GALVANIZING OF AL-SI TRIP-ASSISTED STEELS

GALVANIZING OF AL-SI TRIP-ASSISTED STEELS

By

ERIKA MICHELLE BELLHOUSE, B.A., B.E.Sc.

A Thesis

Submitted to the School of Graduate Studies

in Partial Fulfilment of the Requirements

for the Degree

Doctor of Philosophy

McMaster University

© Copyright by Erika Bellhouse, December 2010

Doctor of Philosophy (2010)		McMaster University
(Materials Science & Engineering)		Hamilton, Ontario
TITLE:	Galvanizing of Al-	Si TRIP-Assisted Steels
AUTHOR:	Erika Michelle Bel	lhouse, B.A., B.E.Sc. (University of
	Western Ontario)	
SUPERVISOR:	Dr. Joseph R. McD	Dermid

NUMBER OF PAGES: xxvi, 268

ABSTRACT

The high strength and ductility of TRIP-assisted steels makes them ideal for automotive lightweighting. However, to be used in automotive exposed parts galvanizing is essential to provide corrosion protection. Galvanizing of TRIP steels poses two major challenges: i) the heat treatment used to obtain the TRIP steel microstructure and mechanical properties is not necessarily compatible with the higher temperatures required for hot-dip galvanizing and ii) selective oxidation of the alloying elements used in TRIP steels; Mn, Si and Al, can result in bare spot defects and unacceptable coatings. Both of these issues have been investigated.

Heat treatments compatible with continuous hot-dip galvanizing were performed on two high Al – low Si TRIP-assisted steels; one having 1.5% Al and the other having 1.0% Al and 0.5% Si. The effect of intercritical annealing (IA) temperature and isothermal bainitic transformation (IBT) time at 465 °C on the development of microstructure and mechanical properties was studied. It was determined that a sufficient quantity of stable retained austenite and an excellent combination of strength and ductility could be obtained using thermal cycles with a 465 °C IBT temperature. For the 1.5% Al steel the best combination of strength and ductility was obtained for the thermal cycle using the 50% austenite (γ) IA temperature and IBT times of 90 s and 120 s. For the IBT time of 90 s the tensile strength was 895 MPa and uniform elongation was 0.26. For the IBT time of 120 s the tensile strength was 880 MPa and uniform elongation was 0.27. For the 1.0% Al – 0.5% Si steel the best combination of strength and ductility was obtained for

iv

the 50% γ IA temperature and IBT time of 120 s. This thermal cycle resulted in a tensile strength of 1009 MPa and a uniform elongation of 0.22.

The effect of process atmosphere oxygen partial pressure on oxidation and reactive wetting during galvanizing was determined for four TRIP-assisted steels having varied Si and Al contents. Three different process atmospheres were studied for each alloy: a -53 °C dew point (dp) or -50 °C dp with $N_2 - 20\%$ H₂, a -30 °C dp with $N_2 - 5\%$ H₂ and a +5 °C dp with $N_2 - 5\%$ H₂. The steel chemistry and oxygen partial pressure of the process atmosphere affected oxide chemistry and morphology. For all alloys the lowest oxygen partial pressure process atmosphere resulted in the highest concentration of Si at the surface (-53 °C dp or -50 °C dp) and the -30 °C dp process atmosphere resulted in the highest concentration of Mn at the surface. The predominant oxide morphology observed at the surface of the two high Al – low Si steels comprised film-type oxides or irregular shaped nodules whereas the two high Si steels had an oxide morphology that generally comprised spherical cap shaped nodules.

Good wetting was obtained for all alloys when using two low oxygen partial pressure process atmospheres (-53 °C dp or -50 °C dp and -30 °C dp) and poor wetting was obtained for a higher oxygen partial pressure process atmosphere (+5 °C dp). At the +5 °C dp a considerably larger percentage bare area in the galvanized coating was obtained for the two high Si steels when compared to the two high Al – low Si steels. For the two high Si steels poor wetting at the +5 °C dp was attributed to the oxide morphology with closely spaced Mn-Si oxide nodules being observed at the surface of

v

these steels. For the 1.5% Al steel and 1.0% Al - 0.5% Si steel the poor wetting was due to thick localized MnO films at the steel surface.

Despite selective oxidation observed at the surface for the -53 °C dp or -50 °C dp and -30 °C dp process atmospheres good reactive wetting was observed. For these processing conditions a number of reactive wetting mechanisms were identified. When oxides remained at the steel/coating interface, the oxides could be bridged by the Zn overlay, $Fe_2Al_5Zn_x$ or Fe-Zn intermetallics. Good wetting was also attributed to aluminothermic reduction of surface oxides by the dissolved Al in the Zn bath. For some processing parameters cracking of the oxide as a result of thermal stresses in the oxide imposed during cooling from the intercritical annealing temperature to the Zn bath temperature allowed the bath metal to reach the steel substrate, thereby improving wetting. Similarly, liquid infiltration of bath metal at the oxide/steel grain boundaries also contributed to good wetting on some samples. Lastly, in some cases wetting of the oxide was observed.

ACKNOWLEDGEMENTS

Most importantly I would like to thank my supervisor Dr. Joe McDermid. He has provided me with excellent guidance and has taught me so much in my time at McMaster. I appreciate his generosity in allowing me to perform many expensive and interesting experiments and analyses (I think we both hope I retain my title as most expensive student). I am grateful for the many opportunities he has provided me with to present my work at international conferences and to meet others in the field of galvanizing. His support and encouragement has been greatly appreciated. I would also like to thank my supervisory committee members Dr. Ken Coley and Dr. David Wilkinson for their valuable suggestions and comments.

The following people are thanked for their assistance with the experimental work: Jason Lavallée and John Thomson from the McMaster Steel Research Centre (Galvanizing Simulator), Fred Pearson (TEM), Carmen Andrei (TEM), Steve Koprich (SEM training), Chris Butcher (EBSD and optical microscopy training) and Julia Huang (FIB) from the Canadian Centre for Electron Microscopy, Doug Culley and John Rodda for their help in the MSE labs and Ed McCaffery for solving my computer problems, Li Sun (XPS) from ArcelorMittal Dofasco and Shihong Xu (SAM) from ACSES, the Alberta Centre for Surface Engineering and Science. I would also like to thank the Academic User Access Facility (AUAF) program of the Materials Technology Laboratory of CANMET for fabrication of the TRIP steels used in the experiments.

I would like to thank U. S. Steel Canada, Xstrata Zinc, the Natural Sciences and Engineering Research Council of Canada (NSERC) and the members of the McMaster Steel Research Centre for their financial support. I am also grateful for the financial support I obtained through scholarships from NSERC, OGS and the Stelco-McMaster Scholarship.

Lastly, I would like to thank my husband, family and friends for their support.

TABLE OF CONTENTS

ABS	TRACT NOWLEDGEMENTS	iv vii
TAR	LE OF CONTENTS	ix
LIST	OFFIGURES	xiii
LIST	TOF TABLES	xxv
1	INTRODUCTION	1
1.1	The use of TRIP-assisted steels for automotive applications	1
1.2	Galvanizing of TRIP-assisted steels	2
2	LITERATURE REVIEW	4
2.1	Continuous galvanizing	4
	2.1.1 Overview of the industrial continuous hot-dip galvanizing process	4
	2.1.2 Gas-metal reactions in the annealing furnace	6
	2.1.3 The Zn (Al, Fe) bath and reactive wetting	11
	2.1.3.1 Inhibition breakdown	17
2.2	TRIP-assisted steels	20
	2.2.1 The TRIP-assisted steel microstructure	20
	2.2.2 Chemical composition and heat treatment of TRIP-assisted steels	22
	2.2.2.1 The replacement of Si by Al	24
	2.2.3 Mechanical properties of TRIP-assisted steels	25
	2.2.4 The effect of using thermal cycles compatible with hot-dip	28
	galvanizing on microstructure and mechanical properties	
	2.2.5 Strengthening mechanisms in TRIP-assisted steels	33
	2.2.5.1 Solid solution strengthening	33
	2.2.5.2 Composite strengthening	35
	2.2.5.3 The TRIP effect	36
	2.2.6 Fracture in TRIP-assisted steels	38
2.3	Selective oxidation and galvanizing of TRIP steels	39
	2.3.1 Thermodynamic predictions of oxidation behaviour	40
	2.3.2 The transition between internal and external oxidation	46
	2.3.2.1 Wagner's model	48
	2.3.2.2 Limitations of Wagner's model	49
	2.3.2.3 Extensions of the Wagner model	50
	2.3.2.4 Formation of solvent metal nodules at the surface as a	52
	result of internal oxidation	
	2.3.3 Selective oxidation of TRIP steels	54
	2.3.4 The relationship between selective oxidation and reactive wetting in	57
	TRIP-assisted steels	

3	RESEARCH OBJECTIVES	65
4	EXPERIMENTAL METHOD	67
4.1	Steel chemistry, fabrication and sample preparation	67
4.2	McMaster Galvanizing Simulator	69
4.3	Heat treatment of TRIP steels for analysis of microstructure and mechanical properties	71
4.4	Analysis of TRIP-assisted steel microstructure and mechanical properties	73
	4.4.1 Scanning electron microscopy analysis of the steel microstructure and fracture surface	73
	4.4.2 X-ray diffraction	75
	4.4.3 Tensile Testing	76
4.5	Selection of heat treatment and annealing atmosphere for surface analysis and galvanizing of experimental steels	77
4.6	Analysis of the steel surface after annealing	80
	4.6.1 Sample preparation and storage	80
	4.6.2 X-ray photoelectron spectroscopy	81
	4.6.3 SEM analysis of the surface oxide morphology	82
	4.6.4 Scanning Auger Microscopy	82
	4.6.5 TEM analysis of the selectively oxidized steel surface	85
4.7	Analysis of galvanized samples	85
	4.7.1 Analysis of bare spots in the galvanized coating	85
	4.7.2 SEM and EBSD analysis of the interfacial layer	86
	4.7.3 TEM sample preparation using focused ion beam (FIB) milling	88
	4.7.4 TEM analysis of the steel-coating interface	89
	4.7.5 Testing of Coating adhesion by 180° Bend tests	90
5	THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HIGH AL – LOW SI TRIP-ASSISTED STEELS USING HEAT TREATMENTS COMPATIBLE WITH HOT-DIP GALVANIZING	92
5.1	As-received microstructures	92
52	SEM analysis of the steel microstructure after annealing	93
5.3	XRD analysis of the volume percent retained austenite and retained austenite carbon content	101
54	Tensile testing	104
5.5	SFM analysis of nost tensile testing specimens	112
5.6	Discussion of microstructure and mechanical properties	117
5.0	Discussion of microsulucture and meenameal properties	11/
6	SELECTIVE OXIDATION AND REACTIVE WETTING OF THE STEEL SURFACE	126

6.1	Select	ive Oxida	ation of the steel surface	126
	6.1.1	XPS An	alysis	126
		6.1.1.1	Identification of oxides on the steel surface	126
		6.1.1.2	Effect of oxygen partial pressure and steel chemistry on the	130
			chemical composition of the steel surface	
		6.1.1.3	Analysis of the steel surface and subsurface by XPS depth	132
			profiles	
	6.1.2	Study of SAM ar	f surface oxide morphology and elemental distribution by nd SEM	140
	6.1.3	TEM an	alysis of the steel surface	166
6.2	Reacti	ve wettin	g during galvanizing of TRIP-assisted steels	175
	6.2.1	Analysi	s of coating quality	176
	6.2.2	Galvani	zed coating adhesion	178
	6.2.3	Analysi	s of the steel-coating interface	179
		6.2.3.1	SEM and EBSD analysis of the interfacial reaction	179
			products	
		6.2.3.2	TEM analysis of the steel/coating interface	187
6.3	Discus	ssion of s	elective oxidation and reactive wetting behaviour	207
	6.3.1	General	trends observed for selective oxidation of experimental	207
		alloys		
	6.3.2	Therma	l stresses in the oxide	211
	6.3.3	Nodules oxidatio	s of metallic iron on the surface as a result of internal	214
	6.3.4	Effect o	f intercritical microstructure on oxide morphology	215
	6.3.5	General	trends observed for reactive wetting of experimental allovs	216
	6.3.6	Reactive	e wetting mechanisms	219
		6.3.6.1	Bridging of oxides by $Fe_2Al_5Zn_x$, Fe-Zn intermetallics or the Zn overlay	219
		6362	Aluminothermic reduction of oxides	220
		6363	Infiltration of the liquid Zn (Al Fe) bath between oxide	220
		0101010	particles and the steel substrate	
		6364	Wetting of the oxide	223
	6.3.7	Mechan	ism of Fe-Zn intermetallic formation	223
7	CON	CLUSIO	NS	228
71	Micro	structure	and mechanical properties of TRIP-assisted steels using heat	228
,. 1	treatm	ents com	patible with hot-dip galvanizing	220
7.2	Select	ive oxida	tion	229
7.3	Reacti	ve wettin	Ig	230
7.4	Future	Work	-	232
8	REFF	RENCE	S	234

Appendix A: Modelling the transition between internal and external oxidation for the experimental alloys	243
Appendix B: XPS binding energies from the literature	249
Appendix C: Effect of annealing time on selective oxidation	250

LIST OF FIGURES

Figure 2.1: Schematic drawing of a continuous hot-dip galvanizing line (Marder 2000).	6
Figure 2.2: The relationship between dew point and the partial pressure of water vapour (Fine and Geiger 1979).	7
Figure 2.3: Thermodynamic stability of oxides with respect to annealing temperature and oxygen partial pressure (Fine and Geiger 1979, Kubaschewski and Alcock 1979, Huang and Rosén 1994, Lenev and Novokhatskiy 1966).	9
Figure 2.4: The oxygen partial pressure of the experimental process atmospheres as a function of annealing temperature. The hydrogen content was 5 volume % for the +5 °C dp and -30 °C dp process atmospheres and 20 volume % for the -50 °C dp and -53 °C dp process atmospheres. The effect of activity of the alloying elements is shown for Mn (Fine and Geiger 1979).	10
Figure 2.5: Zn rich corner of the Zn-Al-Fe phase diagram; L is liquid, ζ is FeZn ₁₃ , δ is FeZn ₁₀ and η is Fe ₂ Al ₅ Zn _x . Indicated on the phase diagram are isoactivity lines for Al and Fe in the liquid phase (McDermid et al. 2007).	12
Figure 2.6: Potential supersaturation of Fe in the Zn (Al, Fe) bath at 450 °C (Nakano 2006).	13
Figure 2.7: Steps in inhibition layer formation on an IF steel galvanized using a 0.2 wt. % dissolved Al bath (Chen et al. 2008).	15
Figure 2.8: Morphology of the $Fe_2Al_5Zn_x$ layer on an IF steel observed by SEM. The steel was galvanized in a 0.2 wt. % dissolved Al bath at 460 °C, the reaction time (dipping time + solidification time) was 5 seconds (Chen et al.2008).	15
Figure 2.9: Schematic drawing of the Zn rich corner of the Zn-Al-Fe phase diagram showing the effect of Fe dissolution from the steel strip (Leprêtre et al. 1998).	16
Figure 2.10: Outbursts on an ultra low carbon steel galvanized in a 0.20 wt. % Al bath at 450 °C for 1800 s (Jordan and Marder 1997).	18
Figure 2.11: Schematic drawing of the inhibition layer. As a result of the epitaxial growth of $Fe_2Al_5Zn_x$ on the steel substrate each substrate grain will have grains of $Fe_2Al_5Zn_x$ of the same orientation separated by low angle grain boundaries. High angle grain boundaries between $Fe_2Al_5Zn_x$ grains will occur at the substrate grain boundaries (Guttmann 1994).	19

Figure 2.12: Typical TRIP-assisted steel microstructure consisting of ferrite (α), 21 bainitic ferrite (α b) and retained austenite (γ) (Girault et al. 2001).

Figure 2.13: On the left is the typical two stage heat treatment used to produce 23 the TRIP-assisted steel microstructure. On the right is a Fe-C phase diagram for a steel with 1.5 wt. % Mn. The T_0 line and M_s temperature as a function of C content have been added to the phase diagram (De Cooman 2004).

Figure 2.14: Effect of Al and Si on the isothermal bainite transformation, the 25 curves are for 75% transformation of austenite to bainite. The Al curve is for an alloy with 0.162 wt. % C, 1.49 wt. % Mn, 0.025 wt.% Si and 1.256 wt.% Al, the Si curve is for an alloy with 0.155 wt.% C, 1.56 wt. % Mn, 1.025 wt. % Si and 0.033 wt. % Al (Fonstein et al. 2003).

Figure 2.15: a) true stress-true strain curves for three Si TRIP steels, b) the 27 corresponding work hardening behaviour as shown by n_{incr} and c) the volume % retained austenite as a function of strain. The HSiI steel has 0.13% C, 1.42% Mn and 1.5% Si, the initial carbon content of the retained austenite was 0.95%. The HSiII steel has 0.29% C, 1.42% Mn and 1.41% Si, the initial carbon content of the retained austenite was 0.73% (all values are in weight %) (Jacques, Girault, Harlet et al. 2001).

Figure 2.16: Comparison of static tensile results with high strain rate results for a 28 TRIP steel with 0.18 wt.% C, 1.56 wt.% Mn, 1.73 wt.% Al and 0.021 wt.% Si (Van Slycken et al. 2007).

Figure 2.17: Summary of mechanical properties for the 1.0% Si steel, LT is for 31 an intercritical annealing temperature of 750 °C (35% intercritical austenite) and HT is for an intercritical annealing temperature of 797 °C (50% intercritical austenite). IBT times are indicated next to each point. Lines for the product of the UTS and maximum uniform elongation equal to 100 and 200 are indicated on the graph (Mertens and McDermid 2006).

Figure 2.18: Summary of mechanical properties for the 1.5% Si steel, LT is for 32 an intercritical annealing temperature of 740 °C (35% intercritical austenite) and HT is for an intercritical annealing temperature of 777 °C (50% intercritical austenite). IBT times are indicated next to each point. Lines for the product of the UTS and maximum uniform elongation equal to 100 and 200 are indicated on the graph (Mertens and McDermid 2006).

Figure 2.19: The influence of various alloying elements on solid solution 34 strengthening in ferrite (Pickering 1978).

Figure 2.20: True stress-true strain curves showing the effect of solid solution 34 strengthening provided by Si (Girault et al. 2001).

Figure 2.21: Nanohardness results for the different phases in a 0.29% C, 1.42% 35 Mn and 1.41% Si TRIP-assisted steel, F = ferrite, B = bainitic ferrite, A = retained austenite and M = marteniste (Furnémont et al. 2002).

Figure 2.22: TEM image of dislocations in ferrite surrounding a strain induced 37 martensite grain (Jacques, Furnémont, Mertens et al. 2001).

Figure 2.23: Fracture mechanisms in TRIP-assisted steels, a) cracking of 39 martensite and cracking at the interface between ferrite and martensite (Furnémont et al. 2001), b) a crack propagating through ferrite, bending around harder phases, M/A indicates martensite or austenite (Zhang et al. 2007).

Figure 2.24: Isothermal section of the MnO-Al₂O₃-SiO₂ phase diagram at 800 41 °C, where M = MnO, $A = Al_2O_3$ and $S = SiO_2$ (Jung et al. 2009).

Figure 2.25: Thermodynamic prediction of phases present during annealing with 42 respect to oxygen partial pressure and annealing temperature, a) for a steel with 0.08% C, 1.5% Mn and 1.5% Si, b) for a steel with 0.0015% C, 1.5% Mn, 1.5% Si and 0.5% A1 (in wt. %), B = BCC, F = FCC, M = MnO, S = SiO₂ and A = Al₂O₃ (Jung et al. 2009). A red box as been added to the figures showing the relevant temperature and oxygen partial pressure range for annealing of advanced high strength steels during the continuous galvanizing process.

Figure 2.26: Thermodynamic prediction of oxides present as a function of dew point when annealing a steel with 0.090 wt. % C, 1.43 wt. % Mn, 0.26 wt. % Si and 0.20 wt. % Cr at 800 °C in a N_2 -5% H₂ process atmosphere (Liu et al. 2009).

Figure 2.27: Effect of Si/Mn ratio on oxides predicted as a function of process 45 atmosphere oxygen partial pressure at 850 °C for steels with a Si content of 0.3-1.5 wt. % and Mn content of 0.15-1.7 wt. %. Corresponding wetting results from the literature are overlaid on the graph. The dew point scale on the right is for a $N_2 - 5\%$ H₂ atmosphere. Me = Mn or Fe. (Suzuki et al. 2009).

Figure 2.28:	Schematic of	trawing of	fexternal	and internal	oxidation.	40	6
0		-0-					

Figure 2.29: The effect of dew point on the Mn concentration as a function of the 52 distance from the steel surface for a steel with 1.235 % Mn and 0.12 % Si. The process atmosphere was $N_2 - 5$ % H_2 and the peak annealing temperature was 800 °C (Huin et al. 2005).

Figure 2.30: Nodules of metallic Ag formed as a result of internal oxidation of 54 Mg in a Ag-Mg alloy (Douglass et al. 1992).

Figure 2.31: Schematic drawing showing the effect of annealing temperature on oxidation (Gong et al. 2008).	56
Figure 2.32: Schematic drawing of surface oxide coverage as a function of steel chemistry after annealing using a -30 °C dp N_2 - 5% H_2 atmosphere (Mahieu et al. 2004).	59
Figure 4.1: Uniform temperature and coating area on galvanized panels.	68
Figure 4.2: The McMaster Galvanizing Simulator (MGS).	70
Figure 4.3: Schematic drawing of the McMaster Galvanizing Simulator (Chen 2007).	71
Figure 4.4: Experimental thermal cycle.	72
Figure 4.5: Interrupted annealing cycle.	79
Figure 4.6: Process of generating a KL_2L_3 Auger electron (adapted from Grant (2003) and Briggs and Rivière (1983)) i) an incident electron of sufficient energy ejects an electron from the K shell leaving a hole, ii) the hole in the K shell is filled by an electron from the L_2 energy level which results in excess energy, iii) the excess energy is used to emit an Auger electron from the L_3 level.	84
Figure 4.7: Kikuchi pattern for $Fe_2Al_5Zn_x$ generated by EBSD, the calculated diffraction pattern is overlaid in blue (Chen et al. 1992).	87
Figure 4.8: Stages in typical FIB sample preparation of galvanized samples a) rough milling of trenches on either side of the sample, b) milling around the sample and welding of the probe to the sample, c) welding of the sample to the Cu grid and removing the probe and d) fine milling of three electron transparent windows on the sample.	89
Figure 4.9: a) picture of the bend test die, b) and c) schematic drawings of the bend test, b) before testing and c) after testing.	91
Figure 5.1: As-received microstructures of the experimental TRIP steels a) 1.5% Al steel, b) 1.0% Al steel, c) 1.0% Si steel and d) 1.5% Si steel.	93
Figure 5.2: SEM images of the 1.5% Al (35% γ) microstructure, tempered at 250 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s (F = ferrite, A = retained austenite, M = thermal martensite and B = bainitic ferrite).	95

Figure 5.3: SEM images of the 1.5% Al (50% γ) microstructure, tempered at 250 96 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s.

Figure 5.4: SEM images of the 1.0% Al $(35\% \gamma)$ microstructure, tempered at 250 97 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s.

Figure 5.5: SEM images of the 1.0% Al $(50\% \gamma)$ microstructure, tempered at 250 98 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s.

Figure 5.6: SEM images of selected samples where carbide precipitation was 99 observed, samples were not tempered and were etched with 2% nital a) 1.5% Al (35% γ) and IBT time of 90 s and b) 1.0% Al (35% γ) and IBT time of 120 s.

Figure 5.7: Percentage of thermal martensite as determined by image analysis of 100 the TRIP steel microstructure, a) 1.5% Al steel and b) 1.0% Al steel for both IA temperatures.

Figure 5.8: Volume % of retained austenite as a function of the IBT time as 102 measured by X-ray diffraction, a) 1.5% Al steel and b) 1.0% Al steel. Error bars were determined through comparison of measured and calculated diffraction patterns.

Figure 5.9: Retained austenite carbon content as a function of the IBT time as 103 determined by X-ray diffraction, a) 1.5% Al steel and b) 1.0% Al steel.

Figure 5.10: Tensile results plotted to the point of necking a) 1.5% Al $(35\% \gamma)$ 107 steel, b) 1.5% Al $(50\% \gamma)$ steel, c) 1.0% Al $(35\% \gamma)$ steel and d) 1.0% Al $(50\% \gamma)$ steel, IBT times (t2) are indicated in the legend of each graph.

Figure 5.11: Summary of mechanical properties with respect to isothermal 109 bainite transformation time, σ_T is the tensile strength, σ_Y is the yield strength and ε_U is uniform elongation, a) 1.5% Al (35% γ) steel, b) 1.5% Al (50% γ) steel, c) 1.0% Al (35% γ) steel and d) 1.0% Al (50% γ) steel.

Figure 5.12: Strain hardening behaviour shown by n_{incr} corresponding to the 111 tensile results shown in Figure 5.10 a) 1.5% Al (35% γ) steel, b) 1.5% Al (50% γ) steel, c) 1.0% Al (35% γ) steel and d) 1.0% Al (50% γ) steel, IBT times (t2) are indicated in the legend of each graph.

Figure 5.13: The steel microstructure after tensile testing (uniform elongation 113 region) tempered at 250 °C for 2 hours and etched using 2% nital a) 1.5% Al ($35\% \gamma$) steel, b) 1.5% Al ($50\% \gamma$) steel, c) 1.0% Al ($35\% \gamma$) steel and d) 1.0% Al ($50\% \gamma$) steel, all samples shown used an IBT time of 120 s.

Figure 5.14: SEM images of the cross-section of fractured tensile samples 115 showing preferential sites for void formation and crack propagation a) 1.5% Al $(35\% \gamma)$ steel and IBT time of 60 s, b) 1.5% Al $(35\% \gamma)$ steel and IBT time of 90 s and c) 1.5% Al $(50\% \gamma)$ steel and IBT time of 90 s.

Figure 5.15: SEM images of the fracture surface a) and b) 1.5% Al (50% γ) steel 117 and IBT time of 120 s, c) 1.5% Al (50% γ) steel and IBT time of 90 s and d) 1.0% Al (50% γ) steel and IBT time of 120 s, arrows indicate regions where a harder phase, such as martensite, is visibly protruding from the ductile ferrite matrix showing decohesion between the phases.

Figure 5.16: Summary of mechanical properties comparing the combination of 122 strength and ductility obtained for the 1.5% Al and 1.0% Al steels investigated in the present study to the 1.0% Si and 1.5% Si steels investigated by Mertens and McDermid (2005, 2006).

Figure 6.1: XPS spectra for depth profiles of Fe showing that iron is oxidized to 129 a depth of 5 nm for the 1.0% Si steel at a) the -50 °C dp, b) the -30 °C dp and c) the +5 °C dp.

Figure 6.2: Chemical composition of the steel surface after annealing as131determined using XPS (5 nm sputtering) a) 1.5% Al steel, b) 1.0% Al steel, c)1.0% Si steel and d) 1.5% Si steel.

Figure 6.3: XPS depth profiles for the 1.5% Al steel a) -53 °C dp, b) -30 °C dp 136 and c) +5 °C dp. 136

Figure 6.4: XPS depth profiles of the 1.0% Al steel a) -53 °C dp, b) -30 °C dp 137 and c) +5 °C dp.

Figure 6.5: XPS depth profiles of the 1.0% Si steel a) -50 °C dp, b) -30 °C dp 138 and c) +5 °C dp. (138)

Figure 6.6: XPS depth profiles of the 1.5% Si steel a) -53 $^{\circ}$ C dp, b) -30 $^{\circ}$ C dp 139 and c) +5 $^{\circ}$ C dp.

Figure 6.7: Oxide morphology of the 1.5% Al -53 °C dp steel using Auger 148 mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Al maps.

Figure 6.8: Oxide morphology of the 1.5% Al -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Al maps.	149
Figure 6.9: SEM analysis of the selective oxidation of the 1.5% Al -30 °C dp steel surface.	150
Figure 6.10: Oxide morphology of the 1.5% Al +5 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Al maps.	151
Figure 6.11: Oxide morphology of the 1.0% Al -53 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.	152
Figure 6.12: Oxide morphology of the 1.0% Al -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.	153
Figure 6.13: Oxide morphology of the 1.0% Al +5 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O and d) Mn maps.	154
Figure 6.14: SEM analysis of the oxidized 1.0% Al +5 °C dp steel a) secondary electron image and b) backscattered electron image.	155
Figure 6.15: Oxide morphology of the 1.0% Si -50 °C dp steel using Auger mapping after sputtering 10 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	156
Figure 6.16: Oxide morphology of the 1.0% Si -30 °C dp steel using Auger mapping for the steel surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.	157
Figure 6.17: Oxide morphology of the 1.0% Si -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.	158
Figure 6.18: Oxide morphology of the 1.0% Si +5 °C dp steel using Auger mapping for the steel surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	159
Figure 6.19: Oxide morphology of the 1.0% Si +5 °C dp steel using Auger mapping after sputtering 40 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	160

Figure 6.20: SEM analysis of the oxide morphology of the 1.0% Si +5 $^{\circ}$ C dp steel.	161
Figure 6.21: SEM analysis of the oxide morphology of the 1.5% Si -53 °C dp steel.	161
Figure 6.22: Oxide morphology of the 1.5% Si -53 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	162
Figure 6.23: Oxide morphology of the 1.5% Si -30 °C dp steel using Auger mapping for the steel surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	163
Figure 6.24: Oxide morphology of the 1.5% Si -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	164
Figure 6.25: Oxide morphology of the 1.5% Si +5 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.	165
Figure 6.26: STEM bright field image of the 1.5% Al +5 °C dp steel after annealing, the three areas indicated correspond to the areas analyzed in greater detail shown in i) Figure 6.27, ii) Figure 6.28 and iii) Figure 6.29.	167
Figure 6.27: TEM EDX mapping of area i) shown in Figure 6.26 a) STEM bright field image, b) Fe, c) Mn, d) Al and e) O maps.	168
Figure 6.28: TEM EDX mapping of area ii) shown in Figure 6.26 a) STEM bright field image, b) Fe, c) Mn, d) Al and e) O maps.	169
Figure 6.29: STEM bright field image of area iii) shown in Figure 6.26.	170
Figure 6.30: TEM analysis of the 1.0% Al -53 °C dp steel (area 1) a) bright field STEM image, corresponding elemental maps for b) Fe, c) Mn, d) Al, e) O, f) Si and g) Au.	172
Figure 6.31: STEM bright field image of the 1.0% Al -53 °C dp steel (area 2).	172
Figure 6.32: STEM bright field image of the 1.0% Al -53 °C dp steel (area 3).	173
Figure 6.33: TEM analysis of the cross-section of the 1.0% Al +5 °C dp a) STEM bright field image, corresponding elemental maps for b) Fe, c) Mn, d) Al and e) O.	175

Figure 6.34: Pictures of galvanized panels, a) the 1.0% Al -30 °C dp steel where 177 good reactive wetting and few bare spots were present and b) the 1.0% Si +5 °C dp steel which had the highest percentage bare area of all experimental conditions.

Figure 6.35: Bend test results for the 1.5% Al steel (sample width is 30 mm).	178
Figure 6.36: Bend test results for the 1.0% Al steel (sample width is 30 mm).	178
Figure 6.37: Bend test results for the 1.0% Si steel (sample width is 30 mm).	179
Figure 6.38: Bend test results for the 1.5% Si steel (sample width is 30 mm).	179
Figure 6.39: SEM analysis of the Fe-Zn interface of the 1.5% Al steel a) -53 °C dp stripped with HNO ₃ , b) -53 °C dp stripped with 10% H ₂ SO ₄ , c) -30 °C dp stripped with HNO ₃ , d) -30 °C dp stripped with 10% H ₂ SO ₄ , e) +5 °C dp stripped with HNO ₃ and f) +5 °C dp stripped with 10% H ₂ SO ₄	181
Figure 6.40: SEM analysis of the Fe-Zn interface of the 1.0% Al steel a) -53 °C dp stripped with HNO ₃ , b) -53 °C dp stripped with 10% H ₂ SO ₄ , c) -30 °C dp stripped with HNO ₃ , d) -30 °C dp stripped with 10% H ₂ SO ₄ , e) +5 °C dp stripped with HNO ₃ and f) +5 °C dp stripped with 10% H ₂ SO ₄ .	182
Figure 6.41: SEM analysis of the Fe-Zn interface of the 1.0% Si steel a) -50 °C dp stripped with HNO ₃ , b) -50 °C dp stripped with 10% H ₂ SO ₄ , c) -30 °C dp stripped with HNO ₃ , d) -30 °C dp stripped with 10% H ₂ SO ₄ , e) +5 °C dp stripped with HNO ₃ and f) +5 °C dp stripped with 10% H ₂ SO ₄ .	183
Figure 6.42: SEM analysis of the Fe-Zn interface of the 1.5% Si steel a) -53 °C dp stripped with HNO ₃ , b) -53 °C dp stripped with 10% H ₂ SO ₄ , c) -30 °C dp stripped with HNO ₃ , d) -30 °C dp stripped with 10% H ₂ SO ₄ , e) +5 °C dp stripped with HNO ₃ and f) +5 °C dp stripped with 10% H ₂ SO ₄ .	184
Figure 6.43: Outbursts shown on the 1.5% Al -30 °C dp steel.	185
Figure 6.44: Identification of Al rich phases at the steel/coating interface of the 1.0% Si -50 °C dp steel by EBSD a) secondary electron image and b) EBSD phase map (blue is Fe_2Al_5 or $Fe_2Al_5Zn_x$, red is $FeAl_3$ and green is ferrite). It should be noted that this sample was galvanized immediately following cooling from the IA temperature rather than after the IBT time of 120 s.	186
Figure 6.45: TEM EDX mapping of the steel/coating interface of the 1.5% Al -30 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Al and f) Zn maps.	188

Figure 6.46: STEM bright field image of the 1.5% Al -30 °C dp steel with colour 189 overlay of EDX elemental maps; Fe in blue, Mn in red and Al in green.

Figure 6.47: TEM analysis of the Fe-Zn interface of the 1.0% Al -53 °C dp steel 192 (area 1) a) bright field image, b) higher magnification bright field image of the interface area indicated in a), EDX elemental maps corresponding to the area shown in a) for c) Fe, d) O, e) Mn, f) Al, g) Zn and h) Si.

Figure 6.48: a) overlay of EDX elemental maps of Al in green and Mn in red on 193 the bright field image from Figure 6.47 a) and b) overlay of EDX elemental maps of Mn in red, Al in blue and Zn in green on the bright field image from Figure 6.47 b).

Figure 6.49: TEM EDX mapping of the 1.0% Al -53 °C dp steel (area 2) a) 194 bright field image, b) Fe, c) O, d) Mn, e) Al, f) Zn and g) Si maps and h) bright field image with the Fe map overlaid in green, the Mn map in red and the Al map in blue.

Figure 6.50: TEM EDX mapping of the steel/coating interface of the 1.0% A1 195 -30 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Al, f) Zn and g) Si maps and h) bright field image with the Fe map overlaid in green, the Mn map in red and the Al map in blue.

Figure 6.51: TEM EDX mapping of the steel/coating interface of the 1.0% Al 198 +5 °C dp steel at the edge of a bare spot a) bright field image, b) Fe, c) O, d) Mn, e) Al and f) Si maps.

Figure 6.52: TEM EDX mapping of the steel/coating interface of the 1.0% Si 200 -30 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Si, f) Al and g) Zn maps and h) bright field image with colour overlay of the Fe map in green, Mn in red and Zn in blue.

Figure 6.53: TEM EDX mapping of the steel/coating interface of the 1.0% Si 202 +5 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Si, f) Al and g) Zn maps.

Figure 6.54: TEM EDX mapping of the steel surface within a bare spot on the 203 1.0% Si +5 °C dp galvanized steel a) bright field image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.

Figure 6.55: TEM EDX mapping of the steel/coating interface of the 1.5% Si206-30 °C dp steel a) bright field image, b) Fe c) O, d) Mn, e) Si, f) Al and g) Zn206maps.-30 °C dp steel a) bright field image, b) Fe c) O, d) Mn, e) Si, f) Al and g) Zn-30 °C dp steel a) bright field image, b) Fe c) O, d) Mn, e) Si, f) Al and g) Zn

Figure 6.56: Summary of bare spot analysis showing the effect of steel chemistry 217 and process atmosphere oxygen partial pressure on the total bare area per panel, the area analyzed for each panel was 8100 mm^2 .

Figure 6.57: Zn rich corner of the Zn-Al-Fe phase diagram (McDermid et al. 225 2007) with arrows added to indicate processes occurring during galvanizing of the experimental TRIP steels. When the steel is immersed in the Zn (Al, Fe) bath Fe dissolution from the substrate occurs as shown by arrow 1. On areas of the steel surface which are free of oxides $Fe_2Al_5Zn_x$ precipitates as shown by arrow 2. At the same time aluminothermic reduction will occur on oxidized areas of the substrate consuming Al as indicated by arrow 3. If aluminium is not replenished Fe-Zn intermetallics will precipitate as shown by arrow 4.

Figure 6.58: The Mn oxidation depth determined using the full width half 226 maximum (FWHM).

Figure C.1: XPS depth profiles for the 1.5% Al -53 °C dp steel, a) O, b) Mn and 251 c) Al.

Figure C.2: XPS depth profiles for the 1.5% Al -30 °C dp steel, a) O, b) Mn and 252 c) Al.

Figure C.3: XPS depth profiles for the 1.5% Al +5 °C dp steel, a) O, b) Mn and 253 c) Al.

Figure C.4: XPS depth profiles for the 1.0% Al -53 °C dp steel, a) O, b) Mn, c) 254 Al and d) Si.

Figure C.5: XPS depth profiles for the 1.0% Al -30 °C dp steel, a) O, b) Mn, c) 256 Al and d) Si.

Figure C.6: XPS depth profiles for the 1.0% Al +5 °C dp steel, a) O, b) Mn, c) 258 Al and d) Si.

Figure C.7: XPS depth profiles for the 1.0% Si -50 °C dp steel, a) O, b) Mn, c) 260 Al and d) Si.

Figure C.8: XPS depth profiles for the 1.0% Si -30 °C dp steel, a) O, b) Mn, c) 262 Al and d) Si.

Figure C.9: XPS depth profiles for the 1.0% Si +5 °C dp steel, a) O, b) Mn, c) Al 264 and d) Si.

Figure C.10: XPS depth profiles for the 1.5% Si -53 °C dp steel, a) O, b) Mn and 266 c) Si.

Figure C.11: XPS depth profiles for the 1.5% Si -30 °C dp steel, a) O, b) Mn and 267 c) Si.

Figure C.12: XPS depth profiles for the 1.5% Si +5 °C dp steel, a) O, b) Mn and 278 c) Si.

LIST OF TABLES

Table 2.1: Gibbs energy minimization for reduction of a MnO film by the dissolved Al in a Zn (Al, Fe) bath (Khondker et al. 2007)	63
Table 4.1: Chemical composition of experimental TRIP steels (weight %)	67
Table 4.2: Summary of experimental heat treatments	73
Table 4.3: Summary of SEM parameters for different sample types	74
Table 4.4: Annealing atmosphere compositions	78
Table 5.1: Summary of optimal mechanical properties	123
Table 6.1: Identification of oxides on the steel surface using XPS (after sputtering 5 nm)	127
Table 6.2: Mass balance results showing the amount of excess oxygen at various depths into the steel surface	140
Table 6.3: TEM EDX quantitative analysis of the 1.5% Al +5 °C dp steel, points A through I are indicated in the STEM bright field images shown in Figure 6.27 a), Figure 6.28 a) and Figure 6.29 (atomic %)	170
Table 6.4: TEM EDX quantitative analysis of the 1.0% Al -53 °C dp steel, points A through I are indicated in the STEM bright field images shown in Figure 6.30 a), Figure 6.31 and Figure 6.32 (atomic %)	173
Table 6.5: TEM EDX quantitative analysis of the 1.0% Al +5 °C dp steel, points A through C are indicated in the STEM bright field image shown in Figure 6.33 a) (atomic %)	174
Table 6.6: Bare spot analysis	176
Table 6.7: TEM EDX point analysis of the 1.5% Al -30 °C dp steel corresponding to the points indicated in Figure 6.45 a) (atomic %)	189
Table 6.8: TEM EDX point analysis of the 1.0% Al -53 °C dp steel corresponding to the points indicated in Figure 6.47 a) and b) and Figure 6.49 a) (atomic %)	193
Table 6.9: TEM EDX point analysis of the 1.0% Al -30 °C dp steel corresponding to the points indicated in Figure 6.50 a) (atomic %)	196

Table 6.10: TEM EDX point analysis of the 1.0% Al +5 °C dp steel corresponding to the points indicated in Figure 6.51 a) (atomic %)	198
Table 6.11: TEM EDX point analysis of the 1.0% Si -30 °C dp steel corresponding to the points indicated in Figure 6.52 a) (atomic %)	200
Table 6.12: TEM EDX point analysis of the 1.0% Si +5 °C dp steel corresponding to the points indicated in Figure 6.53 a) and Figure 6.54 a) (atomic %)	203
Table 6.13: TEM EDX point analysis of the 1.5% Si -30 °C dp steel corresponding to the points indicated in Figure 6.55 a) (atomic %)	205
Table 6.14: Material properties needed to solve equation (6.1)	213
Table 7.1: Summary of reactive wetting behaviour by steel chemistry and process atmosphere	232
Table A.1: : Diffusion data for species in ferrite (α) and austenite (γ) needed for equations (A.1) and (A.2)	245
Table A.2: Diffusion coefficients for Si (D'_{Si}) in ferrite needed for equations (A.1) and (A.2) (Borg and Lai 1970)	245
Table A.3: Molar volumes and stoichiometric ratio (n) for oxide species BO_n needed for equations (A.1) and (A.2) (Weast 1978, Lide 2002)	245
Table A.4: Predicted oxidation mode for experimental alloys	248
Table B.1: XPS binding energies compiled from the literature	249

1 INTRODUCTION

1.1 The use of TRIP-assisted steels for automotive applications

Multiphase TRIP-assisted steels are ideal for automotive lightweighting due to their high strength and ductility. The high strength allows thinner cross-sections of material to be used, decreasing the vehicle weight and thereby increasing fuel efficiency and decreasing greenhouse gas emissions (Traint et al. 2004). Furthermore, the combination of strength and ductility results in excellent energy absorption. At high strain rates, such as those occurring in the event of a collision, the energy absorption capabilities of TRIP-assisted steels are enhanced, resulting in improved passenger safety (De Cooman 2004, Van Slycken et al. 2006, Van Slycken et al. 2007).

TRIP-assisted steel mechanical properties are brought about by the multiphase microstructure which consists of ferrite, bainitic ferrite, retained austenite that transforms to martensite during deformation (*i.e.* the TRIP effect (Zackay et al. 1967)) and sometimes a small amount of thermal martensite (Jacques et al. 1998, Matsumura et al. 1987). The strengthening mechanisms responsible for the high strength and ductility are i) composite strengthening provided by the multiphase microstructure, ii) the TRIP effect and iii) solid solution strengthening by C and Si (Tomota et al. 2004, Jacques et al. 2006, Jacques, Furnémont, Mertens et al. 2001, Jacques, Girault, Harlet et al. 2001, Jacques, Girault, Mertens et al. 2001). The TRIP effect is of particular importance as it strongly influences the work hardening behaviour of the material. The gradual transformation of retained austenite to martensite results in an increasing value of the incremental work

hardening exponent (n_{incr}) or an n_{incr} value that remains high at high values of strain, thereby delaying the onset of necking (Jacques, Furnémont, Mertens et al. 2001). n_{incr} is defined in equation (1.1) (Sachdev 1983).

$$n_{incr} = \frac{d(\ln \sigma)}{d(\ln \varepsilon)}$$
(1.1)

The TRIP effect affects the work hardening behaviour as a result of i) increasing the amount of martensite in the microstructure and ii) the creation of dislocations in ferrite to accommodate the volumetric expansion which accompanies the austenite to martensite transformation (Tomota et al. 2004, Jacques, Furnémont, Mertens et al. 2001).

TRIP steels are one of the advanced high strength steels utilized in the ULSAB-AVC (Advanced Vehicle Concepts) program which is an initiative to increase vehicle fuel efficiency while maintaining or increasing safety and without increasing vehicle cost (ULSAB-AVC Advanced Vehicle Concepts Overview Report 2002). TRIP steels have also been used in A and B-pillars in the Porsche Cayenne (Mehrkens and Fröber 2003).

1.2 Galvanizing of TRIP-assisted steels

To be used in automotive exposed parts corrosion protection of TRIP steels is essential to protect the steel from aqueous corrosion and maintain the structural integrity of the steel. Continuous galvanizing is amongst the most cost-effective means of accomplishing this objective. However, the continuous galvanizing of TRIP steels can be difficult due to selective oxidation of the alloying elements commonly used in TRIPassisted steels; Mn, Si and Al (Drillet et al. 2004, Mahieu et al. 2001, Maki et al. 2003, Mahieu et al. 2004, Mahieu, De Cooman et al. 2002). The process atmosphere used during annealing prior to galvanizing is reducing for iron oxides but not for the oxides of the alloying elements. Selective oxidation of the steel surface can prevent the Zn (Al, Fe) bath from reactively wetting the steel substrate and forming the $Fe_2Al_5Zn_x$ inhibition layer at the steel/coating interface. This can result in unacceptable coatings with many bare spots (Drillet et al. 2004, Mahieu et al. 2001, Mahieu et al. 2004).

Another concern when galvanizing TRIP-assisted steels is that the heat treatment conventionally used to obtain the TRIP steel microstructure is not necessarily compatible with the higher temperatures required for hot-dip galvanizing. The TRIP steel microstructure is obtained using a two stage heat treatment that includes intercritical annealing (IA) and an isothermal bainitic transformation (IBT). The temperature of the zinc bath used for galvanizing requires that higher than nominal temperatures are used for the IBT step of this heat treatment. Using higher temperatures during the IBT can result in carbide precipitation, thereby lowering the retained austenite carbon content and adversely affecting its stability and volume fraction (Pichler et al. 2003).

This thesis addresses both of these issues in the continuous galvanizing of TRIPassisted steels. The microstructure and mechanical properties produced using heat treatments compatible with hot-dip galvanizing will be discussed in Chapter 5. The selective oxidation and galvanizing behaviour of TRIP steels as a function of alloy content and process atmosphere oxygen partial pressure will be discussed in Chapter 6.

3

2 LITERATURE REVIEW

2.1 Continuous galvanizing

2.1.1 Overview of the industrial continuous hot-dip galvanizing process

Continuous hot-dip galvanizing is used to protect steel from aqueous corrosion by two methods: i) barrier protection and ii) galvanic protection. In barrier protection, the Zn coating creates a physical barrier between the steel substrate and the corrosive environment. In galvanic protection, zinc is a sacrificial anode when paired with iron and corrodes preferentially, thereby protecting the iron (Fontana and Greene 1978). Providing corrosion protection of TRIP steels in automotive applications is of particular importance for maintaining the structural integrity of the vehicle due to the thinner crosssections of material used in weight saving applications.

The continuous galvanizing process is described by Marder (2000) and a schematic drawing of a continuous galvanizing line is shown in Figure 2.1. First the steel coils are welded together to form a continuous strip (not shown). Next the steel strip is cleaned using an alkali solution of approximately 2 % NaOH along with brushing of the surface to remove loose dirt and oils remaining on the surface after rolling. This is often followed by electrolytic cleaning which removes the dirt more tightly adhered to the surface. The steel then enters the annealing furnace. In Figure 2.1 there are two furnaces shown; a direct fired furnace and a radiant tube furnace. Typically, industrial galvanizing lines have only one type of furnace; either a direct fired furnace or a radiant tube furnace. The difference between these two types of furnaces is that in the direct

4

fired furnace the process gas is not independent of the heating system and in the radiant tube furnace the process gas is independent of the heating system. The furnace has two purposes: i) to heat treat the steel in order to obtain the desired mechanical properties and microstructures and ii) to reduce iron oxides on the steel surface. In order to reduce iron oxides a N₂/H₂ atmosphere with a controlled dew point (i.e. controlled oxygen partial pressure) is used. This step is critical to ensure that metallic Fe comes in contact with the bath metal in order for good reactive wetting to occur. After annealing the steel strip is cooled to approximately the zinc bath temperature and is then immersed in the zinc bath. Al is added to the galvanizing bath to form the so-called $Fe_2Al_5Zn_x$ inhibition layer at the steel/coating interface. The $Fe_2Al_5Zn_x$ layer delays or "inhibits" the formation of Fe-Zn intermetallics which are brittle and can result in failure of the coating by cracking, flaking or powdering upon forming (Marder 2000). A typical galvanizing bath dissolved Al content ranges from 0.15 to 0.2 wt. % (McDermid et al. 2007, Giorgi et al. 2001, Tang 1999). Upon exiting the zinc bath gas jet wiping using air or nitrogen is used to control the coating thickness (Marder 2000). For galvanized coatings the steel is cooled upon exiting the zinc bath, solidifying the zinc coating. For galvannealing the steel is annealed to develop a fully alloyed coating of Fe-Zn intermetallics prior to cooling the coated steel strip. Only galvanizing will be discussed in the present study. Not shown in Figure 2.1 are several post dipping steps including quality control, temper rolling, chromating (or application of another coating to prevent corrosion of the Zn coating prior to delivery to the customer) and lastly coiling and cutting of the galvanized steel strip (Marder 2000).



Figure 2.1: Schematic drawing of a continuous hot-dip galvanizing line (Marder 2000).

2.1.2 Gas-metal reactions in the annealing furnace

Annealing is done under a protective N₂/H₂ atmosphere with a controlled dew point (dp). This controls the oxygen partial pressure of the annealing atmosphere. Oxygen partial pressure is a strong function of temperature and the temperature varies in different areas of the annealing furnace, therefore the variables of H₂ content and dew point are controlled in the industrial process. The dew point temperature, T_{dp}, is the temperature at which equation (2.1) is in equilibrium (*i.e.* $\Delta G_{2.1} = 0$):

$$H_2O_{(1)} = H_2O_{(g)}$$
 (2.1)

Thus, the partial pressure of $H_2O_{(g)}$ can be determined using equations (2.2) and (2.3).

$$\Delta G_{2,1} = \Delta G_{2,1}^{\circ} + RT_{dp} \ln K_{2,1}$$
(2.2)

Where $\Delta G_{2,1}^{\circ}$ is the standard Gibbs free energy change for the reaction, R is the universal gas constant and $K_{2,1}$ is the equilibrium constant for the reaction and:

$$K_{2.1} = \frac{p_{H_2O_{(g)}}}{a_{H_2O_{(j)}}} = p_{H_2O_{(g)}}$$
(2.3)

It should be noted that $a_{H_2O_{(1)}} = 1$ since $H_2O_{(1)}$ is assumed to be a pure condensed substance and $H_2O_{(g)}$ is assumed to be an ideal gas. The relationship between dew point and the partial pressure of $H_2O_{(g)}$ is shown in Figure 2.2.



Figure 2.2: The relationship between dew point and the partial pressure of water vapour (Fine and Geiger 1979).

Since the hydrogen content of the process atmosphere is fixed the oxygen partial pressure is determined at the annealing temperature, T_A , from the reaction shown in equation (2.4) and by the application of equations (2.5) and (2.6).

$$H_{2(g)} + \frac{1}{2}O_{2(g)} = H_2O_{(g)}$$
 (2.4)

$$\Delta G_{2.4} = \Delta G_{2.4}^{\circ} + RT_{A} \ln K_{2.4}$$
(2.5)

Where

$$K_{2.4} = \frac{p_{H_2O_{(g)}}}{p_{H_{2(g)}} p_{O_{2(g)}}^{1/2}}$$
(2.6)

Evaluated at equilibrium such that $\Delta G_{2.4} = 0$.

The thermodynamic stability of the oxides of iron and the alloying elements with respect to oxygen partial pressure, per the chemical reaction shown in equation (2.7), can be determined using equations (2.8) and (2.9). In equations (2.7) through (2.9) M represents a metallic species.

$$\frac{x}{y}M + \frac{1}{2}O_2 = \frac{1}{y}M_xO_y$$
(2.7)

$$\Delta G_{2.7} = \Delta G_{2.7}^{\circ} + RT_{A} \ln K_{2.7}$$
(2.8)

Where

$$\mathbf{K}_{2.7} = \frac{\mathbf{a}_{M_x O_y}^{1/y}}{\mathbf{a}_M^{x/y} \mathbf{p}_{O_2}^{1/2}} = \frac{1}{\mathbf{a}_M^{x/y} \mathbf{p}_{O_2}^{1/2}}$$
(2.9)

Where at equilibrium $\Delta G_{2.7} = 0$. In this case, $M_x O_y$ is assumed to be a pure condensed species with an activity 1. The thermodynamic stability of the oxides of Fe, Mn, Si and Al is shown in Figure 2.3. In Figure 2.3 an activity of 1 was assumed for all metal species.



Figure 2.3: Thermodynamic stability of oxides with respect to annealing temperature and oxygen partial pressure (Fine and Geiger 1979, Kubaschewski and Alcock 1979, Huang and Rosén 1994, Lenev and Novokhatskiy 1966).

The experimental annealing atmosphere oxygen partial pressures as a function of temperature are shown in Figure 2.4. For the +5 °C dp and -30 °C dp atmospheres the H₂ content of the atmosphere is 5% and for the -50 °C dp and -53 °C dp the H₂ content is 20%. Increasing the H₂ content of the process atmosphere decreases the oxygen partial

pressure as implied by equation (2.6). The lower the dew point the lower the oxygen partial pressure. In the temperature range of 465 °C to 900 °C all experimental annealing atmospheres are predicted to reduce iron oxides but will be oxidizing for the alloying elements, when using an activity of 1 for all metal species.



Figure 2.4: The oxygen partial pressure of the experimental process atmospheres as a function of annealing temperature. The hydrogen content was 5 volume % for the +5 °C dp and -30 °C dp process atmospheres and 20 volume % for the -50 °C dp and -53 °C dp process atmospheres. The effect of activity of the alloying elements is shown for Mn (Fine and Geiger 1979).

The effect of alloying element activity is shown in Figure 2.4 using Mn as an example. An activity of 1 and an activity of 0.015 are shown. The activity of 0.015 was chosen as 0.015 is approximately the mole fraction of Mn in the experimental alloys and assuming an ideal solution, the activity of Mn in the experimental alloys is estimated to
be 0.015. When the activity of Mn is lower than unity, MnO can be reduced at higher temperature and lower oxygen partial pressures as shown in Figure 2.4; *i.e.* for the -53 °C dp and -50 °C dp atmospheres it is possible to reduce MnO at high temperatures (above approximately 855 °C at the -53 °C dp). Even if the steel is annealed at temperatures above 855 °C Mn can be oxidized to form mixed oxides with Al or Si, or MnO can form upon cooling from the peak annealing temperature. Regardless of the annealing temperature or experimental process atmosphere used, selective oxidation of Mn, Si and Al cannot be avoided (Figure 2.3 and Figure 2.4).

Figure 2.2, Figure 2.3 and Figure 2.4 were constructed using the standard Gibbs free energy of formation obtained from the following sources:

H₂O₍₁₎, H₂O_(g), FeO, Fe₃O₄, MnO and Al₂O₃ (Fine and Geiger 1979)
SiO₂ (Kubaschewski and Alcock 1979)
Mn₂SiO₄ and MnSiO₃ (Huang and Rosén 1994)
MnAl₂O₄ (Lenev and Novokhatskiy 1966).

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

In the continuous hot-dip galvanizing process small additions of Al are added to the Zn bath to inhibit the formation of Fe-Zn intermetallics at the steel/coating interface. Fe is also present in the Zn bath as a result of Fe dissolution from the steel strip upon immersion. Fe dissolution occurs because the steel strip is not in equilibrium with the Zn bath (Guttmann 1994). Due to the limited solubility of Al and Fe in liquid Zn, as shown by the Zn rich corner of the Zn-Al-Fe phase diagram in Figure 2.5, intermetallic phases will precipitate from the bath forming particles commonly referred to as a component of "dross". In the vicinity of the steel strip there is a higher metastable Fe solubility, shown in Figure 2.6, resulting in the continuous dissolution of Fe and precipitation of dross (Nakano 2006). For a 0.2 wt. % dissolved Al bath, as used in the present study, the bath will be saturated with respect to Fe₂Al₅Zn_x. Fe₂Al₅Zn_x floats on top of the surface of the bath and can easily be removed from the bath by skimming the surface. At lower bath Al contents FeZn₁₀ (δ) or FeZn₁₃ (ζ) will precipitate from the bath, these Fe-Zn intermetallics have a higher density than liquid Zn and sink to the bottom of the bath and are more difficult to remove. Oxidation of bath metals (ZnO and Al₂O₃) also contributes to dross formation in the bath (Marder 2000).



Figure 2.5: Zn rich corner of the Zn-Al-Fe phase diagram; L is liquid, ζ is FeZn₁₃, δ is FeZn₁₀ and η is Fe₂Al₅Zn_x. Indicated on the phase diagram are isoactivity lines for Al (with respect to pure solid Al) and Fe (with respect to pure solid α -Fe) in the liquid phase (McDermid et al. 2007).



Figure 2.6: Potential supersaturation of Fe in the Zn (Al, Fe) bath at 450 °C (Nakano 2006).

The steps in inhibition layer formation for an IF steel galvanized in a 0.2 wt. % Al bath were described by Chen et al. (2008) and are shown in Figure 2.7. As was discussed above, when the steel is first immersed in the Zn (Al, Fe) bath there is Fe dissolution from the steel strip. This is followed by nucleation and growth of the metastable FeAl₃ phase which forms a compact layer of fine crystals on the steel substrate. Once this layer has formed further dissolution of the steel substrate is prevented. However, Fe does continue to migrate towards the Zn bath by diffusion through the inhibition layer. Similarly, Zn and Al diffuse towards the steel substrate. Next, the metastable FeAl₃ begins to transform to $Fe_2Al_5Zn_x$ via the reaction shown in equation (2.10).

$$\operatorname{FeAl}_{3} + 2\operatorname{Al}_{(\text{bath})} + \operatorname{Fe}_{(\text{substrate})} + xZn_{(\text{bath})} \rightarrow \operatorname{Fe}_{2}\operatorname{Al}_{5}Zn_{x}$$
 (2.10)

This is followed by the growth of an upper, coarser layer of $Fe_2Al_5Zn_x$ and the continued transformation of $FeAl_3$ to $Fe_2Al_5Zn_x$. The final inhibition layer morphology has a two layer structure with a layer of fine compact preferentially oriented $Fe_2Al_5Zn_x$ crystals adjacent to the steel substrate and a layer of coarser randomly oriented $Fe_2Al_5Zn_x$ crystals on top of the fine layer (Figure 2.8). The reactions shown in Figure 2.7 happen very quickly, the nucleation of Fe-Al phases has not been captured experimentally. A continuous Fe-Al layer is formed at the steel/coating interface within two seconds (dipping + solidification time) (Chen et al. 2008). The inhibition layer contains a considerable amount of Zn, for this reason the chemical formula $Fe_2Al_5Zn_x$ will be used to define this phase rather than Fe_2Al_5 (Guttmann 1994, Baril and L'Esperance 1999, Marder 2000, Dionne et al. 2002).



Figure 2.7: Steps in inhibition layer formation on an IF steel galvanized using a 0.2 wt. % dissolved Al bath (Chen et al. 2008).



Figure 2.8: Morphology of the $Fe_2Al_5Zn_x$ layer on an IF steel observed by SEM. The steel was galvanized in a 0.2 wt. % dissolved Al bath at 460 °C, the reaction time (dipping time + solidification time) was 5 seconds (Chen et al. 2008).

For full inhibition to occur (*i.e.* the formation of a continuous Fe-Al alloy layer without the presence of Fe-Zn intermetallics) the bath dissolved Al content should be above 0.15 wt. % (Tang 1998). At 460 °C the bath will be saturated with respect to Fe₂Al₅Zn_x at bath Al compositions above 0.1358 wt. % as shown by point B in Figure 2.5 (McDermid et al. 2007). Although Fe₂Al₅Zn_x is the equilibrium compound expected to precipitate at bath Al compositions from 0.135 to 0.15 wt. %, Fe₂Al₅Zn_x and ζ are often observed at the steel/coating interface (Tang 1998). FeZn₁₃ is found at the steel/coating interface as a result of the Fe dissolution from the steel strip pushing the local bath composition adjacent to the steel strip into the L+ δ region; this is indicated by point 3 in Figure 2.9 (Leprêtre et al. 1998). Although the bath composition for this point is saturated with respect to δ , it is thermodynamically possible for both δ and ζ to form, the formation of ζ is favoured kinetically as it can grow epitaxially on the steel substrate, whereas δ cannot (Tang 1998).



Figure 2.9: Schematic drawing of the Zn rich corner of the Zn-Al-Fe phase diagram showing the effect of Fe dissolution from the steel strip (Leprêtre et al. 1998).

Fe₂Al₅Zn_x or other Fe-Al intermetallics also form at the steel/coating interface at lower Al bath compositions than is expected from the Zn-Al-Fe phase diagram. A discontinuous Al rich layer was found at the steel/coating interface along with Fe-Zn intermetallics when galvanizing using a Zn bath with Al contents as low as 0.10 wt. % (Baril and L'Esperance 1999, McDevitt et al. 1998). In a 0.13 wt. % Al bath Baril and L'Esperance (1999) identified the Al rich layer as Fe₂Al₅Zn_x and Chen et al. (2008) found FeAl₃ and Fe₂Al₅Zn_x. For Zn baths having 0.10 and 0.12 wt. % Al, Baril and L'Esperance (1999) found an Al rich phase at the steel/coating interface but were unable to characterize this phase. The reason for this has been cited as the thermodynamic driving force for the formation of Fe-Al intermetallics being considerably higher than that for the formation of Fe-Zn intermetallics. For example, at 450 °C the free energy of formation for Fe₂Al₅Zn_x and FeAl₃ is approximately an order of magnitude more negative than the free energies of formation for the Fe-Zn intermetallic phases (Guttmann 1994).

2.1.3.1 Inhibition breakdown

Aluminum in the zinc bath delays the formation of Fe-Zn intermetallics but does not prevent these reactions from occurring. Given enough time inhibition breakdown will occur on all coatings with a $Fe_2Al_5Zn_x$ layer (Guttmann 1994, Marder 2000). Inhibition breakdown results in the formation of outbursts of Fe-Zn intermetallics at the steel/coating interface (Figure 2.10) (Jordan and Marder 1997). Outbursts are nucleated at the interface between the inhibition layer and the steel substrate; this is shown by the

.

location of the outbursts in Figure 2.10 beginning below the Fe-Al layer. When an outburst forms the $Fe_2Al_5Zn_x$ layer above the outburst breaks apart leaving fragments of $Fe_2Al_5Zn_x$ within the outburst (Marder 2000).



Figure 2.10: Outbursts on an ultra low carbon steel galvanized in a 0.20 wt. % Al bath at 450 °C for 1800 s (Jordan and Marder 1997).

Outbursts form as a result of Zn diffusion through the inhibition layer and into the steel substrate. Once the Zn concentration in the steel substrate reaches a critical supersaturation level Fe-Zn intermetallics are nucleated. Outbursts are often located at grain boundaries in the steel substrate as Zn diffusion occurs faster at grain boundaries, resulting in a higher Zn concentration at the grain boundaries (Leprêtre et al. 1998, Guttmann 1994, Dionne et al. 2002). There is an epitaxial relationship between the substrate and Fe₂Al₅Zn_x causing the Fe₂Al₅Zn_x grains on a substrate grain to have the same orientation such that these Fe₂Al₅Zn_x grains are separated by low angle grain boundaries. The resulting diffusion of Zn through these low angle grain boundaries will be similar to bulk diffusion of Zn through Fe₂Al₅Zn_x. There will be high angle grain

boundaries between colonies of $Fe_2Al_5Zn_x$ on adjacent steel grains resulting in faster Zn diffusion through the $Fe_2Al_5Zn_x$ layer directly above the steel grain boundaries (Guttmann 1994). It is assumed that the substrate is not preferentially oriented, this is reasonable as the substrate is recrystallized at the high temperatures used during annealing. A schematic drawing showing the effect of substrate grain orientation on $Fe_2Al_5Zn_x$ orientation and grain boundaries is shown in Figure 2.11. The role of substrate grain boundaries on inhibition breakdown is also shown by the effect of C and P on outburst formation. These elements delay the formation of Zn down the grain boundaries (Marder 2000).



Figure 2.11: Schematic drawing of the inhibition layer. As a result of the epitaxial growth of $Fe_2Al_5Zn_x$ on the steel substrate each substrate grain will have grains of $Fe_2Al_5Zn_x$ of the same orientation separated by low angle grain boundaries. High angle grain boundaries between $Fe_2Al_5Zn_x$ grains will occur at the substrate grain boundaries (Guttmann 1994).

The first Fe-Zn phase to nucleate during the formation of outbursts is ζ . This is possibly due to ζ phase having the lowest nucleation barrier as a result of the epitaxial growth of ζ on ferrite (Guttmann 1994). There is, however, some discrepancy in the literature regarding the phases present in outbursts and the order in which they form. For example, Leprêtre et al. (1998) found δ containing outbursts with a thin Γ (Fe₃Zn₁₀) layer at the δ /steel interface. The lack of ζ in these outburst structures was likely due to the short times in which these reactions can take place. The δ phase grows at the expense of ζ (Guttmann 1994) and this reaction may have taken place prior to analysis. It should be noted that there are alternative inhibition breakdown mechanisms proposed in the literature. For example, McDevitt et al. (1998) report that inhibition breakdown occurs not by outburst formation but by consumption of the inhibition layer by the substrate and Γ phase. This mechanism is not likely as Fe₂Al₅Zn_x is thermodynamically more stable than Γ phase at 450 °C (Guttmann 1994), making it unlikely for Fe₂Al₅Zn_x to transform to Γ . Other proposed inhibition breakdown mechanisms have been summarized in Guttmann (1994) and Marder (2000) along with reasons why they are implausible.

2.2 TRIP-assisted steels

2.2.1 The TRIP-assisted steel microstructure

Multiphase TRIP-assisted steels have a microstructure that comprises ferrite, bainitic ferrite, retained austenite that transforms to martensite during deformation (*i.e.* the TRIP effect (Zackay et al. 1967)) and sometimes a small amount of thermal martensite (Figure 2.12). This microstructure is obtained through a combination of alloying elements and a specialized heat treatment. The transformation of retained austenite to martensite during deformation and solid solution strengthening provided by alloying elements such as C and Si results in the excellent combination of strength and ductility exhibited by these steels (Jacques et al. 2006, Jacques, Girault, Harlet et al. 2001, Jacques, Furnémont, Mertens et al. 2001, Jacques, Girault, Mertens et al. 2001, Tomota et al. 2004, Takeuchi 1969, Pickering 1978). The TRIP effect provides strengthening by two methods: i) composite strengthening by continuously introducing harder martensite particles into the microstructure and ii) work hardening of ferrite via the formation of dislocations surrounding newly formed martensite particles to accommodate for the volumetric expansion associated with the austenite to martensite transformation (Tomota et al. 2004, Jacques, Furnémont, Mertens et al. 2001).



Figure 2.12: Typical TRIP-assisted steel microstructure consisting of ferrite (α), bainitic ferrite (α b) and retained austenite (γ) (Girault et al. 2001).

2.2.2 Chemical composition and heat treatment of TRIP-assisted steels

The conventional low alloy TRIP-assisted steel chemistry contains C, Mn and Si (Matsumura et al. 1987, Sakuma et al. 1991, Jacques et al. 1999, De Cooman 2004). This combination of alloying elements and the two stage heat treatment shown in Figure 2.13 is used to produce the TRIP steel microstructure. First the steel is heated to the intercritical annealing temperature (IA) to produce a microstructure of ferrite and austenite. The austenite becomes enriched with carbon as shown by the phase diagram in Figure 2.13. The steel is then rapidly cooled to the isothermal bainitic transformation temperature (IBT) and held at this temperature, usually for several minutes (Matsumura et al. 1987, De Cooman 2004, Jacques, Furnémont, Mertens et al. 2001). During this step some austenite transforms to bainitic ferrite, further enriching the remaining austenite with carbon that is rejected from the bainite. The bainite reaction may proceed at temperatures below T_0 , indicated in Figure 2.13. T_0 is the temperature at which the free energy of ferrite is equal to the free energy of austenite of the same composition (De Cooman 2004). The lower the IBT temperature the higher the maximum attainable carbon content of the retained austenite for a given steel chemistry (Figure 2.13). The IBT temperature typically ranges from 360 °C to 450 °C (Jacques, Girault, Harlet et al. 2001, Tomota et al. 2004, Jacques, Furnémont, Mertens et al. 2001, Jacques, Girault, Mertens et al. 2001, Jacques et al. 1998, Matsumura et al. 1987, Girault et al. 2001, Srivastava et al. 2006, Srivastava et al. 2007, Vasilakos et al. 2002, De Meyer et al. 1999, Mahieu, Maki et al. 2002, Chen et al. 1989). Many of the best combinations of strength and ductility have been reported using IBT temperatures in the range of 360 °C to 410 °C

(Jacques, Girault, Harlet et al. 2001, Tomota et al. 2004, Jacques, Furnémont, Mertens et al. 2001, Jacques, Girault, Mertens et al. 2001, Jacques et al. 1998, Matsumura et al. 1987, Srivastava et al. 2006, Srivastava et al. 2007). This temperature range is below the melting temperature of Zn and, therefore, is not compatible with hot-dip galvanizing.



Figure 2.13: On the left is the typical two stage heat treatment used to produce the TRIPassisted steel microstructure. On the right is a Fe-C phase diagram for a steel with 1.5 wt. % Mn. The T_0 line and M_s temperature as a function of C content have been added to the phase diagram (De Cooman 2004).

Carbon is essential in the TRIP steel chemistry in order to stabilize the retained austenite at room temperature. The carbon content of the retained austenite is of prime importance for determining the rate of the retained austenite to martensite transformation during straining which in turn strongly influences the work hardening behaviour (Jacques, Girault, Harlet et al. 2001). Manganese is added to increase alloy hardenability (De Cooman 2004). Silicon delays carbide precipitation during the IBT step of the heat treatment due to the low solubility of Si in cementite, thereby allowing the austenite to become enriched with carbon (Bhadeshia and Edmonds 1979, Jacques et al. 1999). Silicon is also added to provided solid solution strengthening (Pickering 1978, Girault et al. 2001). However, due to the difficulties in galvanizing Si containing steels, TRIP steels have been developed with Al and/or P partially or completely replacing Si (De Meyer et al. 1999, Jacques, Girault, Mertens et al. 2001, Barbé et al. 2002, Mahieu, Maki et al. 2002). Microalloying with Ti, Nb and/or V has also been explored for increasing the strength of TRIP steels (De Cooman 2004, Krizan et al. 2004).

2.2.2.1 The replacement of Si by Al

Al has a similar effect as Si in delaying carbide precipitation during the IBT step of the heat treatment (Girault et al. 2001). It has been shown that Al either partially or completely replacing Si can produce a sufficient amount of retained austenite having sufficient stability to provide an excellent combination of strength and ductility (Jacques, Girault, Mertens et al. 2001). However, Al containing TRIP steels tend to exhibit lower strengths than Si containing grades as a result of the solid solution strengthening provided by Si versus that of Al (Girault et al. 2001, Jacques, Girault, Mertens et al. 2001).

Al also results in more rapid bainite transformation kinetics when compared to Si (Mertens et al. 2003, Jacques, Girault, Mertens et al. 2001, Fonstein et al. 2003). This difference is particularly pronounced at higher IBT temperatures including the temperature range of 460 °C to 465 °C, which is of interest for hot-dip galvanizing (Figure 2.14) (Fonstein et al. 2003). In particular, the faster bainite transformation kinetics of Al-based alloys are promising for producing sufficient stability retained austenite in the shorter IBT times available on existing industrial galvanizing lines. Al, however, has been shown to be less efficient when compared to Si at preventing carbide precipitation at longer IBT times (Girault et al. 2001).



Figure 2.14: Effect of Al and Si on the isothermal bainite transformation, the curves are for 75% transformation of austenite to bainite. The Al curve is for an alloy with 0.162 wt. % C, 1.49 wt. % Mn, 0.025 wt.% Si and 1.256 wt.% Al, the Si curve is for an alloy with 0.155 wt.% C, 1.56 wt. % Mn, 1.025 wt. % Si and 0.033 wt. % Al (Fonstein et al. 2003).

2.2.3 Mechanical properties of TRIP-assisted steels

TRIP-assisted steels are characterized by their high strength and ductility. This

combination of properties is brought about by the alloy work hardening behaviour. For a

TRIP steel the incremental work hardening exponent, n_{incr} , defined by equation (1.1), increases or remains high at high levels of strain, thereby delaying the onset of necking. Necking occurs when n_{incr} is equal to the true strain as can be derived from the Considère criterion (equation (2.11)).

$$\sigma = \frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon} \tag{2.11}$$

The work hardening behaviour is directly related to the strain induced transformation of retained austenite to martensite (Jacques, Girault, Harlet et al. 2001). True stress-true strain curves, the corresponding n_{incr} versus strain graphs and the volume fraction of retained austenite in the steel as a function of strain are shown for three Si TRIP steels in Figure 2.15. As the retained austenite stability is determined primarily by its carbon content, it was found that the LSi steel had the lowest retained austenite carbon content and, therefore, the majority of retained austenite transformed to martensite at low values of strain (Figure 2.15 c)). This rapid transformation of austenite at low strains resulted in initially higher values of n_{incr} which then decreased rapidly with increasing strain (Figure 2.15 b)). Consequently, the LSi TRIP steel exhibited a lower combination of strength and ductility when compared to the HSiI and HSiII TRIP steels with more stable retained austenite (Figure 2.15 a)), where the higher austenite C content of the HSiI and HSiII steels resulted in a gradual transformation of retained austenite to martensite (Figure 2.15 c)) and a gradually increasing or relatively constant value of n_{incr} with increasing strain (Figure 2.15 b)). In order to provide the best combinations of strength and ductility a



gradual transformation of retained austenite to martensite is desirable (Jacques, Girault,

Harlet et al. 2001).

Figure 2.15: a) true stress-true strain curves for three Si TRIP steels, b) the corresponding work hardening behaviour as shown by n_{incr} and c) the volume % retained austenite as a function of strain. The HSiI steel has 0.13% C, 1.42% Mn and 1.5% Si, the initial carbon content of the retained austenite was 0.95%. The HSiII steel has 0.29% C, 1.42% Mn and 1.41% Si, the initial carbon content of the retained austenite was 0.97%. The LSi steel has 0.16% C, 1.3% Mn and 0.38% Si, the initial carbon content of the retained austenite was 0.73% (all values are in weight %) (Jacques, Girault, Harlet et al. 2001).

At high strain rates, such as those seen in the event of a collision, the excellent

mechanical properties of TRIP steels are further improved, showing an increase in

strength and a dramatic increase in ductility (Van Slycken et al. 2006, Van Slycken et al. 2007). Static and high strain rate tensile curves are shown in Figure 2.16 for an Al TRIP steel. When a material is deformed at high strain rate there is adiabatic heating of the material. This temperature increase causes a more gradual transformation of retained austenite to martensite, resulting in increased strain hardening over a larger range of strain, thereby contributing to the improved strength and ductility (De Cooman 2004).



Figure 2.16: Comparison of static tensile results with high strain rate results for a TRIP steel with 0.18 wt.% C, 1.56 wt.% Mn, 1.73 wt.% Al and 0.021 wt.% Si (Van Slycken et al. 2007).

2.2.4 The effect of using thermal cycles compatible with hot-dip galvanizing on microstructure and mechanical properties

In order for the thermal cycle to be compatible with hot-dip galvanizing, higher than nominal IBT temperatures must be used. The Zn (Al, Fe) bath is generally held in the temperature range of 460 °C to 465 °C and the steel should be at this temperature when entering the Zn bath. Furthermore, to be compatible with existing galvanizing lines the IBT time should be relatively short. A limited number of studies have been carried out that included IBT temperatures greater than 450 °C. Some researchers have shown there was a degradation of mechanical properties when using high IBT temperatures (Pichler et al. 2003, McDermid et al. 2005, Matsuda et al. 2002, Baik et al. 2001, Sakuma et al. 1991). Pichler et al. (2003) found that at IBT temperatures above 450 °C there was a considerable decrease in elongation; this was attributed to carbide precipitation. Carbide precipitation was also observed when using an IBT temperature of 480 °C in combination with a slow cooling rate from the IA temperature to the IBT temperature in a hot rolled Si TRIP steel. This heat treatment resulted in an insufficient quantity of retained austenite and a low product of tensile strength and total elongation (McDermid et al. 2005). Matsuda et al. (2002) also noted a significant decrease in uniform elongation at IBT temperatures of 450 °C and 475 °C with the best combination of strength and ductility being obtained at an IBT temperature of 425 °C for cold rolled Si TRIP steels. Baik et al. (2001) tested IBT temperatures of 400 °C, 450 °C and 500 °C on TRIP steels with 0.14 wt. % C, 2.1 – 2.4 wt. % Mn and 0.5 – 1.0 wt. % Si and found that 500 °C produced a dramatically lower product of the tensile strength and elongation when compared with the lower IBT temperatures.

Some success has been obtained in achieving an excellent combination of strength and ductility when using IBT temperatures ranging from 455 °C to 470 °C and short IBT times (up to 120 s) (Mertens and McDermid 2005, Mertens and McDermid 2006, McDermid et al. 2005, Krizan et al 2004). McDermid et al. (2005) studied the effect of using thermal cycles compatible with hot-dip galvanizing on a hot rolled TRIP steel with 0.18 wt. % C, 1.4 wt. % Mn and 1.5 wt. % Si. When IBT temperatures of 470 °C and 455 °C were used the volume percent retained austenite was found to be 13.5 and 13.2, respectively. The IBT time used in these experiments was 60 s. Both of these thermal cycles provided an excellent combination of strength and ductility. Krizan et al. (2004) studied the effect of microalloying with Ti or Nb on a TRIP steel containing Mn, Si, Al and P. The thermal cycle included a 48 s IBT at 460 °C. The reference steel (no Ti or Nb) produced a good combination of strength and ductility. The Nb added steel had a higher strength with a slight decrease in ductility when compared to the reference steel and the Ti added steel had the highest strength and lowest ductility.

Mertens and McDermid (2005, 2006) investigated the effect of using an IBT temperature of 465 °C on the microstructure and mechanical properties of the 1.0% Si and 1.5% Si TRIP steels used in the present study (Table 4.1). The 1.0% Si steel also contained 0.5 wt.% Al, both steels contained 0.2 wt.% C and 1.5 wt.% Mn. The effect of IA temperature and IBT time on the microstructure and mechanical properties was determined. Two different IA temperatures were tested for each steel chemistry; one corresponding to 35% intercritical γ and the other corresponding to 50% intercritical γ . Five different IBT times were tested; 0, 30, 60, 90 and 120 s. The mechanical properties of the 1.0% Si steel and 1.5% Si steel are summarized in Figure 2.17 and Figure 2.18, respectively. For the 1.0% Si steel the best combination of strength and ductility was obtained when using the 35% γ IA temperature and IBT time of 90 s. Also providing an excellent combination of strength and ductility was the IBT time of 60 s at both the 35% γ and 50% γ IA temperature. For the 1.5% Si steel the best combination of strength and

ductility was obtained for the 50% γ IA temperature and IBT time of 60 s. Also when using the 50% γ IA temperature the IBT times of 90 s and 120 s provided an excellent combination of strength and ductility as did the 35% γ IA temperature and IBT time of 120 s.



Figure 2.17: Summary of mechanical properties for the 1.0% Si steel, LT is for an intercritical annealing temperature of 750 °C (35% intercritical austenite) and HT is for an intercritical annealing temperature of 797 °C (50% intercritical austenite). IBT times are indicated next to each point. Lines for the product of the UTS and maximum uniform elongation equal to 100 and 200 are indicated on the graph (Mertens and McDermid 2006).



Figure 2.18: Summary of mechanical properties for the 1.5% Si steel, LT is for an intercritical annealing temperature of 740 °C (35% intercritical austenite) and HT is for an intercritical annealing temperature of 777 °C (50% intercritical austenite). IBT times are indicated next to each point. Lines for the product of the UTS and maximum uniform elongation equal to 100 and 200 are indicated on the graph (Mertens and McDermid 2006).

As shown by the mixed results obtained to date, processing TRIP steels using thermal cycles compatible with hot-dip galvanizing is an area where more work is required. In particular, the effect of IBT time and IA temperature on microstructure and mechanical properties has yet to be explored for higher Al grades.

2.2.5 Strengthening mechanisms in TRIP-assisted steels

There are three major strengthening mechanisms in TRIP-assisted steels; solid solution strengthening, composite strengthening and the TRIP effect.

2.2.5.1 Solid solution strengthening

The major elements used for solid solution strengthening in TRIP-assisted steels are carbon and silicon. The effect of various alloying elements, including C and Si, on solid solution strengthening of ferrite is shown in Figure 2.19. Carbon and nitrogen provide the most significant solid solution strengthening per unit mass of the element added, closely followed by the effect of phosphorous and then silicon (Pickering 1978).

The effect of solid solution strengthening provided by Si on a TRIP-assisted steel is shown by comparing the mechanical properties of a Si alloyed TRIP steel to an Al alloyed TRIP steel where steps were taken to isolate the effect of solid solution strengthening. Both steels had 0.11 wt. % C and 1.5 wt. % Mn, the initial retained austenite content was 8 volume % and the austenite to martensite transformation rate observed during deformation was the same for both steels. The stress-strain curves for a 1.5% Si TRIP steel and a 1.5% Al TRIP steel are shown in Figure 2.20. The 1.5% Si TRIP steel had a higher strength and this was attributed to the solid solution strengthening provided by Si (Girault et al. 2001). This is in agreement with the results shown in Figure 2.19 with Si providing significant solid solution strengthening and Al having a slight negative effect on the strength of ferrite (Pickering 1978). For this reason some researchers use P in steels with Al completely or partially replacing Si as P also provides excellent solid solution strengthening (De Cooman 2004, Pickering 1978).



Figure 2.19: The influence of various alloying elements on solid solution strengthening in ferrite (Pickering 1978).



Figure 2.20: True stress-true strain curves showing the effect of solid solution strengthening provided by Si (Girault et al. 2001).

2.2.5.2 Composite strengthening

Composite strengthening arises due to the multiphase microstructure that initially consists of a matrix of soft ferrite and a dispersion of harder phases including bainitic ferrite, retained austenite and sometimes a small amount of thermal martensite. This microstructure evolves during deformation as the retained austenite transforms to martensite. The hardness of these phases in a TRIP steel was measured by nanoindentation and the results shown in Figure 2.21 (Furnémont et al. 2002). The hardest phase is martensite, because of the high strength provided by the body centred tetragonal lattice and the high carbon content of this phase. Retained austenite was harder than ferrite and bainite as a result of its high carbon content which provides solid solution strengthening. Bainitic ferrite is shown to be harder than ferrite due to its higher carbon content and higher dislocation density creating a resistance to plastic flow (Furnémont et al. 2002).



Figure 2.21: Nanohardness results for the different phases in a 0.29% C, 1.42% Mn and 1.41% Si TRIP-assisted steel, F = ferrite, B = bainitic ferrite, A = retained austenite and M = marteniste (Furnémont et al. 2002).

Due to the difference in strength between these phases there is stress and strain partitioning between them during deformation (Jacques 2004). Using neutron diffraction Jacques et al. (2006) measured the elastic strains in the individual phases of TRIP steels, from which the stresses in the different phases could be determined. The results show that the stress partitioning between ferrite and retained austenite is small whereas the stress partitioning between ferrite and martensite is much larger. The higher stress was carried by the stronger phase resulting in austenite and martensite enhancing the overall strength of the material. This was shown by a law of mixtures analysis for the phases in TRIP-assisted steels per equation (2.12) (Jacques et al. 2006).

$$\sigma(\varepsilon) = f_{\alpha}\sigma_{\alpha}(\varepsilon) + f_{\alpha_{b}}\sigma_{\alpha_{b}}(\varepsilon) + f_{\gamma}(\varepsilon)\sigma_{\gamma}(\varepsilon) + f_{\alpha'}(\varepsilon)\sigma_{\alpha'}(\varepsilon)$$
(2.12)

Where f_i is the volume fraction of a given phase, σ_i is the stress, ε is the strain, α is ferrite, α_b is bainitic ferrite, γ is austenite and α' is martensite.

2.2.5.3 The TRIP effect

It is well established that the deformation induced transformation of retained austenite to martensite in TRIP steels improves the mechanical properties by increasing the strain hardening exponent over large ranges of strain, thereby delaying the onset of necking. The impact of the TRIP effect on the stress-strain curve and work hardening behaviour is shown in Figure 2.15. Where there is a gradual transformation of retained austenite to martensite, as exhibited by the HSiI and HSiII steels, there is a gradual increase in the value of n_{incr} over a large range of strain. Conversely, transformation of retained austenite to martensite occurred primarily at lower strains in the LSi steel resulting in higher initial values of n_{incr} , however, n_{incr} decreased rapidly with increasing strain, resulting in lower values of strength and ductility.

The TRIP effect affects the work hardening behaviour by two mechanisms i) the formation of harder martensite particles in the ferrite matrix and ii) by the formation of dislocations in ferrite around newly formed martensite grains as a result of the volume expansion during the austenite to martensite phase transformation (Jacques, Furnémont, Mertens et al. 2001, Tomota et al. 2004). The composite strengthening provided by increasing amounts of martensite in the microstructure was discussed previously in §2.2.5.2. Figure 2.22 shows a TEM image of a strain induced martensite grain in a ferrite matrix, the dislocations (indicated by arrows) were generated to accommodate the volume change associated with the phase transformation. These dislocations result in work hardening of the ferrite matrix surrounding newly formed martensite particles (Jacques, Furnémont, Mertens et al. 2001).



Figure 2.22: TEM image of dislocations in ferrite surrounding a strain induced martensite grain (Jacques, Furnémont, Mertens et al. 2001).

2.2.6 Fracture in TRIP-assisted steels

TRIP steels exhibit ductile fracture with the fracture surface having a typical dimpled appearance (De Cooman 2004). Various damage processes leading to fracture have been observed. Furnémont et al. (2001) observed cracking of martensite grains or cracks at the interface between ferrite and martensite as shown in Figure 2.23 a). Zhang et al. (2007) and Yu et al. (2006) found that microvoids nucleated either at ferrite grain boundaries, at the interface between ferrite and harder phases or within ferrite grains. These voids then grow and coalesce, forming cracks which propagate through ferrite and move around the harder phases including bainitic ferrite, retained austenite and martensite. Figure 2.23 b) shows an area with a crack growing in ferrite or at the interface between ferrite and harder phases, where the crack was deflected around a martensite or austenite grain in the middle of the area shown (Zhang et al. 2007). The difference in observations between different groups could be due to the different carbon contents of the steels and retained austenite in the steel, with the steel used by Furnémont et al. (2001) having a higher carbon content and, therefore, a more brittle martensite (Jacques, Furnémont, Pardoen et al. 2001).



Figure 2.23: Fracture mechanisms in TRIP-assisted steels, a) cracking of martensite and cracking at the interface between ferrite and martensite (Furnémont et al. 2001), b) a crack propagating through ferrite, bending around harder phases, M/A indicates martensite or austenite (Zhang et al. 2007).

2.3 Selective oxidation and galvanizing of TRIP steels

Selective oxidation of Mn, Si and Al during annealing prior to galvanizing cannot

be avoided. The process atmosphere used during annealing prior to galvanizing is

reducing for the oxides of iron but not for the oxides of the alloying elements as was

discussed in §2.1.2. As well as the thermodynamic stability of the oxides, the oxidation

kinetics are also important in determining the oxidation behaviour. Oxide chemistry, thickness and morphology are all important factors in determining the reactive wetting behaviour during galvanizing (Mahieu et al. 2004, Drillet et al. 2004, Vanden Eynde et al. 2004).

2.3.1 Thermodynamic predictions of oxidation behaviour

The thermodynamic stability of MnO, Al₂O₃, SiO₂, Mn₂SiO₄, MnSiO₃ and MnAl₂O₄ with respect to annealing temperature and oxygen partial pressure is provided in Figure 2.3. These oxides will be thermodynamically stable at the intercritical annealing temperatures and process atmospheres relevant for hot-dip galvanizing. As well as these oxides, $3Al_2O_3 \cdot 2SiO_2$, $2MnO \cdot 2Al_2O_3 \cdot 5SiO_2$ and $3MnO \cdot Al_2O_3 \cdot 3SiO_2$ may also form as shown by the isothermal section of the MnO-Al₂O₃-SiO₂ phase diagram at 800 °C (Figure 2.24) (Jung et al. 2009). Recently, a few thermodynamic models have been developed which predict the oxide phases expected to form as a function of steel chemistry, annealing temperature and process atmosphere (Jung et al. 2009, Liu et al. 2009, Suzuki et al. 2009).



Figure 2.24: Isothermal section of the MnO-Al₂O₃-SiO₂ phase diagram at 800 °C, where M = MnO, $A = Al_2O_3$ and $S = SiO_2$ (Jung et al. 2009).

Jung et al. (2009) have made thermodynamic predictions for the oxide phases expected when annealing a steel with 0.08% C, 1.5% Mn and 1.5% Si (Figure 2.25 a)). Over the temperature and oxygen partial pressure range relevant to hot-dip galvanizing MnSiO₃ and SiO₂ are expected. When Al is added to the steel chemistry the predicted oxide phases are different, as shown in Figure 2.25 b). For a steel with 0.0015% C, 1.5% Mn, 1.5% Si and 0.5% Al the predicted oxide phases are 2MnO·2Al₂O₃·5SiO₂, 3MnO·Al₂O₃·3SiO₂ and SiO₂ over the temperature and oxygen partial pressure range relevant to galvanizing.



Figure 2.25: Thermodynamic prediction of phases present during annealing with respect to oxygen partial pressure and annealing temperature, a) for a steel with 0.08% C, 1.5% Mn and 1.5% Si, b) for a steel with 0.0015% C, 1.5% Mn, 1.5% Si and 0.5% Al (in wt. %), B = BCC, F = FCC, M = MnO, $S = SiO_2$ and $A = Al_2O_3$ (Jung et al. 2009). A red box as been added to the figures showing the relevant temperature and oxygen partial pressure range for annealing of advanced high strength steels during the continuous galvanizing process.

Liu et al. (2009) predicted the oxide phases expected to form on a steel with 0.090 wt. % C, 1.43 wt. % Mn, 0.26 wt. % Si and 0.20 wt. % Cr, these results are shown in Figure 2.26 as a function of dew point for a $N_2 - 5\%$ H₂ atmosphere at 800 °C. At dew points above -55 °C MnO and Mn₂SiO₄ would be expected, between dew points of -68 °C and -55 °C only Mn₂SiO₄ would be expected and SiO₂ expected only over a small range of dew points below -70 °C. The oxide MnSiO₃ appears to be missing from the analysis which explains the lack of oxide phase predicted in the -70 °C dp region. Comparing the results of Jung et al. (2009) with those of Liu et al. (2009) it is shown that when the Si content is lowered SiO₂ is expected to form only at very low dew points, at higher dew points Si will be consumed by the formation of either Mn₂SiO₄ or MnSiO₃ (Figure 2.25 a) and Figure 2.26). To easily compare Figure 2.25 a) and Figure 2.26 it should be noted that at 800 °C a -70 °C dp N₂ – 5% H₂ process atmosphere has an oxygen partial pressure of 5.22×10^{-27} bar and a -30 °C dp N₂ – 5% H₂ process atmosphere has an oxygen partial pressure of 4.83×10^{-23} bar (Fine and Geiger 1979).



Figure 2.26: Thermodynamic prediction of oxides present as a function of dew point when annealing a steel with 0.090 wt. % C, 1.43 wt. % Mn, 0.26 wt. % Si and 0.20 wt. % Cr at 800 °C in a N_2 -5% H_2 process atmosphere (Liu et al. 2009).

Suzuki et al. (2009) used the Si to Mn ratio to predict the oxides that will form during annealing at 850 °C as a function of oxygen partial pressure of the process atmosphere (Figure 2.27). Comparing the results of Jung et al. (2009) for the steel in Figure 2.25 a) with those of Suzuki et al. (2009) the results are in good agreement for the oxygen partial pressure range of approximately 10^{-26} to 10^{-22} atm, both models predict SiO₂ and MnSiO₃. Below approximately 10^{-26} atm Jung et al. (2009) predict SiO₂ whereas for a Si/Mn ratio of 1.0 Suzuki et al. (2009) predict MnSiO₃. Reactive wetting results compiled from the literature, where wetting is characterized as good, intermediate or bad are overlaid on Figure 2.27. Some of the wetting results overlaid on Figure 2.27 are for steels having significant Al content and therefore are not indicative of the wettability of the oxide phases indicated in Figure 2.27.



Figure 2.27: Effect of Si/Mn ratio on oxides predicted as a function of process atmosphere oxygen partial pressure at 850 °C for steels with a Si content of 0.3-1.5 wt. % and Mn content of 0.15-1.7 wt. %. Corresponding wetting results from the literature are overlaid on the graph. The dew point scale on the right is for a $N_2 - 5\%$ H₂ atmosphere. Me = Mn or Fe. (Suzuki et al. 2009).

These thermodynamic predictions are a good starting point for determining which oxide phases will be expected during annealing. There are, however, discrepancies between the models which indicate that it is difficult to accurately predict which oxides will form. Also, these calculations cannot predict information such as oxide thickness or morphology which will be shown to be critical factors in determining the reactive wetting behaviour.

2.3.2 The transition between internal and external oxidation

Studying oxidation kinetics is important for determining the transition between internal and external oxidation. Improvements in reactive wetting during galvanizing have been observed when the formation of an external surface oxide layer was minimized by inducing the formation of subsurface oxides (Vanden Eynde et al. 2004, Mahieu et al. 2001). Internal oxidation occurs when the flux of oxygen into the steel surface is greater than the flux of alloying elements that can be oxidized to the surface. A schematic drawing showing the difference between internal and external oxidation is provided in Figure 2.28. The criterion for the transition between internal and external oxidation was first developed by Wagner (1959) for a binary alloy single crystal and is discussed in § 2.3.2.1. More recently a number of extensions to the original Wagner model applicable to Fe based alloys have been developed and are discussed in § 2.3.2.3 (Mataigne et al. 1992, Grabke et al. 1995, Shastry et al. 2007, Huin et al. 1996, Huin et al. 2005).



External Oxidation



Figure 2.28: Schematic drawing of external and internal oxidation.
Certain criteria must be satisfied in order for internal oxidation to be possible and are listed below (Birks et al. 2006, Rapp 1965):

- i) For an alloy A-B, where B is the solute metal, the Gibbs energy of formation of the oxide BO_n must be more negative per mole O₂ than the Gibbs energy of formation for the most stable oxide formed by solvent metal A.
- ii) The solubility and diffusivity of O in A must be sufficient for the activity of the dissolved oxygen (\underline{O}) at the reaction front to be high enough for the Gibbs energy of the reaction $B + n\underline{O} = BO_n$ to be negative.
- iii) The concentration of B in A must be such that B does not exceed the critical concentration ($N_B^{(O)} < N_{B,crit}^{(O)}$) resulting in the transition from internal to external oxidation.
- iv) There must not be any surface film or layer which prevents the dissolution of oxygen into the surface at the onset of oxidation.

The first criterion is satisfied for TRIP-assisted steels; the oxides of the alloying elements Mn, Si and Al are more stable than those of Fe as shown in Figure 2.3. Criterion ii) is also satisfied; there is considerable solubility and diffusivity of O in Fe as shown by Swisher and Turkdogan (1967). The conditions necessary to satisfy criterion iii) will be discussed in § 2.3.2.1 and will be calculated for the alloys studied in Appendix A. There should not be any layer blocking the inward diffusion of O into the surface during annealing prior to galvanizing, therefore satisfying criterion iv).

2.3.2.1 Wagner's model

The criterion for the transition from internal to external oxidation was developed by Wagner (1959) and is provided in equation (2.13). Wagner's original publication is in German, but English explanations of the model are widely available (Birks et al. 2006, Rapp 1965).

$$N_{B,crit}^{(O)} = \left[\frac{\pi g^* V N_O^{(S)} D_O}{2n V_{BO_n} D_B}\right]^{1/2}$$
(2.13)

In equation (2.13):

 $N_{B,crit}^{(O)}$ is the critical molar fraction of the alloying element for the transition from internal to external oxidation, where if $N_B < N_{B,crit}^{(O)}$ then internal oxidation will occur, g^* is the critical volume fraction of precipitated oxides resulting in blocking the inward diffusion paths for oxygen, g^* was determined to be 0.3 by Rapp (1965), n is the stoichiometric ratio between the oxygen and metal atoms in the oxide, V is the alloy molar volume,

 $N_{\rm O}^{(S)}$ is the molar fraction of dissolved oxygen at the surface,

 D_0 is the diffusion coefficient for oxygen where $D_o = D'_o \exp\left[\frac{-Q_o}{RT}\right]$,

 V_{BO_n} is the molar volume of the oxide BO_n and

 D_B is the diffusion coefficient of the alloying element where $D_B = D'_B \exp\left[\frac{-Q_B}{RT}\right]$.

2.3.2.2 Limitations of Wagner's model

The original Wagner model is not appropriate for accurately predicting the transition between internal and external oxidation in TRIP steels as this model was developed for a binary alloy and does not take into consideration the multiple alloying elements which can be oxidized in TRIP steels. Also, the Wagner model is for a single crystal and, therefore, does not take into consideration the accelerated diffusion that occurs at grain boundaries in polycrystalline materials. It is well known that grain boundaries provide short circuit diffusion paths for both oxygen and the alloying elements. Another limitation of the Wagner model applicable to TRIP steels is that during intercritical annealing there are two phases present; ferrite and austenite. The diffusivity of oxygen and the alloying elements are known to be significantly different in ferrite and austenite (Takada and Adachi 1986, Oikawa 1983, Borg and Lai 1970, Takada et al. 1986, Takada et al. 1984, Diffusion Data 1969). The Wagner model also assumes a zero solubility product for the oxides of the alloying elements. This is a reasonable approximation for Al₂O₃ and SiO₂, however, this is not appropriate for MnO (Huin et al. 2005). Also, the Wagner model is for isothermal annealing and does not take into consideration heating to and cooling from the peak annealing temperature. In general, there is some uncertainty associated with a number of the parameters used in the calculations, such as the diffusion data, therefore leading to a larger accumulated uncertainty in the predicted result (Mataigne et al. 1992).

2.3.2.3 Extensions of the Wagner model

A number of extensions to the Wagner model relevant to TRIP steels have been developed which deal with some of the limitations of this model discussed in §2.3.2.2 (Mataigne et al. 1992, Shastry et al. 2007, Huin et al. 2005). The issue of multiple alloying elements that can be oxidized was addressed by Mataigne et al. (1992) by assuming an additive effect of the alloying elements (equation (2.14)). If the left side of equation (2.14) is greater than the right side (*i.e.* the inequality is satisfied) then external oxidation will occur. However, it should be noted that with multiple alloying elements there may be interactions between the elements that affects their diffusivities. There may also be complex oxides that form during annealing, such as $MnAl_2O_4$, $MnSiO_3$ and Mn_2SiO_4 in the case of TRIP steels, that are not accounted for by this model (Mataigne et al. 1992).

$$\Sigma_{B} N_{B}^{(O)} \left[n D_{B} V_{BO_{n}} \right]^{1/2} \ge \left[\frac{0.3 \pi V N_{O}^{(S)} D_{O}}{2} \right]^{1/2}$$
(2.14)

Mataigne et al. (1992) also addressed the issue of accelerated diffusion of oxygen and alloying elements at the grain boundaries. This was done by dividing the activation energy for bulk diffusion by two in order to obtain the grain boundary diffusivity as shown in equation (2.15).

$$N_{B,crit.GB}^{(O)} = \left[\frac{\pi g^* V N_O^{(S)} D_O' \exp\left(\frac{-Q_O}{2RT}\right)}{2n V_{BO_n} D_B' \exp\left(\frac{-Q_B}{2RT}\right)}\right]^{1/2}$$
(2.15)

The diffusivities of oxygen and the alloying elements are different in ferrite than they are in austenite. During intercricial annealing ferrite and austenite are present in the microstructure. Shastry et al. (2007) have accounted for the presence of ferrite and austenite using a rule of mixtures formalism. An additive effect of the alloying elements and phases is assumed, as shown in equation (2.16). External oxidation will occur when the inequality in equation (2.16) is satisfied. In equation (2.16) f is the volume fraction of austenite.

$$f\left[\Sigma_{B}N_{B}^{(O)}\left[nD_{B}V_{BO_{n}}\right]^{1/2}\right]_{\gamma} + (1-f)\left[\Sigma_{B}N_{B}^{(O)}\left[nD_{B}V_{BO_{n}}\right]^{1/2}\right]_{\alpha} \geq \left[\frac{0.3\pi V}{2}\right]^{1/2} \left\{\left[f\left[N_{O}^{(S)}D_{O}\right]^{1/2}\right]_{\gamma} + \left[(1-f)\left[N_{O}^{(S)}D_{O}\right]^{1/2}\right]_{\alpha}\right\}$$
(2.16)

Huin et al. (2005) have developed an extension of the Wagner model using a one dimensional finite difference model. This model takes into consideration the oxidation of multiple alloying elements, the formation of complex oxides (oxide species and the sequence in which oxides form must be determined experimentally), a non-zero solubility product for oxides and anisothermal annealing. Rather than simply predicting whether oxidation will be internal or external, elemental concentration profiles versus distance from the steel surface are generated. In the concentration profile the distinction can also be made between the oxidized element and an element dissolved in the matrix. An example of results generated by this model for anisothermal annealing of a steel with 1.235 wt. % Mn and 0.12 wt. % Si are presented in Figure 2.29. The total Mn concentration is shown in Figure 2.29 for a -40 °C dp N₂ – 5% H₂ process atmosphere and a +15 °C dp N₂ – 5% H₂ atmosphere. At the -40 °C dp the oxidized region was thin

(less than 0.1 μ m) and the concentration of oxidized Mn at the surface high. At the +15 °C dp the concentration of oxidized Mn at the surface was found to be lower than at the -40 °C dp and the oxidized region increased to a distance of almost 0.6 μ m from the surface.



Figure 2.29: The effect of dew point on the Mn concentration as a function of the distance from the steel surface for a steel with 1.235 % Mn and 0.12 % Si. The process atmosphere was $N_2 - 5$ % H_2 and the peak annealing temperature was 800 °C (Huin et al. 2005).

The best model available to date for predicting the oxidation kinetics is undoubtedly that of Huin et al. (2005). However, the chemistry of the oxides cannot be predicted as these must be determined experimentally and provided as input to the model. 2.3.2.4 Formation of solvent metal nodules at the surface as a result of internal oxidation

A number of researchers have identified nodules of the noble solvent metal at the surface as a result of internal oxidation (Mackert et al. 1983, Guruswamy et al. 1986, Douglass et al. 1992, Zhang et al. 2009). Douglass et al. (1992) found nodules of metallic Ag at the surface as a result of the internal oxidation of MgO in a Ag-Mg alloy (Figure 2.30). It was found that the nodules of Ag first appeared at the grain boundaries and then on the surface of the bulk grain. It was also observed that nodules increased in size with increased oxidation time. Ag nodules were also observed as a result of the internal oxidation of In in an Ag-In alloy (Guruswamy et al. 1986). Similarly, Mackert et al. (1983) studied a Pd-Ag-Sn-In alloy and found nodules that were a mixture of Pd and Ag at the surface as a result of the internal oxidation of Sn and In. Nodules of the solvent metal form on the surface to accommodate the volume increase resulting from the formation of internal oxide precipitates, thereby relieving the stress generated by these precipitates. Mackert et al. (1983) measured the volume of nodules on the surface and determined that it was equal to the volume increase resulting from internal oxidation. Two different mechanisms have been proposed for the formation of these nodules including a Nabarro-Herring (diffusional) creep mechanism (Mackert et al. 1983) and a slip-assisted diffusion mechanism (Guruswamy et al. 1986). Mackert et al. (1983) proposed that nodules of the solvent metal form at the surface as a result of vacancy diffusion towards the internal oxide particles as a result of a decreased vacancy concentration in this area. Diffusion of vacancies towards the internal oxide precipitates results in the transport of the solvent metal to the surface. Guruswamy et al. (1986), however, found that the volume change associated with internal oxidation cannot be accommodated by lattice vacancy diffusion and proposed that there will be dislocations generated to accommodate the formation of internal oxide precipitates. These dislocations will provide additional fast diffusion paths for the solvent metal to migrate to the surface and are necessary to account for the amount of material transported to the surface. This phenomenon is not limited to Ag based alloys, nodules of metallic iron on the surface of a TRIP steel with 2.0 wt. % Mn, 1.5. wt. % Si and 0.5 wt. % Al were also recently observed as a result of internal oxidation (Zhang et al. 2009).



Figure 2.30: Nodules of metallic Ag formed as a result of internal oxidation of Mg in a Ag-Mg alloy (Douglass et al. 1992).

2.3.3 Selective oxidation of TRIP steels

Selective oxidation of TRIP steels in process atmospheres relevant to continuous hot-dip galvanizing is a complicated process due to the number of oxidizing elements involved and the two phase microstructure. A selection of results from the literature will be presented in this section providing an overview of the effect of steel chemistry, oxygen partial pressure and annealing temperature. Where corresponding galvanizing results are available the oxidation and galvanizing results will be discussed together in §2.3.4.

The effect of annealing temperature was investigated on a CMnSi TRIP steel when using a -30 °C dp $N_2 - 10\%$ H₂ process atmosphere (Gong et al. 2008). The steel chemistry contained 0.11 wt. % C, 1.53 wt. % Mn and 1.46 wt. % Si. The annealing temperatures were chosen to investigate selective oxidation in three different phase regions; 700 °C in the ferrite + cementite region, 870 °C in the ferrite + austenite region (% of each phase was not provided) and 930 °C in the austenite region. It should be noted that the annealing time was 2 hours which is considerably longer than would be used in hot-dip galvanizing. The oxidation was studied by investigating the cross-section of the steel surface using TEM. The different annealing temperatures produced different surface oxide morphologies and oxide species. At 700 °C many nodules of $xMnO \cdot SiO_2$ (x<0.5) and a thin film of xMnO·SiO₂ (1<x<2) were found. At 930 °C only thicker oxide films composed of a layer of amorphous SiO_2 adjacent to the substrate and an upper layer of 2MnO·SiO₂ and MnO·SiO₂ were found. At 870 °C the oxide morphology was similar to that found at 930 °C, however, the SiO₂ layer adjacent to the substrate was not continuous and there were also nodules of MnO at the surface. It was also observed that the value of x for the oxide $xMnO \cdot SiO_2$ determined whether the oxide was crystalline or amorphous with values of x < 0.9 being amorphous and values of x > 1 being crystalline (Gong et al. 2008, Gong, Kim et al. 2009). The oxide chemistry and morphology are summarized in Figure 2.31. This steel has a similar composition to that used by Jung et al. (2009) for the thermodynamic prediction of oxide phases expected to form during annealing (Figure 2.25 a)). Jung et al. (2009) predicted the presence of only SiO_2 and MnSiO₃ for all temperatures studied by Gong et al. (2008). SiO₂ was also observed

experimentally in agreement with the model, however the range of Mn and Si containing oxides was much broader than was predicted.



Figure 2.31: Schematic drawing showing the effect of annealing temperature on oxidation (Gong et al. 2008).

Gong, Kim et al. (2009) studied the same CMnSi TRIP steel as discussed above when using a process atmosphere with a higher oxygen partial pressure in order to promote internal oxidation (+3 °C dp N₂ – 10% H₂). The intercritical annealing temperature was 870 °C and the intercritical annealing time was 220 s. Despite the higher oxygen partial pressure of this atmosphere external oxidation was not prevented and oxide films of xMnO·SiO₂ (1<x<2) and nodules of MnO and xMnO·SiO₂ (2<x<4) formed on the surface. The higher dew point atmosphere did promote internal oxidation with SiO₂ observed at the grain boundaries to a depth of 4 µm from the steel surface and precipitates of xMnO·SiO₂ (1<x<2) observed to a depth of 1 µm from the steel surface. Selective oxidation of TRIP steels with Si partially replaced by Al has also been investigated by TEM (Gong, Lee et al. 2009, Li et al. 2008). Gong, Lee et al. (2009) studied a TRIP steel with 0.158 wt. % C, 1.99 wt. % Mn, 1.01 wt. % Al and 0.31 wt. % Si and used a -25°C dp $N_2 - 10\%$ H₂ process atmosphere. Li et al. (2008) studied a steel with 0.15 wt. % C, 1.55 wt. % Mn, 1.51 wt. % Al, 0.29 wt. % Si and 0.51 wt. % Cu and used a -35 °C dp $N_2 - 5\%$ H₂ process atmosphere and determined that the Cu did not appear to have contributed to the formation of oxides found at the steel surface. Gong, Lee et al. (2009) found Mn₂SiO₄ and MnAl₂O₄ at the surface; these oxides had the morphology of films and nodules. These oxides were also observed as precipitates below the steel surface. It should be noted that the oxides found by Gong, Lee et al. (2009) were crystalline. Li et al. (2008) also identified crystalline MnAl₂O₄ as well as Si containing amorphous oxides which they could not definitively identify. Both groups found AlN below the surface as a result of annealing in a N₂ rich atmosphere.

As shown by these results, the steel chemistry, oxygen partial pressure and annealing temperature all strongly affect the oxidation behaviour. The experimental oxidation results are far more complex than the results predicted by the thermodynamic or kinetic models discussed in §2.3.1 and §2.3.2.

2.3.4 The relationship between selective oxidation and reactive wetting in TRIPassisted steels

A number of studies have investigated the effect of different alloying elements and process atmospheres on the oxidation and galvanizing of TRIP steels. A summary of this work is provided in this section and where appropriate galvanizing results for other Mn and Si containing steels (*i.e.* dual phase and martensitic steels) have been included.

Selective oxidation and galvanizing of a series of Si, Al and P containing TRIP steels have been studied by several authors (Mahieu et al. 2001, Mahieu, De Cooman et al. 2002, Mahieu et al. 2004, Maki et al. 2003). Two process atmospheres were investigated; the first had a -30 °C dp and the second had a +10 °C dp until reaching the peak annealing temperature at which point the dew point was lowered to -50 °C; both used a $N_2 - 5\%$ H₂ atmosphere. Four different groups of steels were studied; i) CMnSi TRIP steels with 1.32% to 1.69% Mn and 1.28% to 1.46% Si, ii) CMnAlSi TRIP steels with 1.57% to 1.69% Mn, 1.23% to 1.34% Al and 0.30% to 0.34% Si, iii) CMnAl TRIP steels with 1.54% to 1.56% Mn and 0.91% to 1.73% Al and iv) a CMnP TRIP steel having 1.49 % Mn and 0.14 % P (all values are in wt. %). Each group of steels produced similar oxidation and reactive wetting results.

The oxides identified at the surface for the CMnSi, CMnAl and CMnP TRIP steels at the -30 °C dp and the morphology of these oxides are summarized in Figure 2.32. The CMnSi steel was completely covered in oxides, the CMnAl steel had partial oxide coverage and the CMnP steel was almost free of oxides. The corresponding galvanizing results showed that the CMnSi steels had the poorest wetting results with many bare spots in the galvanized coating; this was attributed to the full coverage of the steel surface by Mn₂SiO₄ and SiO₂. The CMnAl and CMnP steels had good wetting without any significant bare spot defects as a result of the limited oxide coverage (Mahieu et al. 2004). It should be noted that in these experiments oxide species were identified by X-ray photoelectron spectroscopy and the oxide morphology was determined by SEM EDX analysis. Using SEM EDX analysis an oxide film could be missed due to lack of topographic features and may be too thin to be detected by EDX due to the large interaction volume associated with this technique. The CMnAlSi steels did not show significant Si enrichment at the surface despite having 0.3% Si in the steel chemistry. Only Mn and Al oxidation was detected at the surface (Mahieu, De Cooman et al. 2002). This contradicts the results of Gong, Lee et al. (2009) and Li et al. (2008) who observed Si containing oxides after annealing Al containing TRIP steels having 0.31% Si and 0.29% Si, respectively when using a similar process atmosphere (discussed in §2.3.3). Good reactive wetting was obtained at the -30 °C dp and this was attributed to the absence of Si containing oxides at the surface (Mahieu, De Cooman et al. 2002).



Figure 2.32: Schematic drawing of surface oxide coverage as a function of steel chemistry after annealing using a -30 °C dp N_2 - 5% H_2 atmosphere (Mahieu et al. 2004).

The effect of using the +10 °C/-50 °C dp process atmosphere was studied for a CMnSi steel and the CMnAl steels (Mahieu et al. 2001, Maki et al. 2003). For the CMnSi steel this process atmosphere resulted in improved galvanizing results when compared to the -30 °C dp. Fewer bare spots were observed, however, wetting was still considered poor. Improved galvanizing results were due to internal oxidation promoted

by the +10 °C dp used for the first part of the annealing cycle; this resulted in a lower concentration of Mn and Si at the steel surface prior to galvanizing. The surface oxide morphology was also different when using the +10 °C/-50 °C dp process atmosphere, rather than continuous oxide coverage which was observed at the -30 °C dp, individual oxide particles were present at the surface (Mahieu et al. 2001). For the CMnAl steels the +10 °C/-50 °C dp process atmosphere resulted in wetting problems with bare spots observed in the Zn coating. Prior to galvanizing, the steel surface was covered in MnO particles and these oxides caused the poor wetting observed at this process atmosphere (Maki et al. 2003).

Drillet et al. (2004) investigated the effect of steel chemistry, process atmosphere and annealing time on oxidation and galvanizing. Two Mn and Si containing steels were studied; both had 1.5 wt. % Mn and Si contents of 1.28 wt. % and 2.06 wt. %, respectively. These steels were 100% ferritic to eliminate the effect of having multiple phases present during annealing. When galvanizing these steels after annealing at 810 °C for 42 s using a -35 °C dp N₂ – 5% H₂ process atmosphere, the 1.28 wt. % Si steel had good wetting whereas poor wetting was observed for the 2.06 wt.% Si steel. These galvanizing results indicate that Si content strongly influences reactive wetting behaviour. The effect of annealing time was investigated for the 1.28 wt. % Si steel; when the annealing time was extended from 42 s to 300 s there were bare areas in the galvanized coating. For these steels the poor wetting was attributed to a layer of amorphous SiO₂ identified on the surface. It should be noted that Mn₂SiO₄ was also found on the surface of these steels. To isolate the effect of Si Drillet et al. (2004) studied a binary Fe - 1.5 wt. % Si alloy. Galvanizing results were obtained for three different dew points in order to determine the transition point between good and poor wetting. At the -35 °C dp there was no wetting by the liquid Zn bath, the -30 °C dp showed some wetting with a number of bare areas and the -26 °C dp atmosphere showed good wetting (all process atmospheres contained 5% H₂). As with the Mn-Si steels the poor wetting at the -35 °C dp was attributed to an amorphous SiO₂ film which completely covered the steel surface.

Drillet et al. (2004) also studied the effect of replacing Si with Al in the steel chemistry using a steel with 0.178 wt. % C, 1.6 wt. % Mn and 1.4 wt. % Al. Different process atmospheres were investigated to determine the transition between good and poor wetting. Good wetting was obtained when using a -55 °C dp ($N_2 - 5\%$ H₂) and poor wetting was obtained at a -60 °C dp ($N_2 - 5\%$ H₂). Poor wetting at the -60 °C dp was attributed to a continuous layer of Al₂O₃ with a thickness of 11.3 nm, whereas the Al₂O₃ layer at the -55 °C dp contained holes and had a thickness of 6.5 nm. An unwettable condition was reached when lowering the dew point for both the Si and Mn-Al steels resulting for a continuous oxide film which prevented contact between metallic Fe and the bath metal.

Vanden Eynde et al. (2004) used a surface oxide maturation process to prevent the formation of a continuous layer of Mn and Si rich oxides at the surface of a TRIP steel containing 0.11 wt. % C, 1.54 wt. % Mn and 1.32 wt. % Si. The surface oxide maturation process starts by first annealing the steel in an oxidizing atmosphere for iron $(N_2 - 1 \text{ volume } \% \text{ air with a } -30 \,^{\circ}\text{C} \text{ dp} \text{ at } 650 \,^{\circ}\text{C} \text{ for 1 second})$ in order to form a layer of

iron oxide on the original surface. The second step is to internally oxidize Mn and Si using a process atmosphere which is slightly oxidizing with respect to iron (N₂ with a dp in the range of -30 °C to +10 °C at 820 °C for 60 seconds). The Fe surface oxide was then reduced with the addition of H₂ to the process atmosphere on cooling prior to the steel entering the Zn bath. This process resulted in a low concentration of Mn and Si at the surface as a result of the formation of Mn and Si rich oxides below the steel surface. This in turn resulted in good reactive wetting of the substrate.

Despite the selective oxidation of Mn that occurs during annealing prior to galvanizing (see Figure 2.4) good reactive wetting can readily be obtained on Mn containing dual phase steels (Khondker et al. 2007, Meguerian and McDermid 2007, Meguerian 2007). Meguerian (2007) showed that reactive wetting is possible on substrates with Mn contents as high as 5 wt. %. Khondker et al. (2007) determined that it is thermodynamically possible for a thin MnO film to be reduced by the dissolved Al in the Zn bath as per the reaction shown in equation (2.17).

$$3MnO_{(s)} + 2[A1] \xrightarrow{460^{\circ}C} Al_2O_{3(s)} + 3[Mn]$$

$$(2.17)$$

A Gibbs energy minimization was performed which took into consideration the relative quantities of the reactants (*i.e.* the Zn (Al, Fe) bath is considerably larger than the quantity of MnO at the steel surface). The results of the Gibbs energy minimization are provided in Table 2.1 and indicate that it is possible for a 0.00002 g MnO film to be reduced by the Al in a 100 g Zn (Al, Fe) bath.

Reactants:		
Phase	Composition	Mass (g)
Liquid Zn-Al-Fe	99.78 wt.% Zn + 0.2 wt. % Al + 0.02 wt. % Fe	100
Solid MnO	MnO	0.00002
Products:		
Phase	Composition	Mass (g)
Liquid Zn-Al-Fe	99.799 wt.% Zn + 0.18946 wt. % Al + 0.011241 wt. % Fe + 0.15493×10^{-4} wt. % Mn	99.976
Solid Fe ₂ Al ₅ Zn _x	80.257 wt. % Fe ₂ Al ₅ + 19.743 wt. % Zn	2.4104×10^{-2}
Solid Al ₂ O ₃	Al_2O_3	9.5623×10^{-6}

Table 2.1: Gibbs energy minimization for reduction of a MnO film by the dissolved Al in a Zn (Al, Fe) bath (Khondker et al. 2007)

More recently, the reduction of manganese silicates $(xMnO \cdot SiO_2)$ by the dissolved Al in the Zn bath to form MnAl₂O₄ has been proposed by Gong, Song et al. (2009) according to the series of reactions shown in equations (2.18), (2.19) and (2.20). This two step process takes into account the reduction of Mn₂SiO₄ and MnSiO₃.

$$Mn_{2}SiO_{4(s)} + 2[Al] \rightarrow (MnO)MnSiO_{3(s)} + 2[Al]$$
(2.18)

$$MnSiO_{3(s)} + 2[Al] \rightarrow Al_2O_{3(s)} + [Mn] + [Si]$$
(2.19)

$$Mn_{2}SiO_{4(s)} + 2[Al] \rightarrow MnAl_{2}O_{4(s)} + [Mn] + [Si]$$
(2.20)

Gong, Song et al. (2009) observed $MnAl_2O_4$ at the steel/coating interface after dipping a martensitic steel having 0.15 wt. % C, 2.0 wt. % Mn and 0.33 wt. % Si in Zn baths with 0.13 and 0.2 wt. % Al at 460 °C. Prior to galvanizing amorphous SiO₂, amorphous $xMnO\cdot SiO_2$ (x<0.9) and crystalline $xMnO\cdot SiO_2$ (1<x<2) were identified at the steel surface. It was observed that only the crystalline $xMnO\cdot SiO_2$ phase was reduced to $MnAl_2O_4$.

The following conclusions can be drawn from the previous work on reactive wetting during galvanizing of TRIP steels:

- i) Si containing oxides can be detrimental for hot-dip galvanizing.
- ii) Replacement of Si by Al improves the reactive wetting behaviour.
- iii) Changing the oxygen partial pressure of the process atmosphere used during annealing prior to galvanizing changes the oxidation behaviour, thereby affecting the reactive wetting behaviour.
- iv) It is thermodynamically possible for MnO and crystalline xMnO·SiO₂
 (1<x<2) on the steel surface to be reduced by Al in the Zn bath resulting in good reactive wetting of Mn containing steels.

To date, there is no reliable method of predicting the reactive wetting behaviour for a given alloy and set of processing parameters. This is due to the large number of variables in the galvanizing process such as steel chemical composition, annealing time, annealing temperature and oxygen partial pressure of the process atmosphere. All of these variables will affect the chemistry of the oxides on the surface, the oxide thickness and the oxide morphology; this will in turn affect the reactive wetting behaviour. The relationship between oxide morphology and reactive wetting is one area in the current literature where data is lacking. Furthermore, only a limited number of studies link the steel microstructure or mechanical properties to the galvanizing results (Mahieu et al. 2001, Mahieu, De Cooman et al. 2002, Gong, Song et al. 2009).

3 RESEARCH OBJECTIVES

This study focused on two major areas: i) the effect of heat treatments compatible with hot-dip galvanizing on the microstructure and mechanical properties of TRIPassisted steels and ii) the selective oxidation and reactive wetting of TRIP-assisted steels by liquid Zn-Al-Fe (galvanizing) melts. The overall objectives were to determine processing parameters which provided both the desired TRIP steel mechanical properties and high quality galvanized coatings.

Studying the effect of heat treatments compatible with hot-dip galvanizing on the resulting microstructure and mechanical properties was limited to two high Al-low Si TRIP steels. The objective of this work was to determine whether heat treatments with a higher IBT temperature (465 °C) could produce a microstructure that contained a sufficient amount of high carbon retained austenite to produce the desired combination of strength and ductility. The effects of steel chemistry, intercritical annealing temperature and isothermal bainitic transformation time on microstructure and mechanical properties were investigated. The optimal thermal processing parameters were then used in subsequent oxidation and galvanizing experiments.

Selective oxidation and galvanizing of four TRIP-assisted steels with a variety of Si and Al contents were studied. The objectives were to study the effects of steel chemistry, oxygen partial pressure of the annealing atmosphere, annealing temperature and annealing time on the selective oxidation of the steel surface. The effects of steel chemistry and oxygen partial pressure of the annealing atmosphere on reactive wetting

during galvanizing were determined. The relationship between selective oxidation (including steel surface chemistry and surface oxide morphology) and reactive wetting was determined. The reactive wetting mechanisms were investigated.

4 EXPERIMENTAL METHOD

Experiments were conducted to focus on three major areas of study: i) analysis of the microstructure and mechanical properties of TRIP steels utilizing heat treatments compatible with hot-dip galvanizing, ii) analysis of the selective oxidation of the steel surface after annealing and prior to galvanizing and iii) analysis of galvanized samples.

4.1 Steel chemistry, fabrication and sample preparation

The experimental TRIP steel compositions are given in Table 4.1. Four TRIP steels with varied Si and Al contents were studied. The sum of the Si and Al content was kept constant at 1.5 wt. %. Experimental steels also had 0.2 wt. % C, 1.5 wt. % Mn and 0.02 wt. % Ti. The TRIP steels were fabricated at the CANMET Materials Technology Laboratory. The steel was cast, hot rolled to a thickness of 4 mm, pickled, sandblasted and cold rolled to a thickness of approximately 1.5 mm. The hot rolling start and finish temperatures were 1250 °C and 850 °C, respectively.

Table 4.1. Chemical composition of experimental TRH steels (weight 76)					
Alloy Name	С	Mn	Si	Al	Ti
1.5% Al	0.20	1.55	0.025	1.52	0.025
1.0% Al	0.20	1.52	0.45	1.0	0.021
1.0% Si	0.21	1.52	1.08	0.49	0.02
1.5% Si	0.20	1.50	1.47	0.006	0.018

Table 4.1: Chemical composition of experimental TRIP steels (weight %)

Experimental samples comprised 120 mm x 200 mm panels with the longitudinal axis of the sample parallel to the rolling and dipping direction. A uniform temperature and coating area on the panel of 90 mm \times 90 mm was centred in the lower portion of the

steel panel and only material from this area was analyzed. The uniform temperature and coating area is shown in Figure 4.1.



Figure 4.1: Uniform temperature and coating area on galvanized panels.

Prior to heat treatment, samples were degreased in a 2 % NaOH solution heated to 80 °C, NaOH was used to simulate the industrial process (Marder 2000). While immersed in the NaOH solution, samples were brushed with a plastic brush and wiped with paper towels to remove iron fines, other loose dirt and oils. After degreasing samples were rinsed with water, cleaned ultrasonically in isopropanol and dried with warm air. A final cleaning with acetone was performed immediately prior to the sample entering the galvanizing simulator.

4.2 McMaster Galvanizing Simulator

All heat treatments, oxidation and galvanizing experiments were carried out in the McMaster Galvanizing Simulator (MGS) (Iwatani-Surtec). This apparatus in shown in Figure 4.2 and a schematic drawing of the MGS is shown in Figure 4.3. The MGS consists of an atmosphere controlled column composed of several sections (described from top to bottom of the apparatus) (i) sample loading/cooling, (ii) sample heating, (iii) gas jet wiping and (iv) zinc pot. The sample loading/cooling section contains two parallel gas cooling platens. The heating section uses two furnaces: (i) a quartz lamp infrared (IR) furnace and (ii) a high frequency (HF) furnace; only the former was used in this work and the latter used for galvannealing. The sample heating/cooling thermal cycle was controlled using a type K (0.5 mm) thermocouple welded directly to the sample prior to the start of the experiment (location of the thermocouple is shown in Figure 4.1). Sample temperature measurements are accurate to within ± 2 °C. The two upper sections are separated from the gas jet wiping and zinc pot by an airlock. Gas jet wiping controls the coating weight using a N_2 gas slot jet with a flow rate of 500 L/min. In the present work this yielded an average coating weight of 70 g/m². The zinc pot consists of a resistance heated 50 kg graphite crucible controlled to within ± 2 °C using a conventional process controller. The zinc bath contained 0.20 wt. % dissolved Al and had an Fe content such that the bath was saturated with respect to $Fe_2Al_5Zn_x$ (McDermid et al. 2007). At the zinc bath surface a graphite dross removal system skimmed the surface of the bath immediately prior to immersion of the panel in the zinc bath. This removes $Fe_2Al_5Zn_x$ and oxides (top dross) floating on the surface of the bath, which

could affect the coating quality if not removed. At the right in Figure 4.2 is the dew point control system where a water saturated stream of gas was mixed with a dry stream of gas. Further to the right (not shown) is the gas mixing chamber where the flow rates of H_2 and N_2 were controlled and these gases were mixed to produce the desired gas composition.



Figure 4.2: The McMaster Galvanizing Simulator (MGS).



Figure 4.3: Schematic drawing of the McMaster Galvanizing Simulator (Chen 2007).

4.3 Heat treatment of TRIP steels for analysis of microstructure and mechanical properties

Analysis of the microstructure and mechanical properties using thermal cycles compatible with continuous hot-dip galvanizing was carried out on the two high Al – low Si TRIP steels (1.5% Al and 1.0% Al steels). Experimental heat treatments consisted of heating the sample to the intercritical annealing (IA) temperature at 10 °C/s, holding at the IA temperature for 120 s, cooling at 20 °C/s to the isothermal bainitic transformation (IBT) temperature of 465 °C, holding for 4, 30, 60, 90 or 120 seconds, cooling at 20 °C/s to approximately 150 °C and cooling to room temperature at a slower cooling rate (Figure 4.4 and Table 4.2). Two IA temperatures were tested for each steel, resulting in an intercritical annealing microstructure of 50% ferrite (α) – 50% austenite (γ) or 65% α –

35% γ (volume %). The IA temperatures were determined using Thermocalc software with the TCFE2 database and are summarized in Table 4.2 along with sample designations based on the alloy chemistry and volume percentage of intercritical austenite. The 50% α – 50% γ temperature was chosen to begin with an initially higher percentage of intercritical austenite for the purpose of obtaining a higher amount of retained austenite in the final microstructure. The 65% α – 35% γ temperature was chosen to begin with intercritical austenite with a higher initial carbon content in order to promote the formation of higher C content, metastable retained austenite.



Figure 4.4: Experimental thermal cycle.

Alloy Name	T1, IA Temperature [°C]	t1, IA Time [s]	T2, IBT Temperature [°C]	t2, IBT Time [s]	
1.5% Al (50% γ)	862 (50% γ)	120	165	4 30 60 90 120	
1.5% Al (35% γ)	795 (35% γ)	120	405	4, 50, 00, 90, 120	
1.0% Al (50% γ)	825 (50% γ)	120		4 30 60 00 120	
1.0% Al (35% γ)	770 (35% γ)	120	403	4, 50, 00, 90, 120	

Table 4.2: Summary of experimental heat treatments

4.4 Analysis of TRIP-assisted steel microstructure and mechanical properties

4.4.1 Scanning electron microscopy analysis of the steel microstructure and fracture surface

Scanning electron microscopy (SEM) was performed using a JEOL 7000F field emission SEM. SEM analysis was carried out on five sets of samples: i) cross-sections of the as-received steels (after cold rolling), ii) cross-sections after annealing, iii) crosssections of the post tensile testing samples in the uniform elongation region, iv) crosssections of the post tensile testing samples near the fracture surface and v) the fracture surface. For analysis of the steel cross-sections the samples were mounted in epoxy and polished using standard metallographic techniques with a 1 µm diamond suspension used as the final polishing step. The samples were etched with 2 % nitric acid in ethanol (2% nital); the etching time was approximately 10 seconds.

To distinguish between retained austenite and martensite in the microstructure, some samples were tempered for 2 hours based on the method described in Girault et al. (1998), where a tempering temperature of 250 °C was used in the present case rather than 200 °C. This heat treatment results in the precipitation of ε -carbides from martensite allowing the martensite and retained austenite to be distinguished. Only sample sets ii) and iii) were tempered. Both tempered and untempered samples were investigated for the as annealed microstructures (sample set ii)), to determine if carbide precipitation had occurred during holding at the IBT temperature. Carbide precipitation is a concern when using higher IBT temperatures as noted in § 2.2.4.

For all images of the steel microstructure, the rolling direction is parallel to the horizontal axis of the image. The acceleration voltages and working distances used are summarized in Table 4.3.

		1 21		
Sample type	Tempered or	Acceleration voltage	Working distance	
Sample type	untempered	untempered [keV]		
i) as received	Untempered	15	10	
ii) as annealed	Untempered	15 or 20	10	
ii) as annealed –	Tempered	10	6 or 10	
iii) after tensile testing in the uniform elongation region	Tempered	10	6 or 10	
iv) after tensile testing near fracture surface	Untempered	10	10	
v) fracture surface	Untempered	10	15	

Table 4.3: Summary of SEM parameters for different sample types

For the as annealed microstructures the tempered samples were used to distinguish between retained austenite and martensite. The volume percent of martensite was determined using image analysis. Nine SEM images at 5000X magnification were used for each steel and thermal cycle combination to improve the precision and accuracy of the data. Image analysis was carried out using Clemex Vision - Professional Edition – Version 5.0 image analysis software by Clemex Technologies Inc.

4.4.2 X-ray diffraction

Two-dimensional X-ray diffraction (XRD^2) (collection of powder XRD data with a 2D CCD detector) was used to measure the volume percent of retained austenite and % carbon in the retained austenite. A Smart Apex II system by Bruker AXS Inc. with a Mo Ka source ($\lambda = 0.71073$ Å) was used. The detector distance was 17.0 cm and was calibrated with corundum (Al₂O₃). The X-ray beam diameter was 500 μ m. The sample was rotated while collecting the data to minimize the effects of texture. The method used to calculate the amount of retained austenite followed ASTM E 975 - 03 (2003), but was modified to include martensite, where appropriate, through the addition of the martensite (101), (110), (002), (200), (112) and (211) peaks. The ASTM standard uses the ferrite (110), (200) and (211) peaks and the austenite (111), (200) and (220) peaks to calculate the volume % of retained austenite. The data was first processed using GADDS (General Area Detector Diffraction System) software by Bruker AXS Inc. In GADDS a χ integration was performed over the 2θ range of 18 to 38° to obtain an intensity vs. 2θ graph. The percent retained austenite was calculated using Topas software (Bruker AXS Inc.) from the intensity vs. 2θ data generated in GADDS. Using this software, the measured intensity was normalized with respect to the calculated structure factor for each phase and the percentage of each phase was calculated using the entire diffraction pattern. The error bars in the retained austenite measurement were calculated by Topas through comparison of the calculated and measured diffraction patterns. The austenite lattice

parameter (a) was also determined using Topas. From the measured lattice parameter the % of carbon in austenite could be calculated from equation (4.1). This equation is a combination of the equations of Ruhl and Cohen (1969) for Mn, Si and C and Dyson and Holmes (1970) for Al.

$$a = 3.572 + 0.0012(wt.\% Mn) - 0.00157(wt.\% Si) + 0.0056(wt.\% Al) + 0.033(wt.\% C) Å$$
(4.1)

XRD measurements were made on the steel cross-section to remove the effect of any variations in chemical composition or microstructure through the thickness of the sample. Samples were polished using 4000 grit SiC paper for the final step.

4.4.3 Tensile Testing

Tensile testing was performed on an Instron 10 kN Electromechanical Load Frame with Merlin software. The tensile samples were machined using Electrical Discharge Machining (EDM) to avoid heating or damage to the sample which could alter the microstructure prior to tensile testing. The samples were machined to the dimensions specified in ASTM E 8M-01ɛ2 (2001) for a subsize specimen with a gauge length of 25 mm. The sample width was 6 mm. A constant cross-head speed of 1 mm/minute was used for all tests. All tensile tests were performed at room temperature. An extensometer was used during tensile testing to measure sample extension.

In the study of the mechanical properties of TRIP steels the work hardening behaviour was important as it is an indicator of the retained austenite stability (see § 2.2.3). The work hardening behaviour was assessed by plotting the incremental work

hardening exponent (n_{incr}), calculated using equation (4.2) (Sachdev 1983), versus true strain.

$$n_{incr} = \frac{d(\ln \sigma)}{d(\ln \varepsilon)}$$
(4.2)

The work hardening behaviour, as calculated by n_{incr}, is useful for comparing the present results with the work hardening behaviour of TRIP-assisted steels reported in the literature (Jacques et al. 1998, Jacques, Girault, Harlet et al. 2001, Jacques, Furnémont, Mertens et al. 2001, Krizan et al. 2004, McDermid et al. 2005 and Mertens and McDermid 2005).

4.5 Selection of heat treatment and annealing atmosphere for surface analysis and galvanizing of experimental steels

The experimental thermal cycles used to study the oxidation and reactive wetting during galvanizing of the TRIP steels were chosen based on the mechanical properties results for the 1.5% Al and 1.0% Al steels. These results are discussed in § 5.4. For both of these steels the IA temperature that produced the 50% α – 50% γ microstructure and the IBT time of 120 s produced the desired combination of strength and ductility. These parameters were chosen for the four steel chemistries to be consistent with the amount of intercritical phases and annealing times. IA temperatures corresponding to 50% α – 50% γ (volume %) were calculated using Thermocalc software and the TCFE2 database and are shown in Table 4.4. The heating rate, cooling rate and IA time are the same as those specified in § 4.3. It should be noted that the microstructure and mechanical properties of

the two high Si TRIP steels (1.0% Si and 1.5% Si) were studied by Mertens and McDermid (2005, 2006) and are discussed in § 2.2.4.

In order to determine the effect of process atmosphere oxygen partial pressure on selective oxidation and galvanizing behaviour, three different annealing atmospheres were tested for each steel, as shown in Table 4.4. These annealing atmospheres will be distinguished by their dew point in the subsequent text. Oxygen partial pressure is strongly temperature dependent and was calculated as a function of steel IA temperature using the thermodynamic data of Fine and Geiger (1979) (Table 4.4).

Steel and Process Atmosphere Name	Dew Point [°C]	N ₂ Content [Volume %]	H ₂ Content [Volume %]	IA Temperature [°C]	pO ₂ at IA Temperature [atm]
1.5% Al -53 °C dp	-53	80	20	862	5.08E-25
1.5% Al -30 °C dp	-30	95	5	862	9.93E-22
1.5% Al +5 °C dp	+5	95	5	862	2.80E-19
1.0% Al -53 °C dp	-53	80	20	825	5.08E-25
1.0% Al -30 °C dp	-30	95	5	825	9.93E-22
1.0% Al +5 °C dp	+5	95	5	825	2.80E-19
1.0% Si -50 °C dp	-50	80	20	797	4.13E-26
1.0% Si -30 °C dp	-30	95	5	797	4.05E-23
1.0% Si +5 °C dp	+5	95	5	797	1.41E-20
1.5% Si -53 °C dp	-53	80	20	777	7.16E-27
1.5% Si -30 °C dp	-30	95	5	777	1.40E-23
1.5% Si +5 °C dp	+5	95	5	777	3.95E-21

Table 4.4: Annealing atmosphere compositions

The -30 °C dp process atmosphere was chosen as this dew point and H_2/N_2

content is typical of industrial continuous galvanizing lines. From § 2.3.4 it was shown that the combination dew point of +10 °C/-50 °C used by Mahieu et al. (2001) resulted in improved wetting when compared to a -30 °C dp for a high Si TRIP steel. It was not clear if it was the +10 °C or -50 °C dp that improved wetting. In the present work, both a

higher oxygen partial pressure atmosphere and a lower oxygen partial pressure atmosphere were chosen. The -53 °C or -50 °C dp was chosen as this is one of the lowest oxygen partial pressures that can be obtained in the MGS. The +5 °C dp was chosen to promote the internal oxidation of alloying elements.

An interrupted annealing cycle was used to study the selective oxidation of the steel surface as a function of annealing time and temperature. This interrupted annealing cycle is shown in Figure 4.5. The steel was quenched upon reaching the IA temperature (Heating), following the 120 s hold at the IA temperature (Annealing) and following 30, 60, 90 and 120 s of the IBT hold (30 s, 60 s, 90 s and 120 s, respectively).

Samples that were galvanized were dipped in the Zn (Al, Fe) bath for the final 4 s of the 120 s IBT hold.



Figure 4.5: Interrupted annealing cycle.

4.6 Analysis of the steel surface after annealing

To fully characterize the selective oxidation of the steel surface a variety of techniques were used. X-ray photoelectron spectroscopy (XPS) was used to identify the oxides on the steel surface and obtain elemental depth profiles. SEM was used to observe the surface oxide morphology. Transmission electron microscopy (TEM) was used to investigate the cross-section of the selectively oxidized steel surfaces. Scanning Auger microscopy (SAM) was used to determine the relationship between oxide morphology and elemental distribution on the steel surface. Samples using the interrupted annealing cycle were analyzed with XPS (Figure 4.5). Only samples using an IBT time of 120 s were analyzed with SEM and SAM. TEM analysis was limited to selected samples.

4.6.1 Sample preparation and storage

Samples that were brought through the annealing cycle (without galvanizing) in order to analyze the selective oxidation of the steel surface were polished to eliminate the effect of surface roughness. Samples analyzed with XPS were polished prior to annealing with 4000 grit SiC paper as the final step. For analysis of the oxide morphology by SEM, TEM and SAM the steel was polished to 0.05 µm prior to annealing. After annealing and removal of the sample from the MGS and prior to analysis with XPS, SEM, TEM and SAM, samples were immersed and stored in anhydrous isopropanol to minimize further oxidation of the surface.

4.6.2 X-ray photoelectron spectroscopy

XPS is a surface sensitive technique capable of determining chemical composition and chemical bonding state (for all elements except for H and He). This information is obtained via the photoelectric effect. Under ultra-high vacuum the specimen is bombarded with X-rays, from which a photoelectron is ejected from either a core level electron or a valence level electron when an X-ray is absorbed. The chemical composition of the sample and chemical bonding state are obtained from the binding energy. The kinetic energy of the photoelectron is measured and the binding energy is obtained from equation (4.3) (Briggs 2003, Briggs and Rivière 1983).

$$\mathbf{E}_{\mathbf{K}} = \mathbf{h}\,\boldsymbol{\nu} - \mathbf{E}_{\mathbf{B}} - \boldsymbol{\phi}_{sp} \tag{4.3}$$

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

XPS analysis of the steel surface and subsurface was performed for the six different times in the interrupted annealing cycle (Figure 4.5) to study the effect of annealing time and temperature on selective oxidation. XPS analysis was performed using a PHI Quantera XPS with an Al K α X-ray source (1486.6 eV (Briggs 2003)). XPS data was processed using MultiPak software (Version 6). The spot size used was 100 μ m and the take off angle was 45°. All spectra were calibrated using the metallic iron binding energy peak position of 706.62 eV. The binding energy values obtained are

accurate to within ± 0.1 eV and the accuracy of the chemical composition measurements are ± 5 % of the measured value in atomic % for each element. Depth profiles were obtained by Ar sputtering followed by analysis of the new surface. Depth measurements are accurate to ± 10 % of the sputtered depth.

4.6.3 SEM analysis of the surface oxide morphology

Oxide morphology was determined using SEM. SEM analysis was performed using a JEOL 7000F field emission SEM. An acceleration voltage of 7 keV and a working distance of 10 mm were used for all samples. All samples were sputter coated with gold to avoid sample charging. One exception was the 1.0% Al +5 °C dp steel which was coated with 5 nm platinum to avoid charging and improve the results obtained in backscattered electron mode when compared to those observed on this sample when coated in gold. Backscattered electron mode provides atomic number contrast allowing the film-type oxide rich areas to be identified on the steel surface. The detector used was a JEOL SM-54031 backscattered electron detector.

4.6.4 Scanning Auger microscopy

Scanning Auger microscopy (SAM) is a very surface sensitive technique, providing an elemental analysis of only the first few atomic layers of the sample surface (Grant 2003). SAM also has excellent spatial resolution (a probe diameter as small as 8 nm could be obtained with the instrument used) and was used to determine the relationship between oxide morphology and elemental distribution on the steel surface.
The chemical composition is obtained from the kinetic energy of the Auger electrons, which are characteristic of the atoms from which they were emitted. An Auger electron is generated by the process shown in Figure 4.6 for generating KL_2L_3 Auger electrons (Grant 2003, Briggs and Rivière 1983). An incident electron having sufficient energy ejects a core level electron, leaving a hole in that energy level (K electron energy level in Figure 4.6). This hole is then filled with an electron from an outer shell (in Figure 4.6 an electron from the L_2 level fills the hole) resulting in excess energy which can be used either to emit an X-ray or an Auger electron. The Auger electron comes from either the same energy level as the electron that filled the core level hole or a shallower energy level (L_3 in Figure 4.6). The energy of this electron is measured and is described by equation (4.4), again using the KL_2L_3 Auger electron as an example.

$$E_{KL_2L_3} = E_K - E_{L_2} - E_{L_3}$$
(4.4)

Where $E_{KL_2L_3}$ is the kinetic energy of the Auger electron and E_K , E_{L_2} and E_{L_3} are the binding energies of the electrons involved in the process.



Figure 4.6: Process of generating a KL_2L_3 Auger electron (adapted from Grant (2003) and Briggs and Rivière (1983)) i) an incident electron of sufficient energy ejects an electron from the K shell leaving a hole, ii) the hole in the K shell is filled by an electron from the L₂ energy level which results in excess energy, iii) the excess energy is used to emit an Auger electron from the L₃ level.

SAM data was collected using a JEOL JAMP-9500F Field Emission Auger Microprobe. The energy of the primary electron beam was 15 keV for all samples with the exception of the 1.0% Si +5 °C dp steel where 10 keV was used. The samples were tilted at 30° towards the electron analyzer. Auto probe tracking was used during the collection of elemental maps to eliminate sample drift. The signal intensity (I) was calculated using equation (4.5) to attenuate the effect of topography.

$$I = \frac{peak - background}{background}$$
(4.5)

Auger maps were collected at the steel surface and after Ar sputtering. The accuracy of the sputtering depth is $\pm 10\%$.

4.6.5 TEM analysis of the selectively oxidized steel surface

The cross-section of the steel surface after annealing was analyzed by TEM for selected samples to further investigate the selective oxidation behaviour. The TEM sample preparation technique is described in § 4.7.3 and the same TEM parameters were used as those described in § 4.7.4 for the galvanized samples.

4.7 Analysis of galvanized samples

The reactive wetting of the steel samples by the liquid Zn bath was quantified by analyzing the bare spots in the Zn overlay within the uniform coating and temperature area. SEM, electron backscatter diffraction (EBSD) and TEM analysis of the steel/coating interface were used to identify the interfacial reaction products, to determine if any oxides remained at the interface after galvanizing and to investigate the reactive wetting mechanism. Bend tests were performed to test coating adhesion.

4.7.1 Analysis of bare spots in the galvanized coating

Measurement of bare spots on the galvanized panels was performed using a Carl Zeiss Ltd. Stemi 2000-C Stereoscope and Northern Eclipse Version 6.0 image analysis software by Empix Imaging Inc. Images were captured using a magnification of 5X. The bare spot area was measured by manually selecting the bare spot perimeter. The measured bare spot area is accurate to within $\pm 0.01 \text{ mm}^2$.

4.7.2 SEM and EBSD analysis of the interfacial layer

The reactive wetting behaviour was also investigated by analyzing the steel/coating interface via SEM using an acceleration voltage of 5 or 10 keV. The interfacial layer on the galvanized panels was exposed for SEM analysis by two methods: i) stripping the zinc overlay with 10 volume % H₂SO₄ in water, which leaves both the Fe-Al and Fe-Zn intermetallics intact and ii) stripping with fuming HNO₃, which strips the zinc overlay and Fe-Zn intermetallics leaving any Fe-Al intermetallics intact. The stripping time for the 10% H₂SO₄ solution was approximately 60 s and the stripping time when using fuming HNO_3 was between 10 and 15 s. Samples were removed from the acid solutions periodically during stripping to visually assess the stripping progress. Stripping with 10% H₂SO₄ was stopped when a small amount of the Zn overlay remained at the centre of the sample. This solution did not uniformly strip the coating; at the centre of the sample the Zn overlay remained, around this area was a dark gray ring, which was the exposed layer of Fe-Zn and Fe-Al intermetallics and around the sample edges often only the steel substrate remained. Furning HNO₃ stripped the Zn overlay more uniformly. Samples were removed from the fuming HNO_3 when a bluish grey layer ($Fe_2Al_5Zn_x$) was visible. After dissolving the Zn overlay with acid, samples were rinsed in deionised water, rinsed in acetone and dried with warm air. It was usually optimal for the samples to be stripped with acid on the same day as they were to be studied by SEM or EBSD.

EBSD was used to identify the intermetallics in the Fe-Al inhibition layer. In EBSD the phases are identified by comparing the measured Kikuchi pattern to that

calculated from X-ray diffraction data from the literature. For the inhibition layer the measured Kikuchi patterns were compared with those for Fe₂Al₅ (Schubert et al. 1953), Fe₂Al₅Zn_x (Chen et al. 1992), FeAl₃ (also defined as FeAl_{3.2}) (Black 1955) and α -Fe (Kohlhaas et al. 1967). An example of a measured Kikuchi pattern and a calculated Kikuchi pattern (overlaid in blue) is shown in Figure 4.7 identifying this area as Fe₂Al₅Zn_x.



Figure 4.7: Kikuchi pattern for $Fe_2Al_5Zn_x$ generated by EBSD, the calculated diffraction pattern is overlaid in blue (Chen et al. 1992).

EBSD was performed using the JEOL 7000F field emission SEM which is equipped with an HKL Nordlys detector. Data processing was performed using Channel 5 (service pack 7) software. For EBSD an acceleration voltage of 20 keV was used. The specimen was tilted 70° towards the detector and the working distance was 20.0 mm. Ideally the EBSD samples should be highly polished, this is not possible for the present samples and contributed to the large fraction of the sample surface that could not be indexed.

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

TEM sample preparation was performed using FIB milling with an NVision 40 by Zeiss. FIB samples were prepared by Julia Huang at the Canadian Centre for Electron Microscopy. FIB was chosen as this technique is ideal to make site specific samples of the cross-section of the Fe-Zn interface (Goldstein et al. 2003). FIB works by sputtering material using Ga⁺ ions. Carbon was deposited over the FIB sample location as Zn is sputtered more easily than Fe and the carbon layer minimized preferential thinning of the Zn overlay. In the case of oxidized samples (not galvanized) carbon was deposited to protect the steel surface from any damage during sample preparation.

The different stages of FIB sample preparation are shown in Figure 4.8. First, carbon was deposited over the FIB sample location; this is the dark line that can be seen over the sample in Figure 4.8 a). Next two deep trenches were milled on either side of the sample (Figure 4.8 a)). This is followed by milling away the material around the sample so that only a small area of the sample is attached. The probe is then welded to the sample by carbon deposition (Figure 4.8 b)). The small region of the FIB sample that remained attached to the original specimen was milled away. The FIB sample was then placed on a Cu grid and welded to the grid by carbon deposition. The probe was then cut from the FIB sample (Figure 4.8 c)). Windows in the sample were thinned to be electron transparent for analysis by TEM (three windows are shown in Figure 4.8 d)).



Figure 4.8: Stages in typical FIB sample preparation of galvanized samples a) rough milling of trenches on either side of the sample, b) milling around the sample and welding of the probe to the sample, c) welding of the sample to the Cu grid and removing the probe and d) fine milling of three electron transparent windows on the sample.

4.7.4 TEM analysis of the steel-coating interface

TEM was performed with a JEOL 2010F TEM equipped with an Oxford INCA Pentafet energy dispersive X-ray (EDX) spectrometer. The acceleration voltage was 200 keV. EDX was performed in scanning transmission electron microscopy (STEM) mode with a probe size of 1 nm to obtain good spatial resolution. EDX was used for elemental mapping and for quantitative point analysis. The same procedure was used for TEM analysis of oxidized samples (1.5% Al +5 °C dp, 1.0% Al -53 °C dp and 1.0% Al +5 °C dp steels).

4.7.5 Testing of Coating adhesion by 180° Bend tests

Bend tests were conducted on galvanized panels to test coating adhesion. The bend test procedure followed the method described in ASTM A 653/A 653M - 03 (2003). No standard was available for the steel chemical compositions used in the present study. Parameters were chosen based on the steel substrate thickness and coating weight for a steel with a similar, but lower alloy content. The inner diameter of the bend was 4.5 mm and the width of the galvanized strip tested was 30 mm. The bend test die is shown in Figure 4.9 as well as schematic drawings of the sample before and after a force was applied to bend the sample via an arbor press. Coating adhesion was determined by visual inspection of the outer bend surface. The coating passed if no flaking or cracking of the coating was observed on the outer bend surface.

PhD Thesis – E.M. Bellhouse – McMaster – Materials Science and Engineering – 2010



Figure 4.9: a) picture of the bend test die, b) and c) schematic drawings of the bend test, b) before testing and c) after testing.

5 THE MICROSTRUCTURE AND MECHANICAL PROPERTIES OF HIGH AL – LOW SI TRIP-ASSISTED STEELS USING HEAT TREATMENTS COMPATIBLE WITH HOT-DIP GALVANIZING

The effects of steel chemistry, intercritical annealing (IA) temperature and isothermal bainitic transformation (IBT) time on microstructure and mechanical properties were investigated when using thermal cycles compatible with continuous hotdip galvanizing. The purpose of this work was to develop thermal cycles to be used in subsequent oxidation and galvanizing experiments that produce the desired TRIP steel mechanical properties. This work was performed for the 1.5% Al and 1.0% Al steels. The microstructure and mechanical properties of the 1.0% Si and1.5% Si steels were investigated previously and are discussed in the literature review in § 2.2.4 (Mertens and McDermid 2005, Mertens and McDermid 2006).

5.1 As-received microstructures

The as-received cold rolled microstructures are shown in Figure 5.1. For all alloys the microstructure consisted of ferrite and pearlite. These phases are indicated in Figure 5.1 a) where F = ferrite and P = pearlite. Grains were elongated due to cold rolling. Figure 5.1 a) and b) shows the 1.5% Al steel and 1.0% Al steel, respectively. The microstructure and mechanical properties of these two high Al – low Si TRIP steels were studied as well as the selective oxidation and galvanizing behaviour. The 1.0% Si steel and 1.5% Si steel as-received microstructures are shown in Figure 5.1 c) and d),

respectively. The selective oxidation and galvanizing behaviour of these two higher Si TRIP steels was also studied and will be discussed in Chapter 6.



Figure 5.1: As-received microstructures of the experimental TRIP steels a) 1.5% Al steel, b) 1.0% Al steel, c) 1.0% Si steel and d) 1.5% Si steel (F = ferrite and P = pearlite).

5.2 SEM analysis of the steel microstructure after annealing

The TRIP steel microstructures for each alloy, IA temperature and IBT time are shown in Figures 5.2 through 5.5. Figure 5.2 shows the 1.5% Al ($35\% \gamma$) steel microstructures, Figure 5.3 shows the 1.5% Al ($50\% \gamma$) steel microstructures, Figure 5.4 shows the 1.0% Al ($35\% \gamma$) TRIP steel microstructures and Figure 5.5 shows the 1.0% Al ($50\% \gamma$) TRIP steel microstructures. Figures 5.2 through 5.5 a) are for an IBT time of 4 s,

b) for 30 s, c) for 60 s, d) for 90 s and e) for 120 s. The phases in the microstructure are labelled in Figure 5.2 a) and b) where F = ferrite, A = retained austenite, M = thermal martensite and B = bainitic ferrite. The matrix comprised ferrite, dispersed within the matrix were bainitic ferrite, retained austenite and sometimes thermal martensite. Martensite and retained austenite are shown in relief. Martensite and retained austenite were distinguished from one another by tempering using the procedure described in § 4.4.1; tempering of martensite results in the precipitation of ε -carbides and retained austenite remains unchanged. Ferrite and bainitic ferrite are distinguished from one another by their morphology; ferrite is equiaxed and bainitic ferrite is in the form of lamellae located between plates of retained austenite or martensite.

In general, larger amounts of thermal martensite were observed in the microstructure at the IBT time of 4 s when compared to the higher IBT times (Figure 5.2 through Figure 5.5 a)). This was shown most clearly for the 1.0% Al (50 % γ) steel where a band of thermal martensite grains runs across the lower portion of Figure 5.5 a). For the two steel chemistries and both IA temperatures the microstructures were quite similar for IBT times of 30 s through 120 s (Figure 5.2 through Figure 5.5 b) – e)). For the 1.5% Al (50% γ) steel and 1.0% Al (50% γ) steel a small amount of thermal martensite was still observed in the microstructure at IBT times of 30, 60 and 90 s (Figure 5.3 b) – d) and Figure 5.5 b) – d)). Image analysis and XRD were necessary to study any trends observed in the volume percentage of thermal martensite and retained austenite (Figure 5.7 and Figure 5.8).



Figure 5.2: SEM images of the 1.5% Al $(35\% \gamma)$ microstructure, tempered at 250 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s (F = ferrite, A = retained austenite, M = thermal martensite and B = bainitic ferrite).



Figure 5.3: SEM images of the 1.5% Al $(50\% \gamma)$ microstructure, tempered at 250 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s.



Figure 5.4: SEM images of the 1.0% Al $(35\% \gamma)$ microstructure, tempered at 250 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s.



Figure 5.5: SEM images of the 1.0% Al (50% γ) microstructure, tempered at 250 °C for 2 hours and etched using 2% nital, for IBT times of a) 4 s, b) 30 s, c) 60 s, d) 90 s and e) 120 s.

The untempered microstructures were investigated to determine if carbide

precipitation occurred during the IBT, which is a concern when using higher IBT

temperatures. Carbide precipitation was observed in the 1.5% Al and 1.0% Al steel when using the 35% γ IA temperature at the IBT times of 90 s and 120 s. In these samples, it should be noted that carbides were not a major constituent of the microstructure. Examples of carbide precipitation are shown in Figure 5.6 a) for the 1.5% Al (35% γ) steel and IBT time of 90 s and b) for the 1.0% Al (35% γ) steel and IBT time of 120 s.



Figure 5.6: SEM images of selected samples where carbide precipitation was observed, samples were not tempered and were etched with 2% nital a) 1.5% Al (35% γ) and IBT time of 90 s and b) 1.0% Al (35% γ) and IBT time of 120 s.

Trends in the amount of thermal martensite in the steel microstructure as a function of IA temperature and IBT time for the 1.5% Al and 1.0% Al steel were determined using image analysis of the tempered microstructures. These results are shown in Figure 5.7 a) and b) for the 1.5% Al steel and 1% Al steel, respectively. The error bars in Figure 5.7 represent the 95% confidence interval of the measurements made on nine fields for each thermal cycle. The percentage of thermal martensite generally decreased with increasing IBT time for both steel compositions and IA temperatures. One exception was the 1.5% Al (50% γ) where the amount of thermal martensite

remained almost constant for the IBT times of 4 s through 90 s and then decreased at the IBT time of 120 s.



Figure 5.7: Percentage of thermal martensite as determined by image analysis of the TRIP steel microstructure, a) 1.5% Al steel and b) 1.0% Al steel for both IA temperatures.

5.3 XRD analysis of the volume percent retained austenite and retained austenite carbon content

The volume % retained austenite and the retained austenite carbon content were determined using X-ray diffraction; these results are shown in Figures 5.8 and 5.9, respectively. The volume % retained austenite for the 1.5% Al steel at both IA temperatures did not show a significant dependence on IBT time (Figure 5.8 a)) nor did the carbon content of the retained austenite (Figure 5.9 a)). The volume % retained austenite of the 1.0% Al steel increased with increasing IBT time (Figure 5.8 b)). A larger increase in the amount of retained austenite with increasing IBT time was observed for the 50% γ IA temperature when compared to the 35% γ IA temperature. For the 1.0% Al steel the retained austenite carbon content increased slightly with increasing IBT times for the 50% γ IA temperature and was relatively insensitive to IBT time for the 35% γ IA temperature (Figure 5.9 b)). The smallest amount of retained austenite was observed for the 1.0% Al (50% γ) steel at the 4 s IBT time (Figure 5.8 b)), these process parameters also resulted in the largest amount of thermal martensite in the microstructure (Figure 5.7 b)).



Figure 5.8: Volume % of retained austenite as a function of the IBT time as measured by X-ray diffraction, a) 1.5% Al steel and b) 1.0% Al steel. Error bars were determined by comparison of measured and calculated diffraction patterns.



Figure 5.9: Retained austenite carbon content as a function of the IBT time as determined by X-ray diffraction, a) 1.5% Al steel and b) 1.0% Al steel.

5.4 Tensile testing

The tensile results are shown in Figure 5.10; each graph shows the effect of IBT time on the mechanical properties for a given steel chemistry and IA temperature. Figure 5.10 a) and b) shows results for the 1.5% Al ($35\% \gamma$) steel and 1.5% Al ($50\% \gamma$) steel, respectively. Figure 5.10 c) and d) shows the tensile results for the 1.0% Al ($35\% \gamma$) steel and 1.0% Al ($50\% \gamma$) steel, respectively. All tensile curves are for true stress and true strain and are plotted to the point of necking or plastic instability, as determined by the Considère criterion, shown in equation (5.1):

$$\frac{\mathrm{d}\sigma}{\mathrm{d}\varepsilon} = \sigma \tag{5.1}$$

A summary of the tensile results (yield strength, tensile strength and uniform elongation) for the average of three trials is provided in Figure 5.11, allowing general trends for the effect of steel chemistry, IA temperature and IBT time to be observed more easily. The summary of mechanical properties results for the 1.5% Al ($35\% \gamma$) steel and 1.5% Al ($50\% \gamma$) steel are shown in Figure 5.11 a) and b), respectively. The results for the 1.0% Al ($35\% \gamma$) steel and 1.0% Al ($50\% \gamma$) steel are provided in Figure 5.11 c) and d), respectively.

The general trends when increasing the IBT time for both steels and IA temperatures were an increase in yield strength, an increase in yield point elongation, an increase in uniform elongation and a decrease in tensile strength (Figure 5.10 and Figure 5.11). One exception was the 1.5% Al (50% γ) steel at the IBT times of 30 and 60 s, where the tensile strength was lower at the 30 s IBT time (Figure 5.10 b) and Figure 5.11

b)). Analysis of the effect of IA temperature showed that the 50% γ IA temperature generally resulted in higher uniform elongations than the 35% γ IA temperature. IA temperature had little effect on yield strength or tensile strength. Comparing the two steel chemistries it was observed that the 1.0% Al steel generally had a higher tensile strength and lower ductility than the 1.5% Al steel.

The work hardening behaviour corresponding to the tensile curves in Figure 5.10 is shown in Figure 5.12. The work hardening behaviour as shown by n_{incr} indicates retained austenite stability. A value of n_{incr} that is initially high and decreases rapidly with increasing strain is characteristic of dual phase steels. The same work hardening behaviour is observed in TRIP-assisted steels that have retained austenite with poor stability that transforms to martensite at low values of strain. A value of n_{incr} that is initially lower and increases gradually with increasing strain or remains high at higher strains is characteristic of TRIP steels having retained austenite that transforms gradually with increasing strain (Jacques et al. 2006). The majority of results obtained indicate the presence of retained austenite of low stability which transformed to martensite at low values of strain (Figure 5.12). However, when using the 50% γ IA temperature and longer IBT times, the desired TRIP steel work hardening behaviour and, therefore, an excellent combination of strength and ductility were obtained. For the 1.5% Al (50% γ) steel the desired mechanical properties were obtained for the 90 s and 120 s IBT times. For the 90 s IBT time the tensile strength was 895 MPa and the uniform elongation was 0.26 and for the IBT time of 120 s the tensile strength was 880 MPa and the uniform elongation was 0.27 (Figure 5.11 b)). For the 1.0% Al (50% γ) steel the desired

mechanical properties were obtained at the IBT time of 120 s with a tensile strength of 1009 MPa and a uniform elongation of 0.22 (Figure 5.11 d)).



Figure 5.10: Tensile results plotted to the point of necking a) 1.5% Al (35% γ) steel, b) 1.5% Al (50% γ) steel, c) 1.0% Al (35% γ) steel and d) 1.0% Al (50% γ) steel, IBT times (t2) are indicated in the legend of each graph.



Figure 5.10 continued.



Figure 5.11: Summary of mechanical properties with respect to isothermal bainite transformation time, σ_T is the tensile strength, σ_Y is the yield strength and ε_U is uniform elongation, a) 1.5% Al (35% γ) steel, b) 1.5% Al (50% γ) steel, c) 1.0% Al (35% γ) steel and d) 1.0% Al (50% γ) steel.



Figure 5.11 continued.



Figure 5.12: Strain hardening behaviour shown by n_{incr} corresponding to the tensile results shown in Figure 5.10 a) 1.5% Al (35% γ) steel, b) 1.5% Al (50% γ) steel, c) 1.0% Al (35% γ) steel and d) 1.0% Al (50% γ) steel, IBT times (t2) are indicated in the legend of each graph.



Figure 5.12 continued.

5.5 SEM analysis of post tensile testing specimens

After tensile testing the sample microstructures were analyzed in the uniform elongation region with SEM to verify the occurrence of the TRIP effect. Cross-sections of tensile specimens were analyzed near the fracture surface to study preferential sites of void nucleation and crack formation. Also, the fracture surface was analyzed on samples having the desired TRIP steel mechanical properties.



Figure 5.13: The steel microstructure after tensile testing (uniform elongation region) tempered at 250 °C for 2 hours and etched using 2% nital a) 1.5% Al ($35\% \gamma$) steel, b) 1.5% Al ($50\% \gamma$) steel, c) 1.0% Al ($35\% \gamma$) steel and d) 1.0% Al ($50\% \gamma$) steel, all samples shown used an IBT time of 120 s.

The post tensile testing microstructures in the uniform elongation region are shown in Figure 5.13 for samples using an IBT time of 120 s. Figure 5.13 a) shows the 1.5% Al (35% γ) steel, b) the 1.5% Al (50% γ) steel, c) the 1.0% Al (35% γ) steel and d) the 1.0% Al (50% γ) steel. For all samples the microstructure shows that the majority of retained austenite has transformed to martensite. Any retained austenite that did remain after tensile testing has a lamellar morphology and is located between bainite laths. Retained austenite in this morphology following deformation has also been observed by Mark (2007) and Jacques, Ladrière et al. (2001). It should be noted that samples at all IBT times were analyzed and yielded similar results.

X-ray diffraction was also performed in the uniform elongation region of the post tensile testing samples. The amount of retained austenite in these samples was too small to be quantified accurately, therefore, these results are not shown. This is in agreement with the SEM analysis of the post tensile testing samples shown in Figure 5.13.

SEM images of the cross-section of the tensile samples near the fracture surface are shown in Figure 5.14. It should be noted that these samples were not tempered as it was known that the vast majority of retained austenite had transformed to martensite (Figure 5.13). In Figure 5.14 a) the cross-section of the fracture surface of the 1.5% AI ($35\% \gamma$) steel at the IBT time of 60 s is shown. The fracture surface generally bends around the harder phases, showing that fracture was propagated in the ferrite matrix and at the interface between ferrite and harder martensite grains. Figure 5.14 b) shows the 1.5% AI ($35\% \gamma$) steel with an IBT time of 90 s. The region shown in this sample reveals that voids were nucleated and propagated along bands of closely spaced martensite

particles. For all processing parameters voids generally occurred at the interface between ferrite and a harder phase (likely martensite). Rarely were voids observed within the ferrite matrix or within martensite grains. Figure 5.14 c) shows the 1.5% Al (50% γ) steel with the IBT time of 90 s at a lower magnification, showing that the bands of voids propagated along the tensile axis. The same void formation and crack propagation mechanisms were observed for both alloy compositions and IA temperatures at all IBT times and, therefore, only a selection of samples are shown in Figure 5.14.



c)

Figure 5.14: SEM images of the cross-section of fractured tensile samples showing preferential sites for void formation and crack propagation a) 1.5% Al (35% γ) steel and IBT time of 60 s, b) 1.5% Al (35% γ) steel and IBT time of 90 s and c) 1.5% Al (50% γ) steel and IBT time of 90 s.

The fracture surface was studied via SEM for the three samples that had the desired TRIP steel work hardening behaviour, strength and ductility as discussed in § 5.4 (Figure 5.15). For these processing conditions the fracture surface had a dimpled appearance characteristic of ductile fracture. Figure 5.15 a) and b) shows the fracture surface of the 1.5% Al (50% γ) steel with an IBT time of 120 s. In Figure 5.15 a) there are some hard particles (likely martensite) protruding from the fracture surface, showing decohesion between ferrite and martensite (indicated by an arrow). Hard particles were also observed protruding from the surface (indicated by an arrow) in Figure 5.15 c) which shows the fracture surface of the 1.5% Al (50% γ) steel at the IBT time of 90 s. The fracture surface of the 1.0% Al (50% γ) steel at the IBT time of 120 s is shown in Figure 5.15 d), again the surface had a dimpled appearance characteristic of ductile fracture.



Figure 5.15: SEM images of the fracture surface a) and b) 1.5% Al (50% γ) steel and IBT time of 120 s, c) 1.5% Al (50% γ) steel and IBT time of 90 s and d) 1.0% Al (50% γ) steel and IBT time of 120 s, arrows indicate regions where a harder phase, such as martensite, is visibly protruding from the ductile ferrite matrix showing decohesion between the phases.

5.6 Discussion of microstructure and mechanical properties

The effect of IA temperature and IBT time on the microstructure and mechanical properties was studied for two high Al – low Si TRIP-assisted steels; one having 1.5% Al and almost no Si and the other having 1.0% Al and 0.5% Si. Two different IA temperatures were tested for each alloy corresponding to 35% intercritical austenite and 50% intercritical austenite. Five different IBT times were tested for each alloy and IA

temperature combination. Short IBT times of 4, 30, 60, 90 and 120 s were used at an IBT temperature of 465 °C in order for the thermal cycle to be compatible with hot-dip galvanizing.

The effect of IBT time, IA temperature and steel chemistry on the steel microstructure was determined by SEM (Figure 5.2 to Figure 5.7) and XRD (Figure 5.8 and Figure 5.9). The results revealed that the microstructure consisted of a ferrite matrix with bainitic ferrite, retained austenite and sometimes thermal martensite. At the $35\% \gamma$ IA temperature and IBT times of 90 and 120 s carbide precipitation was observed for both steel chemistries, where carbides comprised only a very minor constituent of the microstructure (Figure 5.6).

As the IBT time was increased the amount of thermal martensite in the microstructure decreased (Figure 5.7). During the bainite reaction C is partitioned to austenite, thereby increasing the austenite stability and decreasing the amount of thermal martensite in the final microstructure (Jacques et al. 1998). The amount of thermal martensite decreased rapidly with increasing IBT time for the 1.5% Al ($35\% \gamma$) steel and the 1.0% Al steel at both IA temperatures. For the 1.5% Al ($50\% \gamma$) steel the amount of thermal martensite in the microstructure remained approximately constant over the IBT times of 4 through 90 s and then decreased to almost zero at the IBT time of 120 s. This could be due to the higher M_S temperature as a result of the higher Al content in the steel (De Cooman 2004) as well as the higher amount of intercritical austenite available to transform to martensite. The amount of thermal martensite was generally higher at the 50% γ IA temperature than at the 35% γ IA temperature for a given IBT time. This is due
to the higher amount of austenite available to transform to martensite upon cooling and the initially lower carbon content of austenite at the 50% γ IA temperature, decreasing the stability of the austenite.

The amount of retained austenite in the microstructure increased with increasing IBT time at both IA temperatures for the 1.0% Al steel (Figure 5.8 b)). The increase in the amount of retained austenite was greater for the 1.0% Al (50% γ) steel, however, the retained austenite content of the 1.0% Al $(35\% \gamma)$ steel was higher. This was likely due to the higher initial carbon content of the austenite at the 35% γ IA temperature. A slight increase in retained austenite carbon content with increasing IBT time was also observed for the 1.0% Al (50% γ) steel (Figure 5.9 b)). The increasing amount of retained austenite and increasing austenite carbon content with increasing IBT times was due to the rejection of C into austenite during the progression of the bainite reaction, thereby increasing the austenite stability (Jacques et al. 1998). The 1.5% Al steel did not show the same dependence on IBT time for the amount of retained austenite or the retained austenite carbon content as was observed for the 1.0% Al steel; *i.e.* both were generally independent of IBT time (Figure 5.8 a) and Figure 5.9 a)). However, the change in n_{incr} with increasing IBT times, particularly for the 50% γ IA temperature, implies that retained austenite stability increased with increasing IBT time for the 1.5% Al steel (Figure 5.12). A value of n_{incr} that increases gradually or remains constant with increasing values of strain implies a sufficient amount of stable retained austenite which transforms gradually to martensite with increasing strain (Jacques et al. 2006, Jacques, Furnémont, Mertens et al. 2001).

The trends for the effect of increasing IBT time on mechanical properties were a decrease in tensile strength, an increase in uniform elongation, an increase in yield strength (Figure 5.11) and an increase in yield point elongation (Figure 5.10). One discrepancy in these trends was for the 1.5% Al (50% γ) steel at the 30 s and 60 s IBT times, where the 60 s IBT time sample showed a higher tensile strength.

The 1.0% Al (50% γ) steel and 4 s IBT time had the highest amount of thermal martensite (Figure 5.7 b)) and lowest amount of retained austenite (Figure 5.8 b)) in the microstructure (i.e. a dual phase steel) and therefore had the mechanical properties of a dual phase steel. This included continuous yielding (Figure 5.10 d)) (Sakaki et al. 1983, Hansen and Pradhan 1981) and an initially high work hardening rate that decreased rapidly with increasing strain (Figure 5.12 d)) (Jacques et al. 2006). The other steels at the 4 s IBT time had higher amounts of thermal martensite in the microstructure when compared to the other IBT times for these steels (Figure 5.7) but did not have continuous yielding (Figure 5.10 a) - c)). A sufficient amount of martensite in the microstructure is necessary for the occurrence of continuous yielding, the exact amount of martensite required will depend on other variables such as ferrite and martensite grain size, ferrite solute carbon content and the cooling rate used below the M_S temperature (Sudo and Tsukatani 1985, Hansen and Pradhan 1981). The work hardening behaviour of these steels at an IBT time of 4 s was characteristic of dual phase steels (Figure 5.12 a) - c)) (Jacques et al. 2006). An increase in yield point elongation was observed for all steels with increasing IBT times (Figure 5.10); this is characteristic of decreasing amounts of

thermal martensite in the microstructure (Sudo and Tsukatani 1985) and is in agreement with the results provided in Figure 5.7.

It was determined that the IA temperature had little effect on yield strength or tensile strength when comparing samples with the same steel chemistry and IBT time. For the 1.5% Al and 1.0% Al steels the 50% γ IA temperature resulted in higher uniform elongation than the 35% γ IA temperature, particularly at longer IBT times (Figure 5.10 and Figure 5.11).

In general, the 1.0% Al steel had a higher strength and lower ductility than the 1.5% Al steel when comparing the same IA temperature and IBT time. The higher strength of the 1.0% Al steel was attributed to the 0.5 wt. % Si in this steel which provided solid solution strengthening (Takeuchi 1969, Pickering 1978). The effect of further increasing the Si content and decreasing the Al content on the mechanical properties obtained using thermal cycles compatible with hot-dip galvanizing is shown when comparing the present results with those of Mertens and McDermid (2005, 2006), discussed in § 2.2.4. The mechanical properties obtained for the 1.0% Si steel and 1.5% Si steel are plotted together with the 1.5% Al steel and 1.0% Al steel in Figure 5.16. The trend of decreased ductility with increasing Si content and decreasing Al content continued when including the mechanical properties of the 1.0% Si and 1.5% Si TRIP steels. Similar strengths were obtained for the 1.5% Si, 1.0% Si and 1.0% Al steels (Figure 5.16). Based on these results it is shown that when using heat treatments compatible with hot-dip galvanizing the high Al – low Si TRIP steels (1.5% Al and 1.0%

Al steels) provide a better combination of strength and ductility than the higher Si grades (1.0% Si and 1.5% Si steels).



Figure 5.16: Summary of mechanical properties comparing the combination of strength and ductility obtained for the 1.5% Al and 1.0% Al steels investigated in the present study to the 1.0% Si and 1.5% Si steels investigated by Mertens and McDermid (2005, 2006).

The thermal processing parameters yielding the best combinations of strength and ductility are summarized in Table 5.1. These thermal cycles resulted in the work hardening behaviour characteristic of TRIP-assisted steels produced using conventional thermal cycles (*i.e.* having lower IBT temperatures) with sufficient amounts of stable retained austenite that transformed gradually during straining to martensite (Jacques, Girault, Harlet et al. 2001, Jacques, Furnémont, Mertens et al. 2001). For both steels the 50% γ IA temperature and an IBT time of 120 s provided the optimal combination of strength and ductility and, therefore, this thermal cycle was used for subsequent oxidation and galvanizing experiments for the 1.5% Al and 1.0% Al steels. The same thermal cycle was used for the 1.0% Si and 1.5% Si steels in the oxidation and galvanizing experiments to isolate the effects of steel chemistry and oxygen partial pressure of the annealing atmosphere. As shown in Table 5.1 the 1.5% Al (50% γ) steel at the 90 s IBT time also provided the desired combination of strength and ductility.

Alloy	IA temperature [°C]	IBT time [s]	UTS [MPa]	uniform elongation	UTS ×uniform elongation [MPa]
1.5% Al	862 (50% γ)	90	895	0.26	233
1.5% Al	862 (50% γ)	120	880	0.27	238
1.0% Al	825 (50% γ)	120	1009	0.22	222

Table 5.1: Summary of optimal mechanical properties

The occurrence of the TRIP effect was verified by SEM and XRD. The SEM results provided in Figure 5.13 show that the majority of retained austenite transformed to martensite during deformation. This is in agreement with the XRD results where the amount of retained austenite was too low to be quantified accurately in the post tensile testing samples. The retained austenite that did remain in the microstructure was observed between bainite lamellae (Figure 5.13). Retained austenite in this morphology following deformation has also been observed by several authors (Mark 2007, Jacques, Ladrière et al. 2001). As well as the carbon content of the retained austenite, it is suggested that the retained austenite stability also depends on the retained austenite grain size and the hardness of the surrounding phases (Mark 2007, Jacques, Ladrière et al. 2001, Wang and Van Der Zwaag 2001, Sugimoto et al. 1993).

The fracture behaviour was investigated by studying the cross-section of the post tensile testing specimens adjacent to the fracture surface to determine the preferential sites for void nucleation and crack growth (Figure 5.14). It was found that voids generally nucleated at the interface between ferrite and martensite (Figure 5.14 b)). These cracks propagated along bands of closely spaced martensite particles along the interface between ferrite and the harder phase (Figure 5.14 b)), where these cracks generally occurred parallel to the tensile axis (Figure 5.14 c)). The cross-section of the fracture surface, shown in Figure 5.14 a), shows that fracture generally propagated in ferrite, bending around martensite particles. This fracture behaviour is in agreement with the observations of several authors (Zhang et al. 2007, Yu et al. 2006, Furnémont et al. 2001) who have also found that cracks propagated in ferrite, bending around the harder propagated in ferrite, bending around the tracks propagated in ferrite, bending around that cracks propagated in ferrite, bending around the tracks propagated in ferrite, bending around the tracks propagated in ferrite, bending around the tracks propagated in ferrite, bending around the harder phases. Cracks formed within martensite grains have also been observed previously (Furnémont et al. 2001).

The fracture surface was investigated on those samples having the desired TRIPassisted steel microstructure and mechanical properties, listed in Table 5.1, where these results are shown in Figure 5.15. It was shown that for these samples the fracture surface had a dimpled appearance characteristic of ductile fracture, in agreement with the fracture behaviour of TRIP steels reported by De Cooman (2004). In Figure 5.15 a) and c) hard particles were observed protruding from the fracture surface and are indicated by arrows. These were likely martensite grains in areas where fracture propagated at the interface between ferrite and martensite.

It was shown that it is possible to obtain a sufficient amount of stable retained austenite using a thermal cycle having an IBT temperature of 465 °C for the 1.5% Al and 1.0% Al TRIP steels. The desired combination of work hardening behaviour, strength and ductility were obtained when using the 50% IA temperature and IBT times of 90 s and 120 s for the 1.5% Al steel and IBT time of 120 s for the 1.0% Al steel.

6 SELECTIVE OXIDATION AND REACTIVE WETTING OF THE STEEL SURFACE

The effect of oxygen partial pressure, annealing time, annealing temperature and steel chemistry on the selective oxidation of the steel surfaces was studied. The selective oxidation behaviour was then related to the reactive wetting results and the reactive wetting mechanism was determined.

6.1 Selective oxidation of the steel surface

The selective oxidation of the steel surface was studied using XPS, SEM, SAM and TEM. Using this variety of techniques the surface chemistry and oxide morphology were determined. All oxidation results presented were obtained following the IBT time of 120 s unless indicated otherwise.

6.1.1 XPS analysis

XPS was used to determine the surface chemistry and perform elemental depth profiles.

6.1.1.1 Identification of oxides on the steel surface

XPS was used to identify the oxides on the steel surface; these results are shown in Table 6.1. The oxides were identified by comparing the measured binding energies to those in the literature for the following oxides: Al₂O₃ (Strohmeier and Hercules 1984), MnO (Strohmeier and Hercules 1984), MnAl₂O₄ (Strohmeier and Hercules 1984), Mn₂SiO₄ (Casey et al. 1993, Parezanović and Spiegel 2005, Vanden Eynde et al. 2004,

Van De Putte et al. 2008) and SiO₂ (Parezanović and Spiegel 2005, Vanden Eynde et al. 2004, Finster 1998, Van De Putte et al. 2008). A list of binding energies compiled from the literature is provided in Appendix B. The major limitation to identifying the oxides using XPS is that binding energy data may not be available for all of the compounds on the surface, for example, complex oxides containing Mn, Si and Al and MnSiO₃. Also, $MnAl_2O_4$ cannot be distinguished from Al_2O_3 and MnO using the binding energy (Strohmeier and Hercules 1984), therefore the SAM results discussed in § 6.1.2 were used to determine whether $MnAl_2O_4$ was present.

Table 6.1: Identification of oxides on the steel surface using XPS (after sputtering 5 nm)							
Steel and		Measured B	Major Oxide Phases				
Atmosphere	Al 2p	Mn 2p _{3/2}	Mn 2p _{1/2}	Si 2p	O 1s	Present (Minor Oxides)	
1.5% Al	74 7	6/1 0	654.1	102.0	531.6	Al ₂ O ₃ , MnO, MnAl ₂ O ₄	
-53 °C dp	/ 4. /	041.9	034.1	102.9		(Mn_2SiO_4, SiO_2)	
1.5% Al	74 3	641.6	653 4	102.2	530.6	Aloo, MnO (MnoSiO)	
-30 °C dp	74.5	041.0	035.4	102.2		A1203, 14110 (141125104)	
1.5% Al	74 5	641 5	653 3	102.3	530.4	Al ₂ O ₃ , MnO (Mn ₂ SiO ₄)	
+5 °C dp	74.5	041.5	055.5	102.5	550.4		
1.0% Al	74 4	612 5	654 4	102.2	5323	Al ₂ O ₃ , MnO, MnAl ₂ O ₄ ,	
-53 °C dp	/4.4	042.5	034.4	105.2	552.5	SiO ₂	
1.0% Al	75.0	612 3	654 1	102.3	531 1	Al ₂ O ₃ , MnO, MnAl ₂ O ₄ ,	
-30 °C dp	75.0	042.5	054.1	102.5	551.1	Mn_2SiO_4	
1.0% Al	74.1	641.5	653.6	102.1	530.4	Al ₂ O ₃ , MnO, Mn ₂ SiO ₄	
+5 °C dp	/ 4.1						
1.0% Si		642.7	654.5	103.4	532.3	SiO_2 , Mn_2SiO_4	
-50 °C dp							
1.0% Si	74 3	642.3	654.2	102.7	531.6	MnO, SiO ₂ , Mn ₂ SiO ₄	
-30 °C dp	74.5	042.5	034.2	102.7	551.0	(Al_2O_3)	
1.0% Si	74 1	642.0	654.0	102.3	530.0	M_{PO} M_{P} $SiO_{2}(Al_{2}O_{2})$	
+5 °C dp	/4.1	042.0	054.0	102.5	550.9	$MIIO, MII_2 SIO_4 (AI_2O_3)$	
1.5% Si		612 1	654.1	102.8	531.6	SiO- Mn-SiO	
-53 °C dp	-	042.4	034.1	102.8	551.0	5102, 141125104	
1.5% Si		642.3	654.3	102.6	531.5	MnO SiO. Mn.SiO.	
-30 °C dp	-					WIIO, 310 ₂ , WII ₂ 310 ₄	
1.5% Si		642.0	654.0	102.4	531.2	Mn-SiO	
+5 °C dp	-	042.0	034.0	102.4	331.2	111125104	

Table 6.1: Identification of oxides on the steel surface using XPS (after sputtering 5 nm)

As a result of cooling the steel to room temperature and removing the panel from the galvanizing simulator, Fe was oxidized at the steel surface. Further oxidation was minimized between removing the panel from the galvanizing simulator and analysis of the sample by storing the annealed steel in anhydrous isopropanol. Examples of the Fe XPS spectra for the 1.0% Si steel for all sputtering depths and annealing atmospheres are shown in Figure 6.1. Fe oxides and/or hydroxides were found at the surface (red curve at the bottom of each graph) and 5 nm below the surface (dark blue curve above the red curve) as shown by the higher Fe binding energy when compared to metallic Fe (Grosvenor et al. 2004). Fe metal was also found 5 nm below the surface as shown by the Fe $2p_{3/2}$ peak position at 706.62 eV (XPS spectra were calibrated using the Fe metal peak at this position as discussed in § 4.6.2). There was some concern about Fe oxidation during the IBT stage of the heat treatment when using the +5 °C dp, however, the Fe oxide was not thicker than was determined for the lower oxygen partial pressure atmospheres. The Fe oxide peak was larger at the +5 °C dp, this is due to the higher Fe content at the surface as shown in Figure 6.2. Similar results were obtained for the other steel chemistries and are not shown.



Figure 6.1: XPS spectra for depth profiles of Fe showing that iron is oxidized to a depth of 5 nm for the 1.0% Si steel at a) the -50 °C dp, b) the -30 °C dp and c) the +5 °C dp.

6.1.1.2 Effect of oxygen partial pressure and steel chemistry on the chemical composition of the steel surface

Plots showing the effect of oxygen partial pressure on surface chemistry for each steel composition after sputtering to a depth of 5 nm are shown in Figure 6.2. Figure 6.2 a) shows the 1.5% Al steel, b) shows the 1.0% Al steel, c) shows the 1.0% Si steel and d) shows the 1.5% Si steel. For all steel chemistries and annealing atmospheres considerable enrichment of oxygen and the alloying elements was observed at the steel surface. When comparing the four steel chemistries some trends were observed regarding the effect of oxygen partial pressure on the steel surface chemistry. It was observed that as the oxygen partial pressure was increased the amount of Fe at the surface increased, in agreement with the occurrence of internal oxidation which is expected at higher oxygen partial pressure atmospheres. Also, it was observed that the amount of Si at the steel surface decreased with increasing oxygen partial pressure. For the four steel chemistries the maximum surface Mn concentration occurred at the -30 °C dp.



Figure 6.2: Chemical composition of the steel surface after annealing as determined using XPS (5 nm sputtering) a) 1.5% Al steel, b) 1.0% Al steel, c) 1.0% Si steel and d) 1.5% Si steel.





6.1.1.3 Analysis of the steel surface and subsurface by XPS depth profiles

XPS depth profiles were used to determine the thickness of the oxide layer and to investigate the subsurface behaviour of the alloying elements. XPS depth profiles for the four steel compositions and three dew points are shown in Figure 6.3 to Figure 6.6. The

depth profiles for the 1.5% Al steel are shown in Figure 6.3; a) shows the -53 °C dp, b) the -30 °C dp and c) the +5 °C dp. Significant enrichment of Mn and Al in the form of oxides is observed at the surface at all annealing atmospheres. Considering the small amount of Si in the bulk composition (0.025 wt. %) a large Si enrichment at the surface was observed, particularly at the -53 °C dp where 5.4 atomic % was observed at the surface (Figure 6.3 a)). At the -30 °C dp the Mn surface enrichment reached the highest concentration. At the +5 °C dp the Mn enrichment penetrated to a greater depth indicating a thicker MnO layer (Table 6.1) for this sample and internal oxidation of Mn which was observed using TEM and will be discussed in § 6.1.3.

Figure 6.4 a), b) and c) shows the XPS depth profiles for the 1.0% Al steel at the -53 °C dp, -30 °C dp and +5 °C dp, respectively. At all annealing atmospheres there was significant enrichment of Mn, Si and Al in the form of oxides at the steel surface. At the +5 °C dp (Figure 6.4 c)) the enrichment of the alloying elements at the surface was the smallest and the oxygen content remained high well below the steel surface, indicating internal oxidation of the alloying elements which was also observed by TEM (§ 6.1.3). Comparing the Si and Al depth profiles it was observed that the Si surface concentration is higher than that of Al, even though the bulk Al content of this alloy is approximately twice that of Si. It was also observed that the surface and subsurface enrichment was lower, but the Al concentration remained above the bulk Al level well below the surface. Mn and Si enrichment was higher at the surface and decreased with increasing depth from the steel surface.

The XPS depth profiles for the 1.0% Si steel are shown in Figure 6.5 a) for the -50 °C dp, b) for the -30 °C dp and c) for the +5 °C dp. At the steel surface significant enrichment of Mn and Si in the form of oxides was observed for all annealing atmospheres. The Mn and Si concentration decreased as the depth from the surface increased. The Si enrichment was highest at the -50 °C dp and the Si surface concentration decreased as the oxygen partial pressure of the annealing atmosphere was increased (Figure 6.2 c)). Al did not provide a significant contribution to surface oxidation.

Figure 6.6 shows the XPS depth profiles obtained for the 1.5% Si steel at a) the -53 °C dp, b) the -30 °C dp and c) the +5 °C dp. Mn and Si were oxidized at the steel surface and the concentration of Mn and Si was many times that of the bulk concentration for all process atmospheres. The Si concentration at the surface decreased as the oxygen partial pressure of the annealing atmosphere was increased (Figure 6.2 d) and Figure 6.6). The maximum Mn concentration at the steel surface occurred at the -30 °C dp (Figure 6.2 d) and Figure 6.6). At the -53 °C dp the higher Si binding energy suggests more SiO₂ and this agrees with the higher Si content observed in Figure 6.6 a). At the -30 °C dp the lower Si binding energy indicates a decrease in the amount of SiO₂ when compared to the amount of Mn₂SiO₄ which agrees with the decrease in Si concentration and increase in Mn concentration observed in Figure 6.6 b). At the +5 °C dp the Si binding energy suggests Mn₂SiO₄ (Table 6.1), however, the ratio of Si to Mn suggests MnSiO₃ (Figure 6.2 d) and Figure 6.6 c)). The XPS depth profiles show that the concentration of Mn and Si decreased as the depth from the steel surface increased (Figure 6.6).

Depth profiles were also obtained for the interrupted annealing cycle shown in Figure 4.5. These depth profiles are shown in Appendix C. The major finding of this work was that the majority of selective oxidation occurred during the 120 s IA stage of the heat treatment as the result of faster oxidation kinetics at high temperature.

A mass balance was performed using O, Al, Mn and Si assuming the surface oxides were stoichiometric Al₂O₃, MnO and SiO₂. This is still valid when the other oxides identified in Table 6.1 were present; MnAl₂O₄ and Mn₂SiO₄, as the ratio of oxygen to the alloying elements is the same (MnAl₂O₄ = MnO·Al₂O₃ and Mn₂SiO₄ = 2MnO·SiO₂). The mass balance results showing the atomic % of excess oxygen is provided in Table 6.2. The amount of oxygen was too high at the surface for all steels and all process atmospheres. This was attributed to Fe oxidation that was observed in all samples to a depth of approximately 5 nm (Figure 6.1). Below the steel surface the oxygen was too high for the 1.0% Si and 1.5% Si steels particularly at the +5 °C dp. This discrepancy between the O concentration and that of the alloying elements was attributed to difficulties in detecting Si. The XPS results show that the Si concentration drops to zero below the surface (Figure 6.3 through Figure 6.6), however, Si rich oxides were observed by TEM below the surface as will be shown in § 6.2.3.2. In general, the mass balance showed good agreement below the surface for the 1.5% Al and 1.0% Al steels.



Figure 6.3: XPS depth profiles for the 1.5% Al steel a) -53 °C dp, b) -30 °C dp and c) +5 °C dp.



Figure 6.4: XPS depth profiles of the 1.0% Al steel a) -53 °C dp, b) -30 °C dp and c) +5 °C dp.



Figure 6.5: XPS depth profiles of the 1.0% Si steel a) -50 °C dp, b) -30 °C dp and c) +5 °C dp.



Figure 6.6: XPS depth profiles of the 1.5% Si steel a) -53 °C dp, b) -30 °C dp and c) +5 °C dp.

	Exce	Maximum			
Sample	5 nm below the	100 nm below	Maximum	sputtered depth	
	surface	the surface	sputtered depth	[nm]	
1.5% Al	17.8	68	0.3	1428.6	
-53 °C dp	17.0	0.8	0.5		
1.5% Al	12 /	11	16	489	
-30 °C dp	15.4	1.1	-1.0		
1.5% Al	23.4	3.2	5.6	1428.6	
+5 °C dp	23.4	5.2	5.0		
1.0% Al	7.6	4.4	-1.0	1428.6	
-53 °C dp	7.0	4.4	-1.0		
1.0% Al	6.8	27	3.2	489	
-30 °C dp	0.0	2.1	-3.2		
1.0% Al	26.8	21	69	1428.6	
+5 °C dp	20.0	2.1	0.7		
1.0% Si	12 1	4.6	_2 5	1428.6	
-50 °C dp	12.1	ч.0	-2.5		
1.0% Si	18.6	03	1.2	1428.6	
-30 °C dp	10.0).5	1.2		
1.0% Si	26.5	10.3	94	1428.6	
+5 °C dp	20.5	10.5	7.4		
1.5% Si	14.4	8 9	37	1428.6	
-53 °C dp	17.7	0.7	5.7		
1.5% Si	12.1	9.8	6.5	1428 6	
-30 °C dp	12.1	2.0	0.5	1720.0	
1.5% Si	25.8	13.4	10.7	1428.6	
+5 °C dp	23.0	13.4	10.7		

Table 6.2: Mass balance results showing the amount of excess oxygen at various depths below the steel surface

6.1.2 Study of surface oxide morphology and elemental distribution by SAM and SEM

The oxide morphology was determined via SEM and the relationship between the oxide morphology and distribution of elements at the surface was determined using SAM. Two sets of elemental maps were collected for each sample; one at the sample surface and the other after sputtering to a specified depth below the surface. For the elemental maps collected at the surface the entire surface was oxidized. The oxidation of

Fe is an artefact of removing the panel from the galvanizing simulator; Fe should not be oxidized when the steel enters the Zn bath. When the elemental maps collected before and after sputtering were very similar (except O) only the maps after sputtering are shown.

The SAM results for the 1.5% Al -53 °C dp steel after sputtering to a depth of 20 nm are shown in Figure 6.7. Elemental maps showed that some areas of the surface were rich in Mn, some in Al and some in both Mn and Al, suggesting that of MnO, Al₂O₃ and MnAl₂O₄ are present (Table 6.1). The oxide morphology consisted of oxide nodules and film-type oxides as shown in the secondary electron image in Figure 6.7 a). The nodules in the lower right corner and running diagonally across the area analyzed coincide with Mn rich areas and were likely MnO (Figure 6.7 a) and d) and Table 6.1). The film-type oxides coincide with Al and sometimes Mn rich regions as shown by comparing Figure 6.7 a), d) and e). The film-type oxides correspond to Al₂O₃ and MnAl₂O₄ (Table 6.1). There were also many Fe rich areas on the surface (Figure 6.7 b)). No Si rich features were identified at the steel surface by SAM as a result of the low Si concentration (Figure 6.2 a)).

The SAM results for the 1.5% Al -30 °C dp steel are shown in Figure 6.8. The oxide morphology is shown in Figure 6.8 a) and consists of oxide nodules forming a network-like structure at grain boundaries and nodules distributed over the steel surface. The oxide nodules were determined to be faceted, as shown in the SEM image in Figure 6.9. The nodules were rich in Mn as shown by comparing Figure 6.8 a) to Figure 6.8 d). The holes in the steel surface shown in Figure 6.8 a) and Figure 6.9 were also rich in Mn

(Figure 6.8 d)). These Mn rich areas correspond to MnO as was determined by XPS (Table 6.1). Within the area analyzed there was one Al rich nodule identified on the steel surface as well as a small amount of Al fairly uniformly distributed on the steel surface (Figure 6.8 e)). The Si concentration was too low to be detected by SAM.

The SAM results for the 1.5% Al +5 °C dp steel are shown in Figure 6.10. The secondary electron image in Figure 6.10 a) shows many large nodules on the surface, when comparing this picture with the elemental maps these nodules coincide with Fe rich areas rather than oxides of Mn or Al. MnO tends to occur at the grain boundaries as well as localized oxide films on the surface (Table 6.1 and Figure 6.10 c) and d)). The XPS depth profiles show that the Mn enrichment penetrated to the greatest depth when compared to the other annealing atmospheres for this steel (Figure 6.3), suggesting that the localized films were relatively thick. The Al surface concentration was low and only a small Al rich area was identified by SAM (Figure 6.10 c)). The Si concentration was too low to be detected by SAM.

Figure 6.11 shows the SAM results for the 1.0% Al -53 °C dp steel. The surface is almost entirely covered in Mn, Si and Al rich oxides (Figure 6.11 c)-f)). Some SiO₂ is present at the grain boundaries (Table 6.1 and Figure 6.11 f)). Only a small amount of Fe is present at the surface, Fe is found at the grain boundaries and small areas distributed on the surface (Figure 6.11 b)). This is in agreement with the XPS results which showed that these experimental conditions resulted in the lowest surface Fe content of all steel chemistries and process atmospheres analyzed (Figure 6.2). The surface oxidation of

this sample was further investigated by TEM to determine if this oxide was continuous, these results are discussed in \S 6.1.3.

Auger elemental mapping of the 1.0% Al -30 °C dp steel after sputtering 20 nm below the surface is shown in Figure 6.12. Results were similar to those obtained for the 1.0% Al -53 °C dp steel; the surface was covered in Mn, Al and Si rich oxides. However, more Fe rich areas were present on the steel surface when compared to the 1.0% Al -53 °C dp steel (Figure 6.11 b) and Figure 6.12 b)). The Fe rich areas coincided with oxide nodules shown at the lower left area of Figure 6.12. The increase in Fe observed at the surface by SAM agrees with the increased Fe concentration measured at the -30 °C dp by XPS (Figure 6.2 b)). Mn and Al enrichment of the surface did not always occur together; Al rich oxide films are found at the right side of the area analyzed (Figure 6.12 a), c) and f)). The lack of features in the SAM Si map (Figure 6.12 e)) suggests Si was uniformly distributed on the steel surface. It was determined by XPS that there was approximately 8 atomic % Si at the surface (Figure 6.2 b)).

The SAM results for the 1.0% Al +5 °C dp steel following sputtering are shown in Figure 6.13. MnO is observed primarily at grain boundaries and adjacent areas (Table 6.1 and Figure 6.13 c) and d)). A large amount of Fe is found at the surface (Figure 6.13 b)), this is in agreement with the XPS results (Figure 6.2 b)) and with internal oxidation of the alloying elements which is expected at the +5 °C dp. No Al or Si rich features were found at the surface, therefore, maps for these elements are not shown. This is in agreement with the drop in Al and Si surface concentration at the +5 °C dp as shown by the XPS results in Figure 6.2 b). Some nodules were observed at the steel surface in

Figure 6.13 a), however, these nodules do not coincide with the Mn and O rich regions. The oxide morphology was further investigated by SEM; comparing images obtained in secondary electron mode with those in backscattered electron mode to determine if the oxide had a film or nodule type morphology (Figure 6.14). The dark areas in Figure 6.14 b) correspond to the MnO regions such as those observed in Figure 6.13. In backscattered electron mode the atomic number contrast is accentuated, the lighter elements such as O appear darker. A high concentration of oxides (dark areas) extending beyond the grain boundaries are shown in the upper left of Figure 6.14 b), these areas continue, moving diagonally across the area analyzed. Comparing these oxidized areas with the corresponding secondary electron image (Figure 6.14 a)) no topographic features are observed, suggesting film-type oxides. The grain boundaries also appear dark in the backscattered electron image as a result of preferential oxidation due to the higher diffusivity of oxygen and alloying elements at the grain boundaries. The oxidation of this steel, including oxide thickness, was also investigated by TEM and will be discussed in § 6.1.3.

Figure 6.15 shows the SAM results for the 1.0% Si -50 °C dp steel. The oxide morphology consisted of large spherical cap shaped nodules (Figure 6.15 a)). These oxide nodules were rich in Mn and Si (Figure 6.15 d) and e)) and likely corresponded to Mn_2SiO_4 as identified by XPS (Table 6.1). Grain boundary oxidation was also observed; grain boundaries were rich in Si and Mn (Figure 6.15 d) and e)). The intensity of Si was the highest at the grain boundaries suggesting grain boundaries are rich in SiO₂ (Figure 6.15 e) and Table 6.1). A considerable amount of metallic Fe was observed between the

oxide nodules (Figure 6.15 b)). No Al rich features were observed at the steel surface, therefore the Al map is not shown. This agrees with the low concentration of Al identified by XPS (Figure 6.2 c)). The Al concentration at the surface of this steel was too low to obtain an accurate binding energy for Al.

The Auger results for the 1.0% Si -30 °C dp steel are shown in Figure 6.16 for the steel surface and in Figure 6.17 after sputtering to 20 nm below the steel surface. Two different oxide morphologies were observed; large spherical cap type nodules and small film-like oxide nodules (Figure 6.16 a) and Figure 6.17 a)). More Fe was present between the large oxide nodules when compared to the region where the small oxide nodules formed a film, however, the film-like oxide was thinner as shown by the increase in Fe in this region after sputtering (comparing Figure 6.16 b) with Figure 6.17 b)). The large nodules, film-like oxide and grain boundary oxides were rich in Mn, Si and Al (Figure 6.16 d), e) and f) and Figure 6.17 d), e) and f)). The major difference between the elemental maps before and after sputtering is that at the steel surface the film-type oxide was rich in Mn, Si and Al, whereas after sputtering this film-type oxide was predominantly rich in Al, with Si enrichment occurring in the boundary of this region. It should be noted that the Al surface enrichment was less than 2 atomic % as determined by XPS (Figure 6.5 b)) and that intensity on the elemental maps is an arbitrary scale. Thus, the Al maps in Figure 6.16 f) and Figure 6.17 f) overemphasize the concentration of Al at the surface. From the XPS results (Table 6.1 and Figure 6.2 c)) it is likely that the large nodules on the surface comprised Mn_2SiO_4 and that SiO_2 was present at the grain boundaries.

The oxide morphology and elemental maps collected using SAM for the 1.0% Si +5 °C dp steel are shown in Figure 6.18 for the steel surface and in Figure 6.19 after sputtering 40 nm below the steel surface. The oxide morphology consisted primarily of small, closely spaced nodules that were rich in Mn and Si (Figure 6.18 d) and e) and Figure 6.19 d) and e)). These oxide nodules were likely Mn₂SiO₄ in agreement with the XPS results (Table 6.1 and Figure 6.2 c)). In the upper right corner was a Mn rich region, likely MnO (Table 6.1), which coincided with a film-like oxide (Figure 6.18 d) and Figure 6.19 d)). Mn oxidation was observed at the grain boundaries with some areas also rich in Si (Figure 6.18 d) and e) and Figure 6.19 d) and e). The small, closely spaced nodules are seen more clearly in the SEM image provided in Figure 6.20. The Al maps are not shown as no Al rich features were observed either before or after sputtering, this is in agreement low Al content found using XPS (Figure 6.2 c)).

SAM results for the 1.5% Si -53 °C dp steel are shown in Figure 6.22 after sputtering 20 nm below the surface. Greater detail of the oxide morphology is shown by SEM in Figure 6.21. The oxide morphology comprised large and small nodules; some nodules were connected, forming a network-type structure (Figure 6.21). The surface was almost completely covered in Mn and Si rich oxides and very little Fe was present at the surface (Figure 6.22). This agrees with the XPS results which showed Mn_2SiO_4 and SiO_2 were present at the steel surface (Table 6.1).

SAM results for the 1.5% Si -30 °C dp steel are shown in Figure 6.23 for the steel surface and in Figure 6.24 after sputtering 20 nm. Two distinct oxide morphologies are observed; some grains contain large oxide nodules and some grains have smaller more

closely spaced oxide nodules (Figure 6.23 a)). The Mn rich areas coincided with the areas having larger nodules (Figure 6.23 d) and Figure 6.24 d)). The steel surface was almost uniformly covered in Si (Figure 6.23 e)). After sputtering more Si was found in large nodules and at grain boundaries when compared to the rest of the surface (Figure 6.24 e)). The decrease in Si after sputtering coincided with areas rich in Fe after sputtering (Figure 6.23 b)), indicating that the Si rich film at the surface, likely SiO₂ (Table 6.1), was very thin. The large nodules were likely Mn_2SiO_4 (Table 6.1).

SAM elemental mapping for the 1.5% Si +5 °C dp steel after sputtering 20 nm below the surface is shown in Figure 6.25. The oxide morphology comprised small closely spaced nodules (Figure 6.25 a)). The surface was uniformly covered in Si (Figure 6.25 e)). Nodules and grain boundaries were rich in Mn (Figure 6.25 d)). The distribution of Mn and Si at the surface indicates that nodules and grain boundary oxides comprised Mn_2SiO_4 in agreement the XPS results in Table 6.1. The oxide morphology was similar to that obtained for the 1.0% Si +5 °C dp steel (Figure 6.20).



Figure 6.7: Oxide morphology of the 1.5% Al -53 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Al maps.



Figure 6.8: Oxide morphology of the 1.5% Al -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Al maps.



Figure 6.9: SEM analysis of the selective oxidation of the 1.5% Al -30 °C dp steel surface.



Figure 6.10: Oxide morphology of the 1.5% Al +5 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Al maps.



Figure 6.11: Oxide morphology of the 1.0% Al -53 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.



Figure 6.12: Oxide morphology of the 1.0% Al -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.



Figure 6.13: Oxide morphology of the 1.0% Al +5 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O and d) Mn maps.


b) Figure 6.14: SEM analysis of the oxidized 1.0% Al +5 °C dp steel a) secondary electron image and b) backscattered electron image.



Figure 6.15: Oxide morphology of the 1.0% Si -50 °C dp steel using Auger mapping after sputtering 10 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.



Figure 6.16: Oxide morphology of the 1.0% Si -30 °C dp steel using Auger mapping for the steel surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.



Figure 6.17: Oxide morphology of the 1.0% Si -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.



Figure 6.18: Oxide morphology of the 1.0% Si +5 °C dp steel using Auger mapping for the steel surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.



Figure 6.19: Oxide morphology of the 1.0% Si +5 °C dp steel using Auger mapping after sputtering 40 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.



Figure 6.20: SEM analysis of the oxide morphology of the 1.0% Si +5 °C dp steel.



Figure 6.21: SEM analysis of the oxide morphology of the 1.5% Si -53 °C dp steel.



Figure 6.22: Oxide morphology of the 1.5% Si -53 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.



Figure 6.23: Oxide morphology of the 1.5% Si -30 °C dp steel using Auger mapping for the steel surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.



Figure 6.24: Oxide morphology of the 1.5% Si -30 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.



Figure 6.25: Oxide morphology of the 1.5% Si +5 °C dp steel using Auger mapping after sputtering 20 nm below the surface, a) Secondary electron image, b) Fe, c) O, d) Mn and e) Si maps.

6.1.3 TEM analysis of the steel surface

TEM was performed on the 1.5% Al +5 °C dp steel, 1.0% Al -53 °C dp steel and 1.0% Al +5 °C dp steel to study the cross-section of the oxidized region. TEM analysis was performed on the 1.5% Al +5 °C dp steel to further investigate the internal oxidation behaviour of this steel and the nodules observed on the steel surface (Figure 6.10 a)). Nodules on the steel surface were identified as metallic Fe by SAM (Figure 6.10). Metallic nodules of the more noble solvent metal on the surface have been associated with internal oxidation of the alloying elements; as was discussed in the literature survey in § 2.3.2.4 (Gurusuamy et al. 1986, Mackert et al. 1983, Zhang et al. 2009).

A lower magnification STEM image of the 1.5% A1 +5 °C dp steel is provided in Figure 6.26, showing the location of the three areas analyzed in greater detail by EDX to determine the composition of the nodules on the steel surface and study the internal oxidation of the alloying elements. Area i) in Figure 6.26 is shown in greater detail in Figure 6.27. Quantitative analysis of points A through D in Figure 6.27 a) is shown in Table 6.3. Area i) includes a nodule on the steel surface, TEM EDX mapping of this area (Figure 6.27) shows that the nodule is Fe rich and does not correspond to areas rich in A1 or Mn. Quantitative analysis of point D (Table 6.3) shows that this area is metallic Fe. At the steel surface, on either side of the Fe nodule, areas of MnO are observed (Figure 6.27 c) and point C in Table 6.3). Mn and A1 rich oxides were observed at the grain boundaries below the steel surface (Table 6.3 point B) and in small particles distributed in the steel matrix (Table 6.3 point A). Area ii) in Figure 6.26 is located well below the steel surface and was used to investigate the internal oxidation of this steel; TEM EDX analysis of this area is shown in Figure 6.28 and Table 6.3. The Mn, Al and O maps in Figure 6.28 and quantitative analysis of points E, F and G from Figure 6.28 a) (Table 6.3) show Mn and Al rich oxides at the grain boundaries. Area iii) in Figure 6.26 shows a region within area ii) at higher magnification to further investigate subsurface oxidation. Area iii) is shown in Figure 6.29 and quantitative analysis of points H and I is shown in Table 6.3. Point H is an Al_2O_3 particle in the matrix and possibly also AlN within the matrix. Point I shows $MnAl_2O_4$ at a grain boundary. Oxides were small, therefore, significant matrix effects were observed in the EDX point analysis as shown by the high Fe content of many points in Table 6.3. The small size of Al rich precipitates also explains the lack of Al rich features observed at the surface by SAM (Figure 6.10). The internal oxidation of Mn and Al agrees with the high concentration of Mn, Al and O below the steel surface observed by XPS (Figure 6.3 c)).



Figure 6.26: STEM bright field image of the 1.5% Al +5 °C dp steel after annealing, the three areas indicated correspond to the areas analyzed in greater detail shown in i) Figure 6.27, ii) Figure 6.28 and iii) Figure 6.29.



image, b) Fe, c) Mn, d) Al and e) O maps.



Figure 6.28: TEM EDX mapping of area ii) shown in Figure 6.26 a) STEM bright field image, b) Fe, c) Mn, d) Al and e) O maps.



Figure 6.29: STEM bright field image of area iii) shown in Figure 6.26.

Table 6.3: TEM EDX quantitative analysis of the 1.5% Al +5 °C dp steel, points A through I are indicated in the STEM bright field images shown in Figure 6.27 a), Figure 6.28 a) and Figure 6.29 (atomic %)

	~					
Point	Fe	О	Mn	Al	Ν	Phase(s) Present
Α	64.1	18.9	2.9	14.0	-	Al_2O_3
В	67.2	17.4	4.7	10.3	-	MnAl ₂ O ₄
С	40.2	34.8	21.4	3.3	-	MnO
D	98.2	1.8	-	-	-	Fe
E	2.5	51.8	14.8	30.3	-	$MnAl_2O_4$
F	30.2	38.2	9.7	22.2	-	$MnAl_2O_4$
G	56.4	19.7	18.9	4.8		MnO
Н	69.5	14.8	2.8	10.9	1.5	Al_2O_3
Ι	25.4	39.6	11.2	22.8	-	MnAl ₂ O ₄

A cross-section of the 1.0% Al -53 °C dp steel was investigated by TEM to determine whether the oxidized layer at the surface was a continuous film as it appears to be in Figure 6.11 or whether it consisted of small nodules separated by metallic Fe. The TEM results showed that both oxide morphologies occurred. In Figure 6.30 a continuous oxide film is shown at the surface. The thickness of the film-type oxide in Figure 6.30 ranged from 35 to 40 nm. Just to the left of point A in Figure 6.30 a) there was a gap in the oxide layer with Fe at the surface. The composition of this oxide is provided by point A in Table 6.4 (Figure 6.30 a)) and shows that the oxide layer contains Mn, Si and Al. The ratio between O and the sum of Mn, Si and Al was approximately 1:1, this was also observed for points D through H in Table 6.4. The oxygen balance is too low for these compounds to be in the MnO, Al_2O_3 and SiO_2 system defined in Jung et al. (2009) (Figure 2.21), implying that these compounds are suboxides. A range of compositions was also observed for these suboxides, for example the concentration of Si at points A, D, E and H was higher than the concentration of Mn and Al and the concentration of Si at point F was lower than the Mn and Al concentrations (Table 6.4). This does not agree with the XPS results reported in Table 6.1. These complex suboxides were not found by XPS due to a lack of binding energy data for these phases. The gold map (Figure 6.30 g)) shows that the black particles at the sample surface in Figure 6.30 a) were the applied gold coating. Figure 6.31 shows the cross-section including a grain boundary in the steel substrate. Above this grain boundary was SiO_x (points B and C in Table 6.4) which agrees with the SAM results showing a higher concentration of Si at the grain boundaries (Figure 6.11 e)). It should be noted that Al and Mn were also identified in this oxide; however, the concentration was lower when compared to the other surface oxides on this sample (points B and C in Table 6.4). Point D in Figure 6.31 is further away from the grain boundary and is a complex suboxide rich in Mn, Si and Al. In Figure 6.32 the oxide morphology comprised spherical cap shaped nodules which were composed of Mn, Si and Al (points E, F and H in Table 6.4). Nodules were separated by either a thin suboxide film as shown by point G or by metallic Fe as shown by point I in Table 6.4.

PhD Thesis – E.M. Bellhouse – McMaster – Materials Science and Engineering – 2010



Figure 6.30: TEM analysis of the 1.0% Al -53 °C dp steel (area 1) a) bright field STEM image, corresponding elemental maps for b) Fe, c) Mn, d) Al, e) O, f) Si and g) Au.



Figure 6.31: STEM bright field image of the 1.0% A1 -53 °C dp steel (area 2).



Figure 6.32: STEM bright field image of the 1.0% Al -53 °C dp steel (area 3).

Table 6.4: TEM EDX quantitative analysis of the 1.0% Al -53 °C dp steel, points A
through I are indicated in the STEM bright field images shown in Figure 6.30 a), Figure
6.31 and Figure 6.32 (atomic %)

Point	Fe	0	Mn	Al	Si	Phase(s) Present
А	6.1	46.2	14.5	9.8	23.4	Mn, Si and Al suboxide
В	1.4	52.9	5.7	2.2	37.8	SiO _x
С	1.1	52.8	2.7	0.8	42.7	SiO _x
D	2.1	48.0	10.7	14.2	25.1	Mn, Si and Al suboxide
E	4.1	48.3	16.4	9.7	21.5	Mn, Si and Al suboxide
F	10.6	46.4	17.7	14.7	10.7	Mn, Si and Al suboxide
G	70.1	14.7	7.0	5.6	2.6	Fe and Mn, Si and Al suboxide
Н	2.1	49.8	16.3	10.2	21.6	Mn, Si and Al suboxide
Ι	91.1	6.6	1.5	0.5	0.4	Fe

The cross-section of the 1.0% Al +5 °C dp steel was analyzed by TEM in order to determine the thickness of the oxidized regions identified on the steel surface by SAM (Figure 6.13 and Table 6.5). The MnO layer at the surface of the area shown in Figure 6.33 reached a thickness of 90 nm as is indicated on the Mn map in Figure 6.33 c). These oxides did not form a continuous layer as shown in the SEM backscattered electron image in Figure 6.14 b) and the SAM results in Figure 6.13. Internal oxidation occurred on this sample as shown by the Mn and Al containing oxides present below the surface (Figure 6.33 c), d) and e)).

Table 6.5: TEM EDX quantitative analysis of the 1.0% Al +5 °C dp steel, points A through C are indicated in the STEM bright field image shown in Figure 6.33 a) (atomic %)

Point	Fe	0	Mn	Al	Si	Phase Present
Α	14.4	41.5	35.9	2.0	1.6	MnO
В	14.7	37.9	38.0	1.7	1.0	MnO
С	15.2	43.4	34.6	2.0	0.9	MnO



Figure 6.33: TEM analysis of the cross-section of the 1.0% Al +5 °C dp a) STEM bright field image, corresponding elemental maps for b) Fe, c) Mn, d) Al and e) O.

6.2 Reactive wetting during galvanizing of TRIP-assisted steels

The reactive wetting behaviour was quantified by counting and measuring any bare spots in the galvanized coating. Coating adhesion was tested by performing 180°

bend tests. The interfacial reaction products were analyzed with SEM, EBSD and TEM. TEM was also used to investigate the reactive wetting mechanism, determine if any oxides remained at the Fe-Zn interface after galvanizing and identify the location and chemical composition of these oxides.

6.2.1 Analysis of coating quality

Analysis of the number of bare spots, size of bare spots and total bare area on the galvanized panels is shown in Table 6.6. Two panels were analyzed for each annealing atmosphere for the 1.5% Al and 1.0% Al steels; the average of these measurements is shown Table 6.6. One panel for each annealing atmosphere for the 1.0% Si and 1.5% Si steels was analyzed. Examples of galvanized panels are shown in Figure 6.34. The 1.0% Al -30 °C dp steel, where few bare spots were observed is shown in Figure 6.34 a) and the 1.0% Si +5 °C dp steel, which had the largest % bare area is shown in Figure 6.34 b).

Sample name	Number of bare spots/panel	Total bare area/panel* [mm ²]	% bare area	Average bare spot size [mm ²]
1.5% Al -53 °C dp	14	2.28	0.028	0.16
1.5% Al -30 °C dp	7.5	1.47	0.018	0.20
1.5% Al +5 °C dp	47	39.50	0.49	0.84
1.0% Al -53 °C dp	6.5	1.17	0.014	0.18
1.0% Al -30 °C dp	5	2.98	0.037	0.60
1.0% Al +5 °C dp	48.5	26.47	0.33	0.55
1.0% Si -50 °C dp	6	1.46	0.018	0.24
1.0% Si -30 °C dp	1	0.37	0.0045	0.37
1.0% Si +5 °C dp	443	209.28	2.58	0.47
1.5% Si -53 °C dp	1	0.50	0.0062	0.50
1.5% Si -30 °C dp	11	1.35	0.017	0.12
1.5% Si +5 °C dp	211	110.72	1.37	0.52

Table 6.6: Bare spot analysis

*The area analyzed on each panel was 8100 mm²



Figure 6.34: Pictures of galvanized panels, a) the 1.0% Al -30 °C dp steel where good reactive wetting and few bare spots were present and b) the 1.0% Si +5 °C dp steel which had the highest percentage bare area of all experimental conditions.

Similar trends were observed for the four steel chemistries when comparing the effect of oxygen partial pressure. At the two low oxygen partial pressure atmospheres (-53 °C dp or -50 °C dp and -30 °C dp) good wetting was observed with few bare spots and a small total bare area. At the higher oxygen partial pressure (+5 °C dp) an increase in the number of bare spots and total bare area was observed. Investigating the effect of steel chemistry, it was observed that a significantly greater number of bare spots occurred at the +5 °C dp for the two high Si TRIP steels when compared to the two high A1 – low Si TRIP steels.

6.2.2 Galvanized coating adhesion

The coating adhesion was tested using 180° bend tests. Pictures of the bent samples are shown for the three annealing atmospheres used for each alloy; the 1.5% Al steel is shown in Figure 6.35, the 1.0% Al steel is shown in Figure 6.36, the 1.0% Si steel is shown in Figure 6.37 and the 1.5% Si steel is shown in Figure 6.38. It should be noted that all samples were 30 mm in width. The coating remained intact along the outer surface of all of the bent samples, no cracking or flaking of the coating was observed, indicating that all samples passed the coating adhesion test.



Figure 6.35: Bend test results for the 1.5% Al steel (sample width is 30 mm).



Figure 6.36: Bend test results for the 1.0% Al steel (sample width is 30 mm).



Figure 6.37: Bend test results for the 1.0% Si steel (sample width is 30 mm).



Figure 6.38: Bend test results for the 1.5% Si steel (sample width is 30 mm).

6.2.3 Analysis of the steel-coating interface

6.2.3.1 SEM and EBSD analysis of the interfacial reaction products

The steel/coating interface was analyzed with SEM following selective stripping of the Zn overlay by two methods: i) 10% H_2SO_4 in water and ii) fuming HNO₃. SEM analysis of the steel/coating interface is shown in Figure 6.39 through Figure 6.42. The 1.5% Al steel is shown in Figure 6.39, the 1.0% Al steel is shown in Figure 6.40, the 1.0% Si steel is shown in Figure 6.41 and the 1.5% Si steel is shown in Figure 6.42. Fe₂Al₅Zn_x and FeZn₁₃ were identified at the iron-zinc interface for the four steel chemistries and three annealing atmospheres. The fine equiaxed crystals are Fe₂Al₅Zn_x and the needlelike crystals are FeZn₁₃. The presence of these phases indicates that reactive wetting occurred during galvanizing. However, FeZn₁₃ is not expected when galvanizing using a Zn bath with 0.2 wt. % Al as full inhibition is expected when the dissolved Al content is greater than 0.15 wt. % (Tang 1998). On some samples the inhibition layer was not continuous, indicating that inhibition breakdown may have occurred. This was observed for the 1.5% Al +5 °C dp steel (Figure 6.39 e)), the 1.0% Al -30 °C dp and +5 °C dp steels (Figure 6.40 c) and e)) and the 1.0% Si and 1.5% Si steels at all annealing atmospheres (Figure 6.41 and Figure 6.42). Larger amounts of FeZn₁₃ were often observed at the +5 °C dp when compared to the lower oxygen partial pressure annealing atmospheres (comparison of Figure 6.39 through Figure 6.42 f) with Figure 6.39 through Figure 6.42 b) and d)). One exception is the 1.0% Al steel where large amounts of FeZn₁₃ were also observed at the Fe-Zn interface at the -53 °C dp (Figure 6.40 b)).



Figure 6.39: SEM analysis of the Fe-Zn interface of the 1.5% Al steel a) -53 °C dp stripped with HNO₃, b) -53 °C dp stripped with 10% H₂SO₄, c) -30 °C dp stripped with HNO₃, d) -30 °C dp stripped with 10% H₂SO₄, e) +5 °C dp stripped with HNO₃ and f) +5 °C dp stripped with 10% H₂SO₄.



Figure 6.40: SEM analysis of the Fe-Zn interface of the 1.0% Al steel a) -53 °C dp stripped with HNO₃, b) -53 °C dp stripped with 10% H₂SO₄, c) -30 °C dp stripped with HNO₃, d) -30 °C dp stripped with 10% H₂SO₄, e) +5 °C dp stripped with HNO₃ and f) +5 °C dp stripped with 10% H₂SO₄.



Figure 6.41: SEM analysis of the Fe-Zn interface of the 1.0% Si steel a) -50 °C dp stripped with HNO₃, b) -50 °C dp stripped with 10% H₂SO₄, c) -30 °C dp stripped with HNO₃, d) -30 °C dp stripped with 10% H₂SO₄, e) +5 °C dp stripped with HNO₃ and f) +5 °C dp stripped with 10% H₂SO₄.



Figure 6.42: SEM analysis of the Fe-Zn interface of the 1.5% Si steel a) -53 °C dp stripped with HNO₃, b) -53 °C dp stripped with 10% H₂SO₄, c) -30 °C dp stripped with HNO₃, d) -30 °C dp stripped with 10% H₂SO₄, e) +5 °C dp stripped with HNO₃ and f) +5 °C dp stripped with 10% H₂SO₄.

For the 1.5% Si -53 °C dp steel, shown in Figure 6.42 b), some interesting features were observed regarding the growth of $FeZn_{13}$ relative to $Fe_2Al_5Zn_x$. On this sample $FeZn_{13}$ was shown growing on top of $Fe_2Al_5Zn_x$ grains as well as growing around $Fe_2Al_5Zn_x$ grains. The $FeZn_{13}$ growing above $Fe_2Al_5Zn_x$ is likely a result of aluminum depletion during solidification. Fe continues to diffuse through the $Fe_2Al_5Zn_x$ layer and will precipitate as $FeZn_{13}$ during solidification of the Zn overlay if the Al concentration is not sufficient for the formation of $Fe_2Al_5Zn_x$ (Leprêtre et al. 1998).

Inhibition breakdown was also observed at the steel/coating interface as shown by the outbursts in Figure 6.43 which likely coincide with substrate grain boundaries. Outbursts only constitute a small portion of the $FeZn_{13}$ observed at the steel/coating interface as shown in Figure 6.43; this was true for all experimental alloys and process atmospheres.



Figure 6.43: Outbursts shown on the 1.5% Al -30 °C dp steel.

EBSD was performed on selected samples stripped with HNO₃ to identify the Fe-Al phases at the steel/coating interface. EBSD analysis of the 1.0% Si -50 °C dp steel galvanized after cooling from the IA temperature rather than after the IBT time of 120 s is shown in Figure 6.44. The large areas which could not be indexed (white areas) were largely due to surface roughness of the sample. Of the areas that could be indexed the predominant phase present is $Fe_2Al_3Zn_x$. A very small amount of FeAl₃ was found at the Fe-Zn interface. Ferrite was found in some areas where the Al-rich interfacial layer was discontinuous. The phases identified by EBSD for this sample were representative of the other samples analyzed by EBSD which included the 1.0% Si -50 °C dp and -30 °C dp samples galvanized after the IBT time of 120 s and the 1.5% Al and 1.0% Al steels for the -53 °C dp and -30 °C dp galvanized after cooling from the IA temperature.



Figure 6.44: Identification of Al rich phases at the steel/coating interface of the 1.0% Si -50 °C dp steel by EBSD a) secondary electron image and b) EBSD phase map (blue is Fe_2Al_5 or $Fe_2Al_5Zn_x$, red is $FeAl_3$ and green is ferrite). It should be noted that this sample was galvanized immediately following cooling from the IA temperature rather than after the IBT time of 120 s.

6.2.3.2 TEM analysis of the steel/coating interface

Cross-sections of the steel/coating interface for selected samples were analyzed with TEM EDX elemental mapping and quantitative point analysis. Samples were studied to investigate the interfacial reaction products, determine if any oxides remained at the Fe-Zn interface after galvanizing and determine the location and morphology of these oxides.

TEM EDX mapping of the 1.5% Al -30 °C dp steel is shown in Figure 6.45 and quantitative point analyses of points A through D in Figure 6.45 a) are shown in Table 6.7. TEM analysis of the cross-section shows that Mn rich grains remained at the Fe-Zn interface after galvanizing. Prior to galvanizing nodules of MnO were found at the surface (Table 6.1 and Figure 6.8). After galvanizing, the oxygen concentration of these grains was not high enough to be MnO, as shown by points B and D in Table 6.7, suggesting the occurrence of partial reduction of these oxides by the dissolved Al in the Zn bath. The location of these Mn rich grains is particularly interesting as in the case of points A and B (Figure 6.45 and Table 6.7), the Mn rich grain was above the Fe₂Al₅Zn_x layer. This was typical of other areas analyzed on this sample. The location of Al and Mn rich areas is shown more clearly in Figure 6.46 where the elemental maps for Fe, Al and Mn are overlaid on the STEM bright field image in blue, green and red, respectively. Point C shows Fe-Zn intermetallics above the Fe₂Al₅Zn_x layer.



Figure 6.45: TEM EDX mapping of the steel/coating interface of the 1.5% Al -30 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Al and f) Zn maps.

points indic	cated in Figu	re 6.45 a) (at	omic %)			
Point	Fe	Zn	Al	Mn	0	Phase Present
Α	37.8	28.1	30.7	1.1	2.3	$Fe_2Al_5Zn_x$
В	7.8	2.4	1.5	78.4	13.9	$MnO_x, x < 1$
С	15.9	81.8	1.2	0.5	1.2	Fe-Zn intermetallic
D	4.6	1.3	4.9	68.0	22.3	$MnO_x, x < 1$

Table 6.7: TEM EDX point analysis of the 1.5% Al -30 °C dp steel corresponding to the points indicated in Figure 6.45 a) (atomic %)



Figure 6.46: STEM bright field image of the 1.5% Al -30 °C dp steel with colour overlay of EDX elemental maps; Fe in blue, Mn in red and Al in green.

TEM EDX analysis of two areas of the 1.0% Al -53 °C dp steel are shown due to the variety of information obtained from this sample; including chemistry and morphology of oxides remaining at the Fe-Zn interface after galvanizing. The TEM EDX mapping of area 1 of the 1.0% Al -53 °C dp steel is shown in Figure 6.47 and quantitative point analysis corresponding to letters A through I indicated in Figure 6.47 a) and b) is shown in Table 6.8. Oxides remained at the Fe-Zn interface and $Fe_2Al_5Zn_x$ was found above or between oxide particles (Figure 6.47, Figure 6.48 and Table 6.8). Figure 6.48

shows the bright field STEM images from Figure 6.47 with elemental maps overlaid to show more clearly the location of oxides relative to the $Fe_2Al_5Zn_x$ inhibition layer. At the top of the area shown in Figure 6.47 were larger oxide particles identified as complex Mn, Si and Al containing suboxides as shown by points C and F in Table 6.8. These suboxides are similar to the suboxide nodules found on the surface of this steel prior to galvanizing (Figure 6.32). $Fe_2Al_5Zn_x$ formed between these suboxide particles (points D and E in Table 6.8, Figure 6.47 c) and f) and Figure 6.48). Smaller oxide grains in the lower portion of the area shown in Figure 6.47 a) were identified as MnO by point I in Table 6.8. Above the MnO a thicker and more continuous $Fe_2Al_5Zn_x$ layer was found (Figure 6.47 c) – f)). The MnO grain shown by point I was small and $Fe_2Al_5Zn_x$ was also present in the area analyzed. When the Mn and Al maps are overlaid on the bright field image it is shown that Al extends into the substrate between the MnO grains (Figure 6.48 a)). Comparing the top and bottom of Figure 6.47 shows that oxide size and chemistry are important for determining if Fe₂Al₅Zn_x is able to form on top or must form between oxides. Below the steel surface Mn, Si and Al containing oxides were identified at a grain boundary (Table 6.8 point G). Further below the surface Al₂O₃ was found at a grain boundary (point B in Table 6.8 and Figure 6.47 d) and f)). Below this region needlelike AlN crystals were found (point A in Table 6.8 and Figure 6.47 f)), where AlN formed as a result of annealing in a high N₂ atmosphere.

Area 2 of the 1.0% Al -53 °C dp steel analyzed by TEM is shown in Figure 6.49 and quantitative point analysis of points J through M is provided in Table 6.8. In this area a continuous Mn, Si and Al rich suboxide film is observed (Figure 6.49 c)-e), g) and
h) and point K in Table 6.8). A continuous $Fe_2Al_5Zn_x$ layer was found immediately above this suboxide layer was (points J and L in Table 6.8). Some $Fe_2Al_5Zn_x$ is also observed below the suboxide layer (Figure 6.49 e) and h)). This film-type suboxide shown by point K (Figure 6.49) had a higher Al content and lower Si content than the nodules identified by points C and F in Figure 6.47. These results show the importance of the oxide chemistry in determining the reactive wetting mechanism. $Fe_2Al_5Zn_x$ was able to form on top of this suboxide shown by point K as well as on top of MnO (Figure 6.47, Figure 6.48 b) and point I in Table 6.8). $Fe_2Al_5Zn_x$ formed between rather than on top of suboxides having higher Si concentrations (Figure 6.47, Figure 6.48 b) and points C and F in Table 6.8). Mn, Si and Al rich oxides were also observed below the steel surface (point M in Table 6.8). The suboxide layer at the steel surface was similar to the continuous suboxide layer observed by TEM on this steel prior to galvanizing (Figure 6.30).



Figure 6.47: TEM analysis of the Fe-Zn interface of the 1.0% Al -53 °C dp steel (area 1) a) bright field image, b) higher magnification bright field image of the interface area indicated in a), EDX elemental maps corresponding to the area shown in a) for c) Fe, d) O, e) Mn, f) Al, g) Zn and h) Si.





a)

b)

Figure 6.48: a) overlay of EDX elemental maps of Al in green and Mn in red on the bright field image from Figure 6.47 a) and b) overlay of EDX elemental maps of Mn in red, Al in blue and Zn in green on the bright field image from Figure 6.47 b).

Table 6.8: TEM EDX point analysis of the 1.0% Al -53 °C dp steel corresponding to the	he
points indicated in Figure 6.47 a) and b) and Figure 6.49 a) (atomic %)	

Point	Point Fe		Zn Al	Mn	0	Si	N	Phase(s)
TOIIIt	re	ZII	AI	IVIII	U	51	1	Present
Α	67.7	0.1	17.2	0.7	2.1	0.6	11.7	AlN
В	46.0	0.1	23.4	0.4	30.0	0.3	-	Al_2O_3
С	1.1	0.5	5.9	30.4	49.3	12.9	_	Mn, Al and
		0.0	0.5		1310			Si suboxide
D	32.5	7.4	54.9	0.1	4.9	0.2	-	$Fe_2Al_5Zn_x$
Е	24.5	13.3	58.3	-	3.7	0.2	-	$Fe_2Al_5Zn_x$
Б	1.0	0.4	5.0	20.2	51 1	12.2		Mn, Al and
Г	1.0	0.4	5.0	29.5	51.1	15.2		Si suboxide
C	22.0	0.6	57	15.2	265	0.1		Mn, Al and
G	32.8	0.0	5.7	13.5	30.3	9.1		Si oxide
Н	30.5	11.1	54.1	0.1	4.1	0.2	_	$Fe_2Al_5Zn_x$
T	20.9	7.0	41.0	141	14.1	15		MnO,
1	20.8	1.8	41.8	14.1	14.1	1.5	-	$Fe_2Al_5Zn_x$
J	25.4	11.8	57.8	0.1	4.9	-	_	$Fe_2Al_5Zn_x$
V	1.0	2.0	0.7	20.7	47 4	7.0		Mn, Al and
K	1.0	3.0	9.7	30.7	47.4	7.0	-	Si suboxide
L	28.6	13.1	54.4	0.1	3.7	0.2	-	Fe ₂ Al ₅ Zn _x
	20.5	0.2	10.0	~ ~	24.2	()		Al, Mn and
M	39.5	0.2	12.2	1.1	34.2	0.3	-	Si oxide



Figure 6.49: TEM EDX mapping of the 1.0% Al -53 °C dp steel (area 2) a) bright field image, b) Fe, c) O, d) Mn, e) Al, f) Zn and g) Si maps and h) bright field image with the Fe map overlaid in green, the Mn map in red and the Al map in blue.



Figure 6.50: TEM EDX mapping of the steel/coating interface of the 1.0% Al -30 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Al, f) Zn and g) Si maps and h) bright field image with the Fe map overlaid in green, the Mn map in red and the Al map in blue.

Permo me		-0					
Point	Fe	Zn	Al	Mn	0	Si	Phase(s) Present
А	7.4	0.3	11.2	12.4	48.1	13.8	Mn, Al and Si rich oxides
В	20.2	12.7	46.5	0.6	15.8	0.6	$Fe_2Al_5Zn_x$
С	24.6	27.6	42.0	0.1	3.5	0.3	$Fe_2Al_5Zn_x$
D	27.2	17.1	46.6	0.1	4.1	0.2	$Fe_2Al_5Zn_x$
Е	4.2	1.0	6.5	27.3	37.7	12.3	Mn and Si rich suboxide

Table 6.9: TEM EDX point analysis of the 1.0% Al -30 °C dp steel corresponding to the points indicated in Figure 6.50 a) (atomic %)

TEM EDX elemental mapping of the 1.0% Al -30 °C dp steel is shown in Figure 6.50 and quantitative analysis of points A through E in Figure 6.50 a) is shown in Table 6.9. Below the steel surface Mn, Al and Si rich oxides were found at a grain boundary as shown by point A in Table 6.9 and Figure 6.50. $Fe_2Al_5Zn_x$ was present at the Fe-Zn interface as shown by points B, C and D in Table 6.9 and by the Al map and bright field image with colour overlay in Figure 6.50 e) and h), respectively. The higher Fe and Zn concentration of point C could be due to interference by $FeZn_{13}$ in the area analyzed. A Mn and Si rich suboxide remained at the Fe-Zn interface, as shown by point E in Table 6.9. The Al content of point E likely comes from the $Fe_2Al_5Zn_x$ in this area. In Figure 6.50 h) the location of the $Fe_2Al_5Zn_x$ layer relative to the oxides is clearly shown by comparing the location of Mn, shown in red and Al, shown in blue; oxides are located both above and below the $Fe_2Al_5Zn_x$ layer.

The galvanized 1.0% Al +5 °C dp steel was analyzed at the edge of a bare spot in the Zn overlay (Figure 6.51 and Table 6.10). The area shown in Figure 6.51 is within a bare spot and an intact Zn overlay and Fe-Al inhibition was observed immediately to the left of the area shown. It should be noted that the sample orientation is different in this figure; here the substrate is on the bottom rather than on the left side as it is in the other TEM images of the Fe-Zn interface. At the edge of the bare spot a continuous layer of MnO was observed on the steel surface as shown by the Mn and O maps in Figure 6.51 c) and d), respectively and by the quantitative analysis of points A, C and D in Table 6.10. Continuous regions of MnO were identified on the 1.0% Al +5 °C dp surface prior to galvanizing by SAM (Figure 6.13) and by TEM (Figure 6.33). The increase in bare area in the galvanized coating was attributed to these localized continuous and thicker oxide films (Table 6.6). The thickness of the oxide film in Figure 6.51 was measured to be 92 nm in the vicinity of point A and 163 nm at point B. Just below this MnO layer an increase in Al and Si content of the Mn rich oxide was observed as shown by quantitative analysis of point B in Table 6.10. Internal oxidation was observed for these processing parameters as shown by the Mn, Al, Si and O observed below the surface (Figure 6.51 c) - f).



Figure 6.51: TEM EDX mapping of the steel/coating interface of the 1.0% Al +5 °C dp steel at the edge of a bare spot a) bright field image, b) Fe, c) O, d) Mn, e) Al and f) Si maps.

Table 6.10: TEM EDX point analysis of the 1.0% Al +5 $^{\circ}$ C dp steel corresponding to the points indicated in Figure 6.51 a) (atomic %)

		0		/			
Point	Fe	Zn	Al	Mn	0	Si	Phase Present
А	16.0	1.0	0.6	32.6	39.6	0.3	MnO
В	11.9	0.3	6.1	25.3	34.9	4.9	Mn, Si and Al rich oxide
С	10.8	0.7	1.8	33.0	37.4	0.5	MnO
D	16.5	0.6	0.6	32.9	38.8	0.4	MnO

TEM EDX mapping of the 1.0% Si -30 °C dp steel is shown in Figure 6.52 and quantitative analysis of points A and B in Figure 6.52 a) is provided in Table 6.11. Mn and Si rich oxides remain at the Fe-Zn interface after galvanizing as shown by Figure 6.52 c) - e. Al did not contribute significantly to the surface oxidation (Figure 6.2 c)), therefore all of the Al detected at the Fe-Zn interface coincides with Fe₂Al₅Zn_x. Prior to galvanizing the oxides on the steel surface had a spherical cap morphology (Figure 6.16 a)). After galvanizing the surface oxide morphology was different; oxides are now flat plates (Figure 6.52), showing that the steel surface was altered during galvanizing. The oxide layer on this sample was not continuous and Fe₂Al₅Zn_x was able to form between oxide particles as shown by comparing the location of Mn and Si with Al (Figure 6.52 d) - f)) or Mn with Fe in the colour overlay of the bright field image (Figure 6.52 h)). Fe-Zn intermetallics formed above the Fe₂Al₅Zn_x layer (Figure 6.52 g) and point B in Table 6.11).



Figure 6.52: TEM EDX mapping of the steel/coating interface of the 1.0% Si -30 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Si, f) Al and g) Zn maps and h) bright field image with colour overlay of the Fe map in green, Mn in red and Zn in blue.

Table 6.11: TEM EDX point analysis of the 1.0% Si -30 °C dp steel corresponding to the points indicated in Figure 6.52 a) (atomic %)

P							
Point	Fe	Zn	Al	Mn	0	Si	Phase Present
Α	4.1	1.5	4.4	21.5	22.4	42.4	Mixed Mn-Si oxide
В	8.7	86.1	0.7	0.1	0.1	0.8	Fe-Zn intermetallic

For the 1.0% Si +5 °C dp steel a TEM sample was made at the edge of a bare spot to capture the transition between wetting and non-wetting (Figure 6.53). The top portion of Figure 6.53 a) shows an area with good wetting. The location of the Zn overlay is shown by the Zn map (Figure 6.53 g)) and the Al map (Figure 6.53 f)) shows the location of the $Fe_2Al_5Zn_x$ layer. At the start of the non-wetting area Mn and Si oxides were detected at and below the steel surface. The surface oxide was likely Mn_2SiO_4 which was found at the surface prior to galvanizing (Table 6.1). Quantitative analysis of point A in Figure 6.53 a) is provided in Table 6.12 showing that the centre of the subsurface oxide particle is SiO₂, a Mn rich shell is found around this particle (Figure 6.53 d)). This type of inhomogeneous oxide structure with a core of SiO₂ and a Mn rich shell was also observed by Gong et al. (2008) and Li et al. (2007). The hole in the sample in the Zn overlay shown on the right side of Figure 6.53 a) is due to the preferential sputtering of Zn during FIB sample preparation and is not associated with poor wetting. An area within the bare spot is shown in Figure 6.54 to further investigate what prevented reactive wetting in this area and to investigate the subsurface oxidation behaviour. At the surface of this sample was a layer of material which was redeposited during FIB sample preparation and is indicated in Figure 6.53 a). The steel surface entering the Zn bath is immediately below this redeposited layer. A Mn and Si rich oxide film, likely Mn_2SiO_4 (Table 6.1), was found at the surface (Figure 6.54 c) – e)). These oxides at the steel surface are what prevented wetting in this area. Many Mn, Si and Al rich oxide particles were found below the surface (Figure 6.54 c) - f). Quantitative analysis of point B (Table 6.12) shows the large oxide particle is SiO_x with a Mn rich shell (Figure 6.54).



g)

Figure 6.53: TEM EDX mapping of the steel/coating interface of the 1.0% Si +5 °C dp steel a) bright field image, b) Fe, c) O, d) Mn, e) Si, f) Al and g) Zn maps.



Figure 6.54: TEM EDX mapping of the steel surface within a bare spot on the 1.0% Si +5 °C dp galvanized steel a) bright field image, b) Fe, c) O, d) Mn, e) Si and f) Al maps.

Table 6.12: TEM EDX point analysis of the 1.0% Si +5 °C dp steel corresponding to the points indicated in Figure 6.53 a) and Figure 6.54 a) (atomic %)

Point	Fe	Zn	Al	Mn	0	Si	Phase Present
Α	18.4	1.0	9.3	5.5	44.0	21.6	SiO ₂
В	5.7	0.4	2.1	1.9	55.4	35.1	SiO _x

TEM analysis of galvanized samples of the 1.0% Si -30 °C dp and +5 °C dp steels also provided information regarding the subsurface oxidation behaviour. Comparison of the 1.0% Si -30 °C dp steel and 1.0% Si +5 °C dp steel showed that the oxides penetrated to a greater depth for the +5 °C dp atmosphere versus the -30 °C dp atmosphere, indicating that internal oxidation occurred for the +5 °C dp (Figure 6.52 and Figure 6.54). At the -30 °C dp the oxides penetrated to a depth of approximately 300 nm as indicated in Figure 6.52 a). At the +5 °C dp many oxides were detected between 400 nm and 1 μ m below the steel surface as shown in Figure 6.54 a). This is in agreement with the increase in Fe concentration at the steel surface as the oxygen partial pressure of the annealing atmosphere increased (Figure 6.2 c)), which is also indicative of internal oxidation of the alloying elements.

TEM EDX analysis of the 1.5% Si -30 °C dp is shown in Figure 6.55 and Table 6.13. Three Mn and Si rich oxide nodules were detected at the steel surface in the upper portion of Figure 6.55. These nodules likely correspond to the large Mn and Si rich nodules found by SAM (Figure 6.23 and Figure 6.24). The Fe₂Al₅Zn_x layer forms around these oxide particles (Figure 6.55 f) and point C in Table 6.13). The Fe content of point C (Table 6.13) is higher than expected for Fe₂Al₅Zn_x. This is likely due to interference from the substrate. In the lower portion of the area shown in Figure 6.55 no oxides remained at the interface. Prior to galvanizing there was considerable oxide coverage of the steel surface (Figure 6.23), and this relatively oxide free interface suggests aluminothermic reduction of the surface oxide by the dissolved Al in the Zn bath. The Fe₂Al₅Zn_x layer was thicker in the area where no oxide remained at the steel

surface (lower half of Figure 6.55). SiO₂ particles were found below the steel surface (Figure 6.55 e) and points A and B in Table 6.13). These oxide particles had a Mn rich shell (Figure 6.55 d)), which was also observed for the 1.0% Si +5 °C dp (Figure 6.53 and Figure 6.54).

Table 6.13: TEM EDX point analysis of the 1.5% Si -30 °C dp steel corresponding to the points indicated in Figure 6.55 a) (atomic %)

Point	Fe	Zn	Al	Mn	0	Si	Phase Present
Α	6.0	1.4	0.2	0.9	58.4	33.2	SiO ₂
В	5.8	1.1	0.2	-	60.0	32.9	SiO ₂
С	37.0	10.0	46.7	-	6.0	0.4	$Fe_2Al_5Zn_x$



g) Figure 6.55: TEM EDX mapping of the steel/coating interface of the 1.5% Si -30 °C dp steel a) bright field image, b) Fe c) O, d) Mn, e) Si, f) Al and g) Zn maps.

6.3 Discussion of selective oxidation and reactive wetting behaviour

6.3.1 General trends observed for selective oxidation of experimental alloys

There were some trends observed for the effect of oxygen partial pressure common to the four experimental TRIP steels. All steels showed significant enrichment of the alloying elements at the steel surface in the form of oxides. As the oxygen partial pressure of the process atmosphere was increased the Si enrichment at the surface decreased. The Fe concentration at the surface increased as the oxygen partial pressure of the process atmosphere was increased (Figure 6.2). At higher oxygen partial pressures the flux of oxygen into the steel surface is higher resulting in precipitation of oxides below the steel surface thereby decreasing the selective oxidation of the alloying elements at the steel surface. For all alloys the maximum Mn surface enrichment was observed for the -30 °C dp process atmosphere (Figure 6.2).

It was observed that the surface and subsurface enrichment behaviour of Al is different when compared to that of Mn and Si. Mn and Si both show surface enrichment many times that of the bulk concentration, with the concentration decreasing rapidly with increasing depth into the steel surface (Figure 6.3 through Figure 6.6). Enrichment of Al at the steel surface was smaller relative to the bulk concentration, immediately below the surface there was a slight decrease in Al concentration followed by an increase in Al content with the Al concentration remaining high well below the steel surface (Figure 6.3 and Figure 6.4). The subsurface enrichment of Al can be partially attributed to the formation of AlN below the steel surface as a result of annealing in a N_2 rich atmosphere.

AlN was observed by TEM for the 1.0% Al -53 °C dp steel (Figure 6.47 and point A in Table 6.8) and has been observed previously in Al rich steels by Mahieu et al. (2004) and Gong, Lee et al. (2009). At the +5 °C dp process atmosphere for the 1.5% Al and 1.0% Al steels internal oxidation of Al also contributed to the high Al concentration below the steel surface (Figure 6.28, Figure 6.33 and Figure 6.51).

In Figure 6.2 through Figure 6.6 it was observed that there was significant excess oxygen at the surface when performing a mass balance assuming the formation of Al_2O_3 . MnO and SiO₂. At 5 nm below the steel surface (Figure 6.2) the amount of excess O was approximately equal to the Fe content, which is in agreement with the oxidation of Fe at this depth per Figure 6.1. Further below the surface the oxygen content was occasionally higher than expected, particularly for the 1.0% Si and 1.5% Si steels at the +5 °C dp. It was also observed in the XPS depth profiles (Figure 6.3 through Figure 6.6) that the Si content often drops to zero below the surface. However, it was observed by TEM that large Si containing oxide precipitates occur well below the steel surface. For example, at approximately 1 µm below the surface of the 1.0% Si +5 °C dp steel Si containing oxides are observed (Figure 6.54). This suggests that the oxygen measurements by XPS were accurate and that there were problems detecting lower concentrations of Si by XPS below the steel surface. At the surface of the 1.0% Al steel for the -53 °C dp and -30 °C dp process atmospheres Mn, Si and Al containing suboxides were identified (Table 6.4, Table 6.8 and Table 6.9), and therefore, it was not appropriate to use Al_2O_3 , MnO and SiO_2 for the mass balance. This was shown by the 1.0% Al -30 °C dp steel where the

amount of excess oxygen (6.8 atomic %) was significantly less than the amount of Fe at the surface (16.3 atomic %) (Table 6.2 and Figure 6.2).

The oxides identified on the steel surface were dependent on steel chemistry and oxygen partial pressure of the annealing atmosphere. One trend observed regarding the effect of oxygen partial pressure on oxides identified at the steel surface was that the Si binding energy increased as the oxygen partial pressure was decreased (Table 6.1). The increase in Si binding energy suggests the presence of SiO₂ at the steel surface or an increase in the amount SiO₂ when compared to the amount of Mn₂SiO₄. This agrees with the higher Si concentration at the surface observed at lower oxygen partial pressures for all steel chemistries (Figure 6.2). The SiO₂ observed at lower oxygen partial pressures also agrees with the general trends of the thermodynamic predictions of Liu et al. (2009) where SiO₂ is only found at very low oxygen partial pressures for a steel with 0.26 wt. % Si and of Suzuki et al. (2009) where SiO₂ is favoured at low oxygen partial pressures when the Si to Mn ratio is above 2.

A direct comparison of the experimental results to the thermodynamic predictions from the literature can only be made for the 1.5% Si steel at the -53 °C dp and -30 °C dp with the results of Jung et al. (2009) shown in Figure 2.22 a). At the annealing temperature of 777 °C Jung et al. (2009) predict MnSiO₃ and SiO₂ at the -53 °C dp (7.3×10^{-27} bar) and at the -30 °C dp (1.4×10^{-23} bar) as shown in Figure 2.22 a). Experimentally SiO₂ was found which is in agreement with this thermodynamic prediction, however, Mn₂SiO₄ rather than MnSiO₃ was found by XPS (Table 6.1 and Table 6.13), but it should be noted that no MnSiO₃ was found because the binding energy data for this oxide could not be found in the literature. The identification of the manganese silicate phases at the surface is complicated as shown by the results of Gong et al. (2008) and Gong, Kim et al. (2009) who show that the ratio of MnO to SiO₂ does not have a fixed composition; oxides were characterized as $xMnO \cdot SiO_2$ where x could be less than 0.5 or as high as 4. The experimental results for the 1.5% Si +5 °C dp steel could not be compared to the thermodynamic prediction as this process atmosphere was off the oxygen partial pressure scale shown in Figure 2.22.

When investigating the effect of steel chemistry, a difference in oxide morphologies was observed when comparing the two high Si TRIP steels with the two high A1 – low Si TRIP steels. The 1.0% Si and 1.5% Si steels generally had oxides at the surface with a spherical cap morphology (Figure 6.15 and Figure 6.25). The 1.5% Si -53 °C dp steel was one exception; the smaller nodules in Figure 6.21 were not spherical cap shaped. Also, many large nodules were connected to form a network type structure (Figure 6.21). Many spherical cap shaped nodules were still observed on this steel (Figure 6.22 a)).

The 1.5% Al and 1.0% Al steels had a mixture of nodules and film-type oxides (Figure 6.7 to Figure 6.14). The nodules often had a faceted or irregular shape rather than a spherical cap shape. Some small spherical cap shaped nodules were found on the 1.0% Al -53 °C dp steel (Figure 6.32) and on the 1.0% Al -30 °C dp steel (lower left of Figure 6.12). For the 1.5% Al -53 °C dp steel both film and nodule type oxides were observed (Figure 6.7). The 1.5% Al -30 °C dp steel had a unique oxide morphology; faceted nodules of MnO were observed primarily at grain boundaries forming a network

type of structure (Figure 6.8 and Figure 6.9). The oxide morphologies of the 1.0% Al -53 °C dp and -30 °C dp steels were similar and consisted primarily of film-type oxides (Figure 6.11 and Figure 6.12). At the +5 °C dp for the 1.5% Al and 1.0% Al steels oxidation was observed at the grain boundaries and as localized film-type oxides (Figure 6.10 and Figure 6.13).

There was also a size difference in subsurface oxide particles observed between the high Si and high Al – low Si steels. TEM analysis of the oxidized 1.5% Al +5 °C dp steel showed very small precipitates of Al rich oxides in the matrix (Figure 6.28 and Figure 6.29). For the 1.0% Si +5 °C dp steel, considerably larger Si and Mn rich oxides were observed below the steel surface (Figure 6.54). It is expected that the Al rich oxides will be smaller due to the higher thermodynamic stability of Al₂O₃ and MnAl₂O₄ versus SiO₂ and Mn₂SiO₄ (Figure 2.2) and it is known that oxide precipitate size tends to decrease as the stability of the oxide increases (Fine and Geiger 1979, Kubaschewski and Alcock 1979, Huang and Rosén 1994, Lenev and Novokhatskiy 1966, Birks et al. 2006).

6.3.2 Thermal stresses in the oxide

The 1.5% Al -53 °C dp steel and 1.5% Al -30 °C dp steel exhibited some features which suggest that cracking or spalling of the oxide occurred during cooling from the IA temperature as a result of a difference in thermal expansion coefficients of the oxide and steel substrate. The oxide morphology of the 1.5% Al -53 °C dp steel comprised primarily Al_2O_3 films and MnO nodules (Figure 6.7). The film-type oxide was not continuous on this steel as shown by the Fe rich areas observed in Figure 6.7 b). Some of these Fe rich areas may be a result of cracking of the Al_2O_3 film caused by thermal stresses imposed upon cooling. The thermal stress in the oxide can be calculated using equation (6.1) (Birks et al. 2006), which is valid for systems in which the oxide is considerably thinner than the substrate:

$$\sigma_{\text{oxide}} = \frac{-E_{\text{oxide}} \left(\alpha_{\text{oxide}} - \alpha_{\text{Fe}}\right) \Delta T}{\left(1 - \nu_{\text{oxide}}\right)}$$
(6.1)

where σ_{oxide} is the stress imposed in the oxide upon cooling, E_{oxide} is the Young's modulus of the oxide, v_{oxide} is the Poisson's ratio of the oxide, α_{oxide} is the linear coefficient of thermal expansion of the oxide, α_{Fe} is the linear coefficient of thermal expansion of iron and ΔT is the temperature difference. The stress in Al₂O₃ ($\sigma_{\text{Al}_2O_3}$) when cooling from the IA temperature (862 °C) to the IBT temperature (465 °C) was calculated to be -1528 MPa using equation (6.1) and the relevant material properties shown in Table 6.14. This stress is larger than the modulus of rupture for Al₂O₃ which is between 350 and 580 MPa (Richerson 1982) and it is reasonable that cracks could have formed in the oxide film prior to the sample being immersed in the Zn (Al, Fe) bath.

The oxide morphology of the 1.5% Al -30 °C dp sample comprised MnO nodules (Figure 6.8). There were also Mn and O rich holes observed at the steel surface (Figure 6.8 a), c) and d)) where there were likely nodules which were removed during cooling as a result of the thermal stress imposed due to the difference in thermal expansion between the oxide and substrate. The stress in MnO (σ_{MnO}) was calculated to be -836 MPa when cooling from 862 °C to 465 °C using equation (6.1) and the relevant material properties from Table 6.14. This stress is large and it is likely that cracks developed between the oxide nodules and the substrate prior to immersion in the Zn bath allowing the bath metal

to reach below the nodules which is suggested by the formation of $Fe_2Al_5Zn_x$ below Mn rich grains as observed in Figure 6.45 and Figure 6.46.

Variable	Value	Reference
α _{Fe}	$15.3 \times 10^{-6} \text{ K}^{-1}$	Birks et al. 2006
$E_{Al_2O_3}$	380 GPa	Callister 2007
$ u_{ m Al_2O_3}$	0.22	Callister 2007
$lpha_{{ m Al}_2{ m O}_3}$	$7.4 \times 10^{-6} \text{ K}^{-1}$	Callister 2007
E _{MnO}	175 GPa	Simmons and Wang 1971
V _{MnO}	0.31	Simmons and Wang 1971
α _{MnO}	$7.0 \times 10^{-6} \text{ K}^{-1}$	Wanke 1973
E_{SiO_2} (fused – amorphous)	73 GPa	Callister 2007
$v_{\rm SiO_2}$ (fused – amorphous)	0.17	Callister 2007
$\alpha_{\rm SiO_2}$ (fused – amorphous)	$0.4 \times 10^{-6} \text{ K}^{-1}$	Callister 2007

Table 6.14: Material properties needed to solve equation (6.1)

The thermal stress in SiO₂ was also determined as this oxide was also identified on the surface of the experimental TRIP steels. The relevant material properties for amorphous SiO₂ needed to solve equation (6.1) are found in Table 6.14. Data for amorphous rather than crystalline SiO₂ was used as it has been determined that the SiO₂ formed at the surface of TRIP steels during annealing is amorphous (Drillet et al. 2004, Gong et al. 2008, Gong, Kim et al. 2009). When cooling from 862 °C to 465 °C the stress in SiO₂ (σ_{siO_2}) was determined to be -520 MPa. This stress is considerably lower than the thermal stresses calculated for MnO and Al₂O₃ and it should be noted that no features were observed at the surface of the higher Si TRIP steels which would suggest cracking or spalling of the oxide upon cooling. The calculated thermal stress is however larger than the modulus of rupture for fused SiO₂ which is 110 MPa (Richerson 1982). The cracking of the oxide film (1.5% Al -53 °C dp steel) or removal of MnO nodules (1.5% Al -30 °C dp steel) likely contributed to the good wetting exhibited by these steels (Table 6.6) allowing Al to reach the substrate and form the desired $\text{Fe}_2\text{Al}_5\text{Zn}_x$ layer. If a SiO₂ film stays intact upon cooling to the Zn bath temperature this may have contributed to the poor wetting often reported for higher Si steels (Mahieu et al. 2001, Mahieu et al. 2004, Drillet et al. 2004, Suzuki et al. 2009).

6.3.3 Nodules of metallic iron on the surface as a result of internal oxidation

The 1.5% Al +5 °C dp steel surface morphology in Figure 6.10 a) shows a number of large nodules present at the surface primarily at grain boundaries. Comparing the location of nodules with the elemental maps shows that nodules correspond to metallic Fe rather than to oxides of the alloying elements. Analysis of point D in Figure 6.27 (Table 6.3) confirms that these nodules comprised metallic Fe. These nodules of metallic Fe were attributed to internal oxidation of the alloying elements which was observed by TEM analysis of the cross-section of the steel surface and subsurface (Figure 6.26 through Figure 6.29). Al₂O₃, MnO and MnAl₂O₄ were observed at grain boundaries and as particles within the matrix below the surface (Table 6.3).

In order to accommodate the volume of the oxides formed below the steel surface, the more noble metal, in this case Fe, was extruded to the surface via grain boundaries or dislocation pipes. The volume of nodules of the noble metal at the surface should be equal to the increase in volume resulting from the oxides formed below the surface (Guruswamy et al. 1986, Mackert et al. 1983). The molar volumes of the oxides MnO and Al_2O_3 are 13.221 cm³/mol and 25.575 cm³/mol, respectively, which is considerably

larger than that of either ferrite (7.0918 cm³/mol) or austenite (7.299 cm³/mol) (Weast 1978, Lide 2002). This caused strain on the lattice in the internal oxidation region, resulting in the migration of Fe to the surface and the formation of nodules. Metallic nodules of the noble metal on the surface as a result of internal oxidation were observed by Gurusuamy et al. (1986) in the Ag-In system and Mackert et al. (1983) in a Pd-Ag-Sn-In alloy. This phenomenon was recently observed in a 2.0 wt.% Mn, 1.5 wt.% Si and 0.5 wt.% Al TRIP steel by Zhang et al. (2009).

6.3.4 Effect of intercritical microstructure on oxide morphology

Two oxide morphologies were observed on the 1.5% Si -30 °C dp steel surface. Some grains had large oxide nodules and between these nodules was a Si rich film whereas other grains had small closely spaced nodules that formed a film-like oxide (Figure 6.23 and Figure 6.24). The difference in oxide morphologies could be due to the two different phases (ferrite and austenite) present during annealing and the difference in diffusivities of oxygen and the alloying elements in these two phases as shown in Table A.1. Comparing the present results to those obtained by Gong et al. (2008) it is likely that the grains with large oxide nodules were ferrite during intercritical annealing and the grains with small closely spaced nodules were austenite. Gong et al. (2008) studied the effect of annealing temperature on the oxidation of a steel of similar chemistry using a similar process atmosphere (-30 °C dp and 10% H₂ – 90% N₂) but using a significantly longer annealing time. When annealing in the ferrite region the oxide morphology consisted of lens or spherical cap shaped oxide nodules with an oxide film between the

nodules. When annealing in the austenite region an oxide film was found on the steel surface (Figure 2.28).

6.3.5 General trends observed for reactive wetting of experimental alloys

The Fe₂Al₃Zn_x inhibition layer was found at the Fe-Zn interface of all samples, indicating reactive wetting occurred. The Fe₂Al₃Zn_x layer was observed by SEM and EBSD (Figure 6.39 through Figure 6.42 and Figure 6.44). EBSD analysis identified a small amount of FeAl₃ at the Fe-Zn interface. Fe₂Al₅Zn_x and FeAl₃ are commonly reported at the Fe-Zn interface (Chen et al. 2008, McDevitt et al. 1997, Morimoto et al.1997). Fe₂Al₅Zn_x (without FeAl₃) was also reported at the Fe-Zn interface (Baril and L'Esperance 1999, Guttmann 1994, Leprêtre et al. 1998). Larger quantities of FeAl₃ were associated with short reaction times between the substrate and the Zn (Al, Fe) bath (Chen et al. 2008). The reaction time in the present experiments was not short and the presence of FeAl₃ could be a result of an additional step during wetting such as aluminothermic reduction of surface oxides. FeZn₁₃ was also found at the Fe-Zn interface of all samples (Figure 6.39 to Figure 6.43) and the mechanism for the formation of FeZn₁₃ on these samples will be discussed in § 6.3.7.

Good wetting was obtained for the four TRIP steels at the two low oxygen partial pressure annealing atmospheres (-53 °C dp or -50 °C dp and -30 °C dp) with few bare spots in the Zn overlay and a small total bare area. The mechanisms by which good reactive wetting occurred on these samples are discussed in § 6.3.6. For the +5 °C dp process atmosphere there was an increase in the number and area of bare spots for all alloys. For the 1.5% Al and 1.0% Al steels the increase in the number of bare spots was

small (47 bare spots for the 1.5% Al steel and 48.5 bare spots for the 1.0% Al steel) (Table 6.6). The increase in the number of bare spots for the 1.5% Al steel and 1.0% Al steel was due to a thicker MnO film present on localized areas of the steel surface (Figure 6.3 c), Figure 6.10, Figure 6.13, Figure 6.33 and Figure 6.51). A large increase in the number of bare spots was observed for the 1.0% Si and 1.5% Si steels at the +5 °C dp (443 bare spots for the 1.0% Si steel and 211 bare spots for the 1.5% Si steel) (Table 6.6). The considerably poorer wetting of the 1.0% Si and 1.5% Si steels was attributed to large portions of the steel surface being covered by closely spaced Mn and Si rich oxide nodules making it difficult for $Fe_2Al_5Zn_x$ to form between nodules. The wetting results are summarized in Figure 6.56 showing the total bare area as a function of steel chemistry and peak annealing temperature process atmosphere oxygen partial pressure.



Figure 6.56: Summary of bare spot analysis showing the effect of steel chemistry and process atmosphere oxygen partial pressure on the total bare area per panel, the area analyzed for each panel was 8100 mm^2 .

Some of the wetting results are contradictory to those reported previously which showed that promoting internal oxidation improved reactive wetting (Vanden Eynde et al. 2004, Mahieu et al. 2001), whereas the present results show poor wetting at the +5 °C dp. The results of Vanden Eynde et al. (2004) cannot be directly compared to the present results as the process atmosphere was considerably different than that used in the present work (§ 2.3.4). Mahieu et al. (2001) showed a +10 °C/-50 °C dp process atmosphere had improved wetting when compared to a -30 °C dp process atmosphere for a high Si TRIP steel as a result of internal oxidation at the +10 °C/-50 °C dp process atmosphere. There were still many bare spots in the galvanized coating observed at the $\pm 10 \text{ °C}/50 \text{ °C}$ dp process atmosphere. The present results, however, show good wetting for the 1.5% Si steel at the -30 °C dp, it should be noted that this steel has a similar chemical composition to the high Si TRIP steel studied by Mahieu et al. (2001). Galvanizing results for the 1.5% Al -30 °C dp steel were similar to those of Mahieu et al. (2004) for a high Al steel where good wetting was observed when galvanizing in a process atmosphere having a -30 °C dp.

Bend tests were conducted on all galvanized samples to determine the coating adhesion (Figure 6.35 and Figure 6.38). Good coating adhesion was obtained despite the $FeZn_{13}$ identified at the Fe-Zn interface (Figure 6.39 through Figure 6.42). Fe-Zn intermetallics are known to be brittle (Marder 2000), therefore there was some concern regarding the formability of the galvanized coatings.

6.3.6 Reactive wetting mechanisms

Despite the selective oxidation of the steel surface good reactive wetting occurred for the four steel chemistries at the -53 or -50 °C dp and at the -30 °C dp. Several different reactive wetting mechanisms were identified by comparing the results obtained for the selective oxidation of the steel surface prior to galvanizing with the TEM results of the Fe-Zn interface after galvanizing.

6.3.6.1 Bridging of oxides by $Fe_2Al_5Zn_x$, Fe-Zn intermetallics or the Zn overlay

For all samples analyzed by TEM following galvanizing, oxides were observed at the Fe-Zn interface (Figure 6.45 through Figure 6.55). On samples where good reactive wetting occurred, these oxides were observed either below, between or above the Fe₂Al₅Zn_x laver (Figure 6.45 through Figure 6.50, Figure 6.52 and Figure 6.55). Oxide size and chemistry determined whether or not oxides could be fully covered by $Fe_2Al_5Zn_x$. Small oxide particles of MnO could be fully covered by $Fe_2Al_5Zn_x$ as demonstrated by the 1.0% Al -53 °C dp steel (point I in Figure 6.47 and Figure 6.48). Areas were also observed on the galvanized samples where oxides were not covered by $Fe_2Al_5Zn_x$. $Fe_2Al_5Zn_x$ formed between nodules of Mn_2SiO_4 and these oxides were covered by Fe-Zn intermetallics in the case of the 1.0% Si -30 °C dp steel (Figure 6.52). Fe-Zn intermetallics were also observed above the Mn rich particles that remained at the Fe-Zn interface after galvanizing on the 1.5% Al -30 °C dp steel (Figure 6.45). Fe₂Al₅Zn_x also formed between Mn and Si rich suboxide nodules in the upper portion of the area analyzed for the 1.0% Al -53 °C dp steel in Figure 6.47 and Figure 6.48 (points C and F in Table 6.8) and these nodules were bridged by the Zn overlay.

6.3.6.2 Aluminothermic reduction of oxides

On a number of samples the surface oxide morphology was clearly altered during galvanizing. For the 1.0% Si -30 °C dp steel the oxide morphology prior to galvanizing consisted of spherical cap shaped nodules (Figure 6.16) and after galvanizing these nodules were significantly flattened (Figure 6.52). The change in oxide morphology could be due to dissolution of the oxide in the Zn bath, possibly via aluminothermic reduction. Similar results were obtained for the 1.5% Si -30 °C dp steel where the surface was almost completely covered in oxide prior to galvanizing (Figure 6.23) whereas after galvanizing it was shown that the lower portion of the area analyzed by TEM was free of oxides (Figure 6.55). Another sample that supports the occurrence of aluminothermic reduction is the 1.5% Al -30 °C dp sample. After galvanizing, the Mn rich particles that remain at the Fe-Zn interface do not have a high enough O content to be identified as MnO, suggesting partial reduction of the oxide (points B and D in Table 6.7).

Thermodynamically it is possible for the dissolved Al in the Zn bath to reduce MnO per the reaction shown in equation (6.2) as was discussed in § 2.3.4 (Khondker et al. 2007).

$$3MnO_{(s)} + 2[Al] \xrightarrow{460 \, ^{\circ}C} Al_2O_{3(s)} + 3[Mn]$$
(6.2)

Similarly the reduction of manganese silicates by Al in the Zn bath to $MnAl_2O_4$ was proposed by Gong, Song et al. (2009) by the reaction shown in equation (6.3).

$$Mn_2SiO_{4(s)} + 2[Al] \rightarrow MnAl_2O_{4(s)} + [Mn] + [Si]$$
(6.3)

Thermodynamically it is also possible for the dissolved Al in a 0.2 wt. % Al bath at 460 °C to reduce SiO_2 as per the reaction shown in equation (6.4). For example, using

a Si activity of one, which is considerably higher than the Si activity in the Zn bath, the activity of Al in the bath required for ΔG for the reaction in equation (6.4) to be zero was calculated to be 7.14×10^{-11} (Fine and Geiger 1979, Kubaschewski and Alcock 1979). The activity of Al in the present Zn (Al, Fe) bath was 0.026, which is orders of magnitude higher than that required to reduce SiO₂ (McDermid et al. 2007). For this calculation it was assumed that the activities of SiO₂ and Al₂O₃ were one as these were assumed to be pure condensed species.

$$3SiO_{2(s)} + 4[A1] \xrightarrow{460^{\circ}C} 2Al_2O_{3(s)} + 3[Si]$$
 (6.4)

It is very difficult to provide evidence of aluminothermic reduction due to the small quantities of Mn, Si and Al₂O₃ involved relative to the size of the bath. Also, Al₂O₃ is expected to form as dross as a result of the dissolved Al in the bath being oxidized at the surface of the bath, and therefore, detecting Al₂O₃ in the bath cannot be used as evidence of aluminothermic reduction. Wang et al. (2009) found Al₂O₃ at the grain boundaries of Fe₂Al₅Zn_x and attributed this to the reduction of surface oxides on the dual phase steels that were galvanized. They suggest that Al₂O₃ became trapped in the Fe₂Al₅Zn_x layer as the grains grow and coalesce. Small quantities of Mn were detected in an industrial Zn bath by Dubois (1998) after galvanizing many coils of Mn containing steels. These results do not necessarily support aluminothermic reduction as Mn is also in solid solution in the substrate and will dissolve into the bath with the Fe matrix in the initial stages of contact with the Zn (Al, Fe) bath.

6.3.6.3 Infiltration of the liquid Zn (Al, Fe) bath between oxide particles and the steel substrate

In some samples Fe₂Al₅Zn_x was found between oxide particles and the substrate surface. Two possible mechanisms are proposed to account for the formation of Fe₂Al₅Zn_x between oxides and the metallic substrate: i) liquid infiltration of bath metal assisted by cracking of the oxide due to thermal stresses and ii) liquid infiltration at grain boundaries between the oxide and substrate. The best example of liquid infiltration due to cracking of the oxide arising from thermal stresses was for the 1.5% Al -30 °C dp steel. Surface analysis of this steel showed that there were many Mn and O rich holes in the surface of the samples analyzed after annealing (Figure 6.8 and Figure 6.9). The holes in the surface were a result of cracking or spalling of the oxide due to thermal stresses imposed upon cooling as was discussed in § 6.3.2. The cracking occurring in the oxide upon cooling to the zinc bath temperature allowed the Al from the liquid Zn bath to reach the substrate below the nodules resulting in the formation of Fe₂Al₅Zn_x below the Mn rich grains as shown in Figure 6.45 and Figure 6.46. Cracks in the oxide film caused by thermal stresses may have contributed to the good reactive wetting observed for the 1.5% Al -53 °C dp steel (Figure 6.7 and Table 6.6).

Another mechanism which can result in the formation of $Fe_2Al_5Zn_x$ below oxides on the steel surface was infiltration of bath metal down grain boundaries between the oxide and the substrate. This likely occurred for the 1.5% Si -30 °C dp steel where the $Fe_2Al_5Zn_x$ layer was observed under and around oxide nodules that remained at the steel surface after galvanizing as shown by comparing the Mn and Al maps in Figure 6.55 d) and f), respectively. Other samples where $Fe_2Al_5Zn_x$ was observed partially below

oxides were the 1.0% Al -53 °C dp steel (Figure 6.48 b)), the 1.0% Al -30 °C dp steel (Figure 6.50 h)) and the 1.0% Si -30 °C dp steel (Figure 6.52).

6.3.6.4 Wetting of the oxide

TEM analysis of the Fe-Zn cross-section of the 1.0% A1 -53 °C dp steel revealed that Fe₂Al₅Zn_x formed directly above a complex Mn, Si and Al containing film-type suboxide (Figure 6.49). This film, which showed good wetting, had a higher Al content and lower Si content as shown by point K (Figure 6.49 and Table 6.8) than the nodule type oxides shown by points C and F (Figure 6.47 and Table 6.8) on the same sample where the Fe₂Al₅Zn_x generally formed between oxides. These results show the importance of oxide chemistry on determining the reactive wetting behaviour. This wetting mechanism may have also contributed to the good wetting observed for the 1.0% A1 -30 °C dp steel, which had a surface morphology similar to that of the 1.0% Al -53 °C dp steel (Figure 6.11 and Figure 6.12).

6.3.7 Mechanism of Fe-Zn intermetallic formation

FeZn₁₃ was found at the Fe-Zn interface of all samples (Figure 6.39 to Figure 6.42) even though FeZn₁₃ is not expected when galvanizing using a 0.2 wt. % dissolved Al bath (Tang 1998). As noted in § 2.1.3 full inhibition is expected when the bath dissolved Al content is greater than 0.15 wt. %. Thus, the presence of FeZn₁₃ could indicate inhibition breakdown or a localized Al depletion in the Zn bath. Some inhibition breakdown did occur during galvanizing as shown by the outburst structures in Figure

6.43. However, the majority of $FeZn_{13}$ observed at all experimental conditions was not associated with outbursts (Figure 6.39 to Figure 6.43).

The formation of FeZn₁₃ at the Fe-Zn interface could be caused by the consumption of Al by a reaction other than the formation of Fe₂Al₅Zn_x such as aluminothermic reduction of surface oxides. In the galvanizing simulator the Zn bath is not stirred and Al in the mass transport boundary layer may not be replenished during the dipping time. Growth of the interfacial layer continues after the galvanized panel is removed from the Zn bath until the Zn coating is solidified. During this time the Al will not be replenished and Fe will continue to diffuse from the substrate through the $Fe_2Al_5Zn_x$ layer. The effect of aluminothermic reduction on the local bath chemistry for a 0.2 wt.% dissolved Al bath is shown in Figure 6.57. When the steel is immersed in the Zn (Al, Fe) bath, Fe dissolution occurs from the strip as shown by arrow 1 in Figure 6.57. When aluminothermic reduction does not occur, $Fe_2Al_5Zn_x$ will precipitate, as shown by arrow 2. If aluminothermic reduction occurs, consuming Al and assuming Al cannot be replenished, the bath composition may be shifted to the L + ζ region as shown by arrow 3 in Figure 6.57. When the local bath composition is in the $L + \zeta$ region FeZn₁₃ will precipitate at the Fe-Zn interface shown by arrow 4 in Figure 6.57. This is the mechanism by which $FeZn_{13}$ precipitates on top of the $Fe_2Al_5Zn_x$ layer as shown in many of the SEM and TEM samples of the Fe-Zn interface (Figure 6.39 b) and d), Figure 6.40 d), Figure 6.41 b) and d), Figure 6.42 b) and d), Figure 6.45 and Figure 6.52). It should be noted that FeZn₁₃ may not precipitate when galvanizing these steels on a continuous hot-dip galvanizing line. In the continuous galvanizing process the Zn bath is stirred by the movement of the steel strip through the bath allowing Al to be replenished at the Fe-Zn interface during dipping.



Figure 6.57: Zn rich corner of the Zn-Al-Fe phase diagram (McDermid et al. 2007) with arrows added to indicate processes occurring during galvanizing of the experimental TRIP steels. When the steel is immersed in the Zn (Al, Fe) bath Fe dissolution from the substrate occurs as shown by arrow 1. On areas of the steel surface which are free of oxides $Fe_2Al_5Zn_x$ precipitates as shown by arrow 2. At the same time aluminothermic reduction will occur on oxidized areas of the substrate consuming Al as indicated by arrow 3. If aluminium is not replenished Fe-Zn intermetallics will precipitate as shown by arrow 4.

Larger amounts of FeZn₁₃ were observed at the +5 °C dp for all steels as well as for the 1.0% Al -53 °C dp steel (Figure 6.39 to Figure 6.42). With the exception of the 1.0% Al -53 °C dp steel the increase in FeZn₁₃ was associated with samples where poor wetting was observed (Table 6.6). The 1.0% Al -53 °C dp steel had the smallest amount of Fe present at the steel surface after annealing (Figure 6.2 b)) and the surface was almost completely covered in oxide (Figure 6.11) implying that a significant amount of oxide must be removed for good wetting to occur. The full width half maximum (FWHM) of the Mn depth profiles (Figure 6.3 to Figure 6.6) was used to estimate the thickness of the Mn containing oxide (Figure 6.58). It is expected that a thicker Mn containing oxide layer will result in more $FeZn_{13}$ as more Al will be consumed to reduce this oxide in order for wetting to occur. For the 1.5% Al steel and 1.0% Al steel there was good agreement between those samples having a thicker Mn containing oxide layer according to the FWHM and a large amount of $FeZn_{13}$ (Figure 6.39, Figure 6.40 and Figure 6.58). For the 1.0% Si steel and 1.5% Si steel the Mn containing oxide thickness did not correlate well with the amount of $FeZn_{13}$. This is likely due to the primarily nodule-type oxide morphology observed on these steels, whereas a film-type morphology is assumed by this analysis.





Outbursts form as a result of saturation of the substrate by Zn resulting in the precipitation of Fe-Zn intermetallics below the $Fe_2Al_5Zn_x$ layer. Outbursts are often located at substrate grain boundaries as Zn diffusion at grain boundaries is faster
(Leprêtre et al. 1998, Guttmann 1994, Dionne et al. 2002). The outbursts observed in Figure 6.43 likely coincide with substrate grain boundaries. The diffusion of Zn into the steel substrate at grain boundaries is demonstrated by the Zn maps for the TEM analysis of the 1.5% Al -30 °C dp steel (Figure 6.45 f)) and the 1.5% Si -30 °C dp steel (Figure 6.55 g)).

7 CONCLUSIONS

7.1 Microstructure and mechanical properties of TRIP-assisted steels using heat treatments compatible with hot-dip galvanizing

The microstructure and mechanical properties of the 1.5% Al and 1.0% Al TRIP steels were investigated using heat treatments compatible with continuous hot-dip galvanizing. The effects of steel chemistry, IA temperature (% intercritical austenite) and IBT time were investigated. The IA temperature had little effect on ultimate tensile strength or yield strength. The higher IA temperature, which produced an intercritical microstructure having 50% α – 50% γ , resulted in higher uniform elongations than the IA temperature which produced an intercritical microstructure of 65% γ – 35% γ . As the IBT time was increased the yield strength increased, the yield point elongation increased, the tensile strength decreased and the uniform elongation increased. For the same IA temperatures and IBT times the 1.0% Al steel had a higher strength than the 1.5% Al steel; this was attributed to the solid solution strengthening provided by Si.

For the 1.5% Al steel the thermal cycles that provided the best combinations of strength and ductility were the 50% γ IA temperature and the IBT times of 90 s and 120 s. The IBT time of 90 s resulted in a tensile strength of 895 MPa and uniform elongation of 0.26. The IBT time of 120 s resulted in a tensile strength of 880 MPa and uniform elongation of 0.27. For the 1.0% Al steel the best combination of strength and ductility was obtained for the 50% γ IA temperature and IBT time of 120 s. This thermal cycle produced a tensile strength of 1009 MPa and a uniform elongation of 0.22. For

thermal cycles that provided the best combinations of strength and ductility there was a sufficient amount of stable retained austenite in the microstructure and the work hardening behaviour, as described by n_{incr} , was typical of conventionally processed TRIP-assisted steels.

7.2 Selective oxidation

For the four steel chemistries studied enrichment of Mn and Si in the form of oxides was observed at the steel surface for all process atmospheres. For the 1.5% Al steel and 1.0% Al steel and all process atmospheres, Al enrichment in the form of oxides was observed at the steel surface. The surface enrichment behaviour of Al was different versus that of Si and Mn due to the formation of AlN below the steel surface. Mn and Si had larger surface enrichments than Al relative to their bulk concentrations and the Mn and Si concentration decreased with increasing depth from the steel surface. The Al surface enrichment decreased slightly just below the steel surface, increased and remained above the bulk Al content well below the steel surface.

Similar trends were observed regarding the effect of process atmosphere oxygen partial pressure for the four TRIP steel chemistries. The lowest oxygen partial pressure (-53 °C dp or -50 °C dp) resulted in the highest concentration of Si at the steel surface and the surface Si concentration decreased with increasing oxygen partial pressure. The Fe concentration at the steel surface was lowest at the lowest oxygen partial pressure and the Fe surface concentration increased with increasing oxygen partial pressure due to internal oxidation of the alloying elements. The maximum Mn concentration at the surface always occurred at the -30 °C dp annealing atmosphere.

Steel chemistry and oxygen partial pressure affected the oxide morphology. The oxide morphology for the 1.0% Si steel and 1.5% Si steel comprised spherical cap shaped nodules. The nodule size and spacing was affected by the steel chemistry and process atmosphere. For the 1.5% Al steel and 1.0% Al steel the oxide morphology generally comprised films or irregular shaped nodules. Exceptions were the 1.0% Al -53 °C dp steel and the 1.0% Al -30 °C dp steel where small spherical cap shaped nodules were identified as well as film-type oxides. The steel chemistry also affected the oxide precipitates below the surface at the +5 °C dp. The Si rich oxides below the surface of the 1.0% Si +5 °C dp steel were much larger than the Al rich oxides below the surface of the 1.5% Al +5 °C dp steel and 1.0% Al +5 °C dp steel. This was due to the higher thermodynamic stability of the Al rich oxides.

7.3 Reactive wetting

For all steel chemistries and process atmospheres $Fe_2Al_5Zn_x$ and $FeZn_{13}$ were identified at the Fe-Zn interface indicating that reactive wetting occurred. Good reactive wetting with few bare spots in the galvanized coating was obtained for all four steel chemistries at the -53 °C or -50 °C dp and the -30 °C dp process atmospheres. An increase in the number and area of bare spots was observed when using the +5 °C dp process atmosphere for all alloys. For the +5 °C dp atmosphere, the 1.5% Al and 1.0% Al steels had a smaller number of bare spots than the 1.0% Si and 1.5% Si steels. The increase in bare spots at the +5 °C dp for the 1.5% Al and 1.0% Al steels was attributed to localized thick films of MnO. For the 1.0% Si and 1.5% Si steels poor wetting at the +5 °C dp was attributed to the closely spaced nodules of Mn₂SiO₄. It was determined

that the $Fe_2Al_5Zn_x$ layer cannot form over Mn_2SiO_4 . For the high Al - low Si TRIP steels the oxide thickness was of prime importance for determining wetting behaviour whereas for the high Si TRIP steels oxide morphology determined the wetting behaviour.

For the samples that were successfully galvanized a number of reactive wetting mechanisms were identified. When oxide nodules on the steel surface were separated by metallic Fe on the steel surface, $Fe_2Al_5Zn_x$ could form between oxides and the oxides could be bridged either by the growth of the $Fe_2Al_5Zn_x$ layer, Fe-Zn intermetallics or by the Zn overlay. Thermodynamically it is possible for the dissolved Al in the Zn bath to reduce MnO, SiO_2 and Mn_2SiO_4 on the steel surface. Comparing the steel surfaces before and after galvanizing it was determined that the surface structure was altered during galvanizing supporting the occurrence of aluminothermic reduction. This allowed the bath metal to come in contact and react with metallic Fe on the steel substrate. Aluminothermic reduction also resulted in the formation of Fe-Zn intermetallics at the steel/coating interface as a result of local aluminium depletion in the bath. Due to the differences in thermal expansion between Fe and the oxides formed on the steel surface it is possible that cracks developed in the oxide when cooling from the IA temperature to the Zn bath temperature exposing metallic Fe at the steel surface. Cracking of the oxide contributed to the good wetting observed for the 1.5% Al -53 °C dp and -30 °C dp steels. The oxide chemistry strongly affected wetting behaviour with $Fe_2Al_5Zn_x$ forming above a Mn, Al and Si containing suboxide. Fe₂Al₅Zn_x generally formed between rather than on top of oxides having a higher Si content. Infiltration of bath metal at grain boundaries between oxides and the substrate also contributed to good reactive wetting. It is believed

that aluminothermic reduction and bridging of the oxides remaining at the steel/coating

interface occurred on all samples whereas cracking of the oxide due to thermal stresses

and wetting of the oxide were limited to specific processing parameters, summarized

below in Table 7.1.

Table 7.1: Summary of reactive wetting behaviour by steel chemistry and process atmosphere

Steel and process atmosphere	Wetting behaviour and proposed reactive wetting mechanism(s)
1.5% Al -53 °C dp	Good wetting due to bridging of oxides, aluminothermic reduction and thermal stresses
1.5% Al -30 °C dp	Good wetting due to bridging of oxides, aluminothermic reduction and thermal stresses
1.5% Al +5 °C dp	Poor wetting due to thick localized MnO films
1.0% Al -53 °C dp	Good wetting due to bridging of oxides, aluminothermic reduction, wetting of oxides and infiltration of bath metal at grain boundaries between oxides and substrate
1.0% Al -30 °C dp	Good wetting due to bridging of oxides, aluminothermic reduction, wetting of oxides and infiltration of bath metal at grain boundaries between oxides and substrate
1.0% Al +5 °C dp	Poor wetting due to thick localized MnO films
1.0% Si -50 °C dp	Good wetting due to bridging of oxides and aluminothermic reduction
1.0% Si -30 °C dp	Good wetting due to bridging of oxides and aluminothermic reduction
1.0% Si +5 °C dp	Poor wetting due to closely spaced Mn and Si rich oxide nodules
1.5% Si -53 °C dp	Good wetting due to bridging of oxides and aluminothermic reduction
1.5% Si -30 °C dp	Good wetting due to bridging of oxides and aluminothermic reduction
1.5% Si +5 °C dp	Poor wetting due to closely spaced Mn and Si rich oxide nodules

7.4 Future Work

One area which should be studied in the future is improving the mechanical

properties of TRIP-assisted steels when using thermal cycles compatible with hot-dip

galvanizing. One method which should be explored is microalloying using combinations of Ti, Nb and V (De Cooman 2004). These small additions should not affect the surface chemistry and galvanizing, but could provide significant increases in strength.

Selective oxidation and galvanizing of TRIP steel should also continue to be studied. Improvements can be made to reactive wetting behaviour by testing a larger range of process atmospheres. Testing more process atmospheres, intercritical annealing temperatures and steel chemistries may also make it possible to accurately predict the oxidation and reactive wetting behaviour for a given set of experimental conditions. Galvannealing of TRIP steels should also be studied as galvannealed coatings provide superior paintability over galvanized coatings (Marder 2000).

Selective oxidation and galvanizing studies should be expanded to include higher alloy steels including TWIP steels having Mn contents in excess of 20 wt. % and steel grades with alloy contents between that of TRIP and TWIP steels such as the steels studied by Suh et al. (2010) having approximately 5 wt. % Mn and 1-3 wt. % Al. These steels are of interest to the automotive industry as they are capable of providing excellent combinations of strength and ductility.

8 REFERENCES

- ASTM Standard A 653/A 653M 03. 2003. Standard Specification for Steel Sheet, Zinc-Coated (Galvanized) or Zinc-Iron Alloy-Coated (Galvannealed) by the Hot-Dip Process. West Conshocken, PA, USA: ASTM International.
- ASTM Standard E 8M 01ɛ2. 2001. Standard Test Methods for Tension Testing of Metallic Materials [Metric]. West Conshocken, PA, USA: ASTM International.
- ASTM Standard E 975 03. 2003. Standard Practice for X-Ray Determination of Retained Austenite in Steel with Near Random Crystallographic Orientation. West Conshocken, PA, USA: ASTM International.
- Baik, S.C., S. Kim, Y.S. Jin and O. Kwon. 2001. ISIJ Int. 41: 290-297.
- Barbé, L., L. Tosal-Martinez and B.C. De Cooman. 2002. Int. Conf. on TRIP-Aided High Strength Ferrous Alloys, Ghent, Belgium, June 19-21, 2002. Bad Harzburg, Germany: GRIPS: 147-152.
- Baril, E. and G. L'Esperance. 1999. Metall. Mater. Trans. A 30: 681-695.
- Bhadeshia, H.K.D.H., and D.V. Edmonds. 1979. Met. Trans. A 10: 895-907.
- Birks, N., G.H. Meier and F.S. Pettit. 2006. Introduction to the High-Temperature Oxidation of Metals. Cambridge, UK: Cambridge University Press: 101-143, 327-331.
- Black, P. 1955. Acta Cryst. 8: 43-48.
- Borg, R.J. and D.Y. Lai. 1970. Journal of Applied Physics 41: 5193-5200.
- Briggs, D. 2003. XPS: Basic Principles, Spectral Features and Qualitative Analysis.
 Chapter 2 of *Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy*, ed.
 D. Briggs and J. Grant. Chichester, UK: IM Publications and SurfaceSpectra: 31-56.
- Briggs, D. and J.C. Rivière. 1983. Spectral Interpretation. Chapter 3 of *Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, ed. D. Briggs and M.P. Seah. Chichester, UK: John Wiley & Sons: 87-139.
- Callister, W.D. 2007. Materials Science and Engineering: An Introduction, 7th Edition. New York, USA: John Wiley & Sons: A8-A19.

- Casey, W.H., M.F. Hochella Jr. and H.R. Westrich. 1993. Geochimica et Cosmochimica Acta 57: 785-793.
- Chen, L. 2007. Master's Thesis, McMaster University, Hamilton, Ontario, Canada.
- Chen, L., R. Fourmentin and J.R. McDermid. 2008. Metall. Mater. Trans. A 39: 2128-2142.
- Chen, H.C., H. Era and M. Shimizu. 1989. Metall. Trans. A 20: 437-445.

Chen, Z., J. Gregory, R. Sharp. 1992. Metall. Trans. A 23: 2393-2400.

- De Cooman, B.C. 2004. Current Opinion in Solid State and Materials Science 8: 285-303.
- De Meyer, M., D. Vanderschueren and B.C. De Cooman. 1999. ISIJ Int. 39: 813-822.

Diffusion Data. 1969. Vol. 3: 270.

- Dionne, S., M. Charest, G. Botton and F. Goodwin. 2002. 44th MWSP Conference Proceedings, Vol. XL: 405-415.
- Douglass, D.L., B. Zhu and F. Gesmundo. 1992. Oxidation of Metals 38: 365-384.
- Drillet, P., Z. Zermout, D. Bouleau, J. Mataigne, S. Claessens. 2004. Proc. 6th Int. Conf. on Zinc Alloy Coated Steel Sheet, Galvatech'04, Chicago, IL, USA, April 4-7, 2004, Association for Iron and Steel Technology: 1123-1134.
- Dubois, M. 1998. Zinc-Based Steel Coating Systems: Production and Performance. TMS, Warrendale, PA, USA: 39-50.

Dyson, D. and B. Holmes. 1970. J. Iron Steel Inst. 208: 469-474.

Fine, H. A. and G. H. Geiger. 1979. Handbook on Material and Energy Balance Calculations in Metallurgical Processes. Warrendale, Pennsylvania, USA: The Metallurgical Society of AIME: 385, 428, 431, 432, 446.

Finster, J. 1988. Surf. Interface Anal. 12: 309-314.

Fonstein, N., N. Pottore, S.H. Lalam and D. Bhattacharya. 2003. Austenite Formation and Decomposition. ed. E.B. Damm and M.J. Merwin. Warrendale, Pennsylvania, USA: TMS, Iron & Steel Society: 549-561.

- Fontana, M.G. and N.D. Greene. 1978. Corrosion Engineering, 2nd Ed. New York, USA: McGraw-Hill: 38.
- Furnémont, Q., P.J. Jacques and T. Pardoen. 2001. Journal de Physique IV 11: Pr5-325-Pr5-332.
- Furnémont, Q., M. Kempf, P. Jacques, M. Göken, F. Delannay. 2002. Materials Science and Engineering A 328: 26-32.
- Giorgi, M.-L., J.-B. Guillot and R. Nicolle. 2001. Calphad 25: 461-474.
- Girault, E., P. Jacques, Ph. Harlet, K. Mols, J. Van Humbeeck, E. Aernoudt and F. Delannay. 1998. Materials Characterization 40: 111-118.
- Girault, E., A. Mertens, P. Jacques, Y. Houbaert, B. Verlinden and J. Van Humbeeck. 2001. Scripta Mater. 44: 885-892.
- Goldstein, J., D. Newbury, D. Joy, C. Lyman, P. Echlin, E. Lifshin, L. Sawyer and J. Michael. 2003. Scanning Electron Microscopy and X-Ray Microanalysis, 3rd Ed. New York, NY, USA: Springer: 553-557.
- Gong, Y.F., H.S. Kim and B.C. De Cooman. 2008. ISIJ Int. 48: 1745-1751.
- Gong, Y.F., H.S. Kim and B.C. De Cooman. 2009. ISIJ Int. 49: 557-563.
- Gong, Y.F., Y.R. Lee, H.S. Kim and B.C. De Cooman. 2009. Proceedings of the Asia-Pacific Galvanizing Conference, The Corrosion Science Society of Korea, Jeju, Korea, November 8-12, paper A-41.
- Gong, Y.F., T. J. Song, H. S. Kim, J. H. Kwak, B. C. De Cooman. 2009. Proceedings of the Asia-Pacific Galvanizing Conference, The Corrosion Science Society of Korea, Jeju, Korea, November 8-12, paper B-15.

Grabke, H.J., V. Leroy and H. Viefhaus. 1995. ISIJ Int. 35: 95-113.

- Grant, J.T. 2003. AES: Basic Principles, Spectral Features and Qualitative Analysis.Chapter 3 of Surface Analysis by Auger and X-Ray Photoelectron Spectroscopy, ed.D. Briggs and J. Grant. Chichester, UK: IM Publications and SurfaceSpectra: 57-87.
- Grosvenor, A.P., B.A. Kobe, M.C. Biesinger and N.S. McIntyre. 2004. Suf. Interface Anal. 36: 1564-1574.

Guruswamy, S., S.M. Park, J.P. Hirth and R.A. Rapp. 1986. Oxid. Met. 26: 77-100.

Guttmann, M. 1994. Mater. Sci. Forum 155-156: 527-548.

- Hansen, S.S. and R.R. Pradhan. 1981. Proc. Symp. At the 110th AIME Annual Meeting, TMS-AIME, Warrendale, PA, USA: 113-144.
- Huang, J.-H. and E. Rosén. 1994. Phys. Chem. Minerals 21: 228-233.
- Huin, D., P. Flauder and J.-B. Leblond. 2005. Oxidation of Metals 64: 131-167.
- Huin, D., V. Lanteri, D. Loison, P. Autesserre and H. Gaye. 1996 Microscopy of Oxidation 3 Proceedings of the Third International Conference on the Microscopy of Oxidation, Eds. S. B. Newcomb and J. A. Little, University of Cambridge, UK, 16-18 September: 573-586.
- Jacques, P. 2004. Current Opinion in Solid State and Materials Science 8: 259-265.
- Jacques, P., X. Cornet, Ph. Harlet, J. Ladrière and F. Delannay. 1998. Metall. Trans. A 29: 2383-2393.
- Jacques, P., Q. Furnémont, S. Godet, T. Pardoen, K. Conlon and F. Delannay. 2006. Philos. Mag. 86: 2371-2392.
- Jacques, P., Q. Furnémont, A. Mertens and F. Delannay. 2001. Phil. Mag. A 81: 1789-1812.
- Jacques, P., Q. Furnémont, T. Pardoen and F. Delannay. 2001. Acta mater. 49: 139-152.
- Jacques, P., E. Girault, T. Catlin, N. Geerlofs, T. Kop, S. van der Zwaag and F. Delannay. 1999. Mater. Sci. Eng. A 273-275: 475-479.
- Jacques, P.J., E. Girault, Ph. Harlet and F. Delannay. 2001. ISIJ Int. 41: 1061-1067.
- Jacques, P., E. Girault, A. Mertens, B. Verlinden, J. van Humbeeck and F. Delannay. 2001. ISIJ Int. 41: 1068-1074.
- Jacques, P.J., J. Ladrière and F. Delannay. 2001. Metall. Mater. Trans. A 32: 2759-2768.
- Jordan, C.E. and A.R. Marder. 1997. Metall. Mater. Trans. A 28: 2683-2694.
- Jung, I.-H., M. Paliwal, Y.-M. Kim, S.-K. Lee and J.-S. Kim. 2009. Proceedings of the Asia-Pacific Galvanizing Conference, The Corrosion Science Society of Korea, Jeju, Korea, November 8-12, paper A-34.

Khondker, R., A. Mertens and J.R. McDermid. 2007. Mat. Sci. Eng. A 463: 157-165.

- Kohlhaas, R., P. Dünner and N. Schmitz-Pranghe. 1967. Zeitschrift für angewandte Physik 23: 245-249.
- Krizan, D., B.C. De Cooman and J. Antonissen. 2004. International Conference on Advanced High Strength Sheet Steels for Automotive Applications Proceedings. Winter Park, CO, USA, July 6-9, 2004, Association for Iron and Steel Technology, Warrendale, PA, USA: 205-216.
- Kubaschewski, O. and C. B. Alcock. 1979. Metallurgical Thermochemistry. 5th Ed. Oxford, UK: Pergamon Press: 382.
- Lenev, L.M. and I.A. Novokhatskiy. 1966. Russian Metallurgy (abridged English translation of Izvetiya Akademii Nauk SSSR, Mentally) 3: 40-41.
- Leprêtre, Y., J.M. Mataigne, M. Guttmann and J. Philibert. 1998. Zinc-Based Steel Coating Systems: Production and Performance. TMS, Warrendale, PA, USA: 95-106.
- Li, X.S., S.-I. Baek, C.-S. Oh, S.-J. Kim, and Y.-W. Kim. 2007. Scripta Mater. 57: 113-116.
- Li, X.S., S.-I. Baek, C.-S. Oh, S.-J. Kim, and Y.-W. Kim. 2008. Scripta Mater. 59: 290-293.
- Lide, D.R. (Ed.). 2002. CRC Handbook of Chemistry and Physics. 83rd Ed. Boca Raton, FL, USA: CRC Press, Inc.
- Liu, H., Y. He, L. Li. 2009. Appl. Surf. Sci. 256: 1399-1403.
- Mackert, J.R., R.D. Ringle and C.W. Fairhurst. 1983. J. Dent. Res. 62: 1229-1235.
- Mahieu, J., S. Claessens and B.C. De Cooman. 2001. Metall. Mat. Trans. A 32: 2905-2908.
- Mahieu, J., S. Claessens, B.C. De Cooman and F. Goodwin. 2004. Proc. 6th Int. Conf. on Zinc Alloy Coated Steel Sheet, Galvatech'04, Chicago, IL, USA, April 4-7, 2004, Association for Iron and Steel Technology, Warrendale, PA, USA: 529-538.
- Mahieu, J., B.C. De Cooman, J. Maki and S. Claessens. 2002. Iron and Steelmaker 29: 29-34.
- Mahieu, J., J. Maki, B.C. De Cooman and S. Claessens. 2002. Metall. Mater. Trans. A 33: 2573-2580.

- Maki, J., J. Mahieu, B.C. De Cooman and S. Claessens. 2003. Materials Science and Technology 19: 125-131.
- Marder, A. 2000. Progress in Materials Science 45: 191-271.
- Mark, A. 2007. Doctoral Thesis, Queen's University, Kingston, ON, Canada.
- Mataigne, J.M., M. Lamberigts and V. Leroy. 1992. Developments in the Annealing of Sheet Steels, Eds. R. Pradhan and I. Gupta. Warrendale, PA, USA: Minerals, Metals & Materials Society: 512-528.
- Matsuda, H., F. Kitano, K. Hasegawa, T. Urabe and Y. Hosoya. 2002. Steel Res. 73: 211-217.
- Matsumura, O., Y. Sakuma and H. Takechi. 1987. Trans. ISIJ 27: 570-579.
- McDermid, J., S. Dionne, O. Dremailova, B. Voyzelle, E. Essadiqi, E. Baril and F. Goodwin. 2005. The effect of continuous galvanizing process parameters on the user properties of hot-rolled transformation induced plasticity steels, paper 2005-01-0495, 2005 SAE World Congress, Society for Automotive Engineers, Detroit, Michigan, USA.
- McDermid, J.R., M.H. Kaye and W.T. Thompson. 2007. Metall. Mater. Trans. B 38: 215-230.
- McDevitt, E., Y. Morimoto and M. Meshii. 1997. ISIJ Int. 37: 776-782.
- McDevitt, E., Y. Morimoto and M. Meshii. 1998. Proc. 4th Int. Conf. on Zinc and Zinc Alloy Coated Steel Sheet (GALVATECH'98), Chiba, Japan: 153-160.
- Meguerian, R. 2007. M.A.Sc. Thesis, McMaster University, Hamilton, ON, Canada.
- Meguerian, R. and J. McDermid. 2007. Proc. 7th Int. Conf. on Zinc and Zinc Alloy Coated Steel Sheet, Osaka, Japan, November 18-22: 448-453.
- Mehrkens, M. and J. Fröber. 2003. Steel Grips 1: 249-251.
- Mertens, A., P.J. Jacques, L. Zhao, S.O. Kruijver, J. Sietsma and F. Delannay. 2003. Journal De Physique IV 112: 305-308.
- Mertens, A. and J. McDermid. 2005. Materials Science & Technology 2005 Developments in Sheet Products for Automotive Applications, September 25-28, Pittsburgh, Pennsylvania, USA: 199-210.

Mertens, A. and J.R. McDermid. 2006. Materials Science and Technology (MS&T) 2006: Materials and Systems – Volume 2, October 15-19, Cincinnati, OH, USA: 131-142.

Morimoto, Y., E. McDevitt and M. Meshii. 1997. ISIJ Int. 37: 906-913.

Nakano, J. 2006. Doctoral Thesis, McMaster University, Hamilton, Ontario, Canada.

Oikawa, H. 1983. Technology Reports, Tohoku Univ. 48: 7-77.

Parezanović, I. and M. Spiegel. 2005. Steel Research Int. 76: 832-839.

- Pichler, A., S. Traint, G. Arnolder, P. Stiaszny, M. Blaimschein and E.A. Werner. 2003. Iron and Steelmaker 30: 21-31.
- Pickering, F.B. 1978. Physical Metallurgy and the Design of Steels. London, UK: Applied Science Publishers Ltd.: 11.
- Rapp, R.A. 1965. Corrosion 21: 382-401.
- Richerson, D.W. 1982. Modern Ceramic Engineering: Properties, Processing, and Use in Design, Marcel Dekker Inc., New York, USA: 92-93.
- Ruhl, R. and M. Cohen. 1969. Trans. Met. Soc. AIME 245: 241-251.
- Sachdev, A.K. 1983. Acta Metall. 31: 2037-2042.
- Sakaki, T., K. Sugimoto and T. Fukuzato. 1983. Acta Metall. 31: 1737-1746.
- Sakuma, Y., O. Matsumura and H. Takechi. 1991. Metall. Trans. A 22: 489-498.
- Schubert, K., U. Roesler, M. Kluge, K. Anderko and L. Haerle. 1953. Naturwissenschaften 40: 437.
- Shastry, C.R., J.A. Rotole and T.W. Kaiser. 2007. Proc. 7th Int. Conf. on Zinc and Zinc Alloy Coated Steel Sheet, Osaka, Japan, November 18-22: 403-408.
- Simmons, G. and H. Wang. 1971. Single Crystal Elastic Constants and Calculated Aggregate Properties: A Handbook, 2nd ed., The M.I.T. Press, Cambridge, MA, USA: 216.
- Srivastava, A.K., D. Battacharjee, G. Jha, N. Gope and S.B. Singh. 2006. Mater. Charact. 57: 127-135.

Srivastava, A.K., D. Battacharjee, G. Jha, N. Gope and S.B. Singh. 2007. Mater. Sci. Eng. A 445-446: 549-557.

Strohmeier, B.R. and D.M. Hercules. 1984. J. Phys. Chem. 88: 4992-4929.

- Sudo, M. and I. Tsukatani. 1985. Technology of Continuously Annealed Cold-Rolled Sheet Steel, Proceedings of a Symposium held at the TMS-AIME Fall Meeting. Warrendale, PA, USA: TMS-AIME: 341-360.
- Sugimoto, K., M. Misu, M. Kobayashi and H. Shirasawa. 1993. ISIJ Int. 33: 775-782.
- Suh, D.-W., S.-J. Park, T.-H. Lee, C.-S. Oh and S.-J. Kim. 2010. Metall. Mater. Trans. A 41: 397-408.
- Suzuki, Y., T. Yamashita, Y. Sugimoto, S. Fujita and S. Yamaguchi. 2009. ISIJ Int. 49: 564-573.
- Swisher, J. H. and E. T. Turkdogan. 1967. Transactions of the Metallurgical Society of AIME 239: 426-431.
- Takada, J. and M. Adachi. 1986. Journal of Material Science 21: 2133-2137.
- Takada, J., K. Kashiwagi and M. Adachi. 1984. Journal of Materials Science 19: 3451-3458.
- Takada, J., S. Yamamoto, S. Kikuchi and M. Adachi. 1986. Oxidation of Metals 25: 93-105.
- Takeuchi, S. 1969. J. Phys. Soc. Jpn. 27: 929-940.
- Tang, N.-Y. 1998. Zinc-Based Steel Coating Systems: Production and Performance. TMS, Warrendale, PA, USA: 3-12.
- Tang, N.-Y. 1999. Metall. Mater. Trans. B 30: 144-148.
- Tomota, Y., H. Tokuda, Y. Adachi, M. Wakita, N. Minakawa, A. Moriai, Y. Morii. 2004. Acta Mater. 52: 5737-5745.
- Traint, S., A. Pichler, M. Blaimschein, B. Röthler, C. Krempaszky and E. Werner. 2004. International Conference on Advanced High Strength Sheet Steels for Automotive Applications Proceedings, June 6-9, 2004, Winter Park, Colorado, USA, Association for Iron & Steel Technology: 79-98.
- ULSAB-AVC Advanced Vehicle Concepts Overview Report. 2002.

- Vanden Eynde, X., J.P. Servais and M. Lamberigts. 2004. Proc. 6th Int. Conf. on Zinc Alloy Coated Steel Sheet, Galvatech'04, Chicago, IL, USA, April 4-7, 2004, Association for Iron and Steel Technology: 361-372.
- Van De Putte, T., D. Loison, J. Penning and S. Claessens. 2008. Metall. Mater. Trans. A 39: 2875-2884.
- Van Slycken, J., P. Verleysen, J. Degrieck, J. Bouquerel and B.C. De Cooman. 2006. Proc. Inst. Mech. Eng. Part D J. Automob. Eng. 220: 391-400.
- Van Slycken, J., P. Verleysen, J. Degrieck, J. Bouquerel and B.C. De Cooman. 2007. Mater. Sci. Eng. A 460-461: 516-524.
- Vasilakos, A.N., J. Ohlert, K. Giasla, G.N. Haidemenopoulos and W. Bleck. 2002. Steel Res. 73: 249-252.
- Wagner, C. 1959. Zeitschrift für Elektrochemie 63: 772-782.

Wang, J. and S. Van Der Zwaag. 2001. Metall. Mater. Trans. A 32: 1527-1539.

- Wang, K.-K., H.-P. Wang, L. Chang, D. Gan, T.-R. Chen and H.-B. Chen. 2009. Proceedings of the Asia-Pacific Galvanizing Conference, The Corrosion Science Society of Korea, Jeju, Korea, November 8-12, paper A-32.
- Wanke, R. 1973. Schweissen und Schneiden 25: 252-254.
- Weast, R.C. (Ed.). 1978. CRC Handbook of Chemistry and Physics. 59th Ed. West Palm Beach, FL, USA: CRC Press, Inc.
- Yu, H., S. Li and Y. Gao. 2006. Mater. Charact. 57: 160-165.
- Zackay, V.F., E.R. Parker, D. Fahr and R.A. Busch. 1967. ASM Trans. Q. 60: 252-259.
- Zhang, M., L. Li, Y. Su, R. Fu, Z. Wan and B.C. De Cooman. 2007. Steel Res. Int. 78: 501-505.
- Zhang, Z.T., I.R. Sohn, F.S. Pettit, G.H. Meier and S. Sridhar. 2009. Metall. Mater. Trans. B 40: 567-584.

Appendix A: Modelling the transition between internal and external oxidation for the experimental alloys

Selective oxidation can occur as either internal oxidation; forming oxides below the gas-metal interface or as external oxidation; forming oxides at the gas-metal interface. The mode of oxidation will depend on whether the flux of oxygen into the surface is greater than the flux of alloying elements to the surface; the former will result in internal oxidation and the latter will result in external oxidation.

The transition between internal and external oxidation was modelled by Wagner (1959) for single crystals. Extensions of this model have been developed by many authors and were discussed in § 2.3.2.3 (Mataigne et al. 1992, Grabke et al.1995, Shastry et al. 2007, Huin et al. 1996, Huin et al. 2005). For the alloys used in the present study, the transition between internal and external oxidation was calculated for the individual alloying elements in the bulk steel and at the grain boundaries for both ferrite and austenite. The following equations were used to calculate the transition between internal and external oxidation were discussed in detail in § 2.3.2. For individual elements in the bulk alloy equation (A.1) was used (Wagner 1959):

$$N_{B,crit}^{(O)} = \left[\frac{\pi g^* V N_O^{(S)} D_O}{2n V_{BO_n} D_B}\right]^{1/2}$$
(A.1)

In equation (A.1):

 $N_{B,crit}^{(O)}$ is the critical molar fraction of the alloying element that will be oxidized, if $N_{R} < N_{B,crit}^{(O)}$ then internal oxidation will occur, g^{*} is the critical volume fraction of precipitated oxides resulting in blocking the inward diffusion paths for oxygen, g^{*} was determined to be 0.3 by Rapp (1965), n is the stoichiometric ratio between the oxygen and metal atoms in the oxide, V is the alloy molar volume,

 $N_{\Omega}^{(S)}$ is the molar fraction of dissolved oxygen at the surface,

 D_0 is the diffusion coefficient for oxygen where $D_o = D'_o \exp\left[\frac{-Q_o}{RT}\right]$,

 V_{BO_n} is the molar volume of the oxide BO_n and

 D_B is the diffusion coefficient of the alloying element where $D_B = D'_B \exp\left[\frac{-Q_B}{RT}\right]$.

For individual elements at the grain boundaries equation (A.2) was used (Mataigne et al. 1992):

$$N_{B,crit.GB}^{(O)} = \left[\frac{\pi g^* V N_O^{(S)} D_O' \exp\left(\frac{-Q_O}{2RT}\right)}{2n V_{BO_n} D_B' \exp\left(\frac{-Q_B}{2RT}\right)}\right]^{1/2}$$
(A.2)

The appropriate diffusion data was obtained from the literature for oxygen, manganese, silicon and aluminium in ferrite and austenite and is provided in Table A.1. The pre-exponential term, D'_{Si} , for Si in ferrite is dependent on the concentration of Si in the alloy and, therefore, varied for the three alloys containing Si, values for D'_{Si} are shown in Table A.2. When more than one set of diffusion data was available for an element, the data was chosen which was collected at a similar temperature to that used in the present experiments and/or had a similar concentration in the alloy. The molar

volumes for the matrix and oxides of alloying elements and the stoichiometric ratio (n)

are provided in Table A.3.

Table A.1: Diffusion data for species in ferrite (α) and austenite (γ) needed for equations (A.1) and (A.2)

Element and phase	$D'_i [cm^2/s]$	Q _i [kJ/mol]	Reference
O in α	0.00291	89.5	Takada and Adachi 1986
Mn in α	0.756	224.35	Oikawa 1983
Si in a	$0.735(1 + 12.4X_{Si})$	219.786	Borg and Lai 1970
Al in α	5.15	245.8	Takada et al. 1986
O in γ	0.642	159	Takada et al. 1984
Mn in γ	0.178	264.2	Oikawa 1983
Si in γ	0.21	242	Takada et al. 1984
Al in γ	5.9	241.58	Diffusion Data 1969

Table A.2: Diffusion coefficients for Si (D'_{Si}) in ferrite needed for equations (A.1) and (A.2) (Borg and Lai 1970)

Alloy	D'_{si} [cm ² /s]
1.0% Al steel	0.825
1.0% Si steel	0.914
1.5% Si steel	1.003

Table A.3: Molar volumes and stoichiometric ratio (n) for oxide species BO_n needed for equations (A.1) and (A.2) (Weast 1978, Lide 2002)

Phase	Molar volume (V_{BO_n}) [cm ³ /mol]	n	
MnO	13.221	1	
SiO ₂	26.12	2	
Al ₂ O ₃	12.7875	1.5	
Ferrite (a)	7.0918	_	
Austenite (y)	7.299		

The molar fraction of dissolved oxygen at the steel surface ($N_{\rm O}^{(S)}$) is determined

by equation (A.3) (Mataigne et al. 1992):

$$N_{O}^{(S)} = \left(\frac{1}{100}\right) \left(\frac{\text{molar mass Fe}}{\text{molar mass O}}\right) (\text{wt.}\%O_{\text{dissolved}})$$
(A.3)

The dissolved oxygen at the steel surface is calculated from the equilibrium constant, K, for the reaction shown in equation (A.4), where K is defined using equation (A.5):

$$\mathbf{H}_2 + \left[\mathbf{O}\right] = \mathbf{H}_2 \mathbf{O} \tag{A.4}$$

$$K = \frac{P_{H_2O}}{P_{H_2}[wt. \% O_{dissolved}]}$$
(A.5)

The value of K is calculated in equation (A.6) for ferrite and equation (A.7) for austenite (Swisher and Turkdogan 1967):

$$\log K = \frac{5000}{T} - 0.79 \tag{A.6}$$

and

$$\log K = \frac{4050}{T} + 0.06 \tag{A.7}$$

The predicted oxidation mode for the experimental alloys is provided in Table A.4 for individual phases and elements, oxidation in the matrix and at grain boundaries are treated separately. External oxidation of the grain boundaries is generally expected for all process atmospheres with the exception of Mn at austenite grain boundaries at the +5 °C dp. External oxidation at the grain boundaries agrees with the experimental results, where all samples showed oxidation at the grain boundaries (Figure 6.7 through Figure 6.25). However, the modelling results for Mn in ferrite and austenite should be treated with caution due to the high solubility product of MnO whereas Wagner's model assumes

a very low solubility product. This issue was addressed by Huin et al. (2005), who showed that the amount of MnO precipitated will increase with time for a given distance from the surface whereas the Wagner model predicts a fixed amount of oxide precipitated for a given position once the oxidation front has passed that point. At the +5 °C dp internal oxidation in the matrix is expected for all alloys (except Al in austenite for the 1.5% Al steel). For the 1.5% Al steel and 1.0% Al steel there is good agreement with the experimental results. At the +5 °C dp the majority of the surface oxidation occurred at the grain boundaries, however, there were also grains where oxide films were observed on the surface (Figure 6.10 and Figure 6.13). For the 1.0% Si steel and 1.5% Si steel the experimental results did not agree with the model as external oxidation was observed by SAM at the +5 °C dp (Figure 6.18 and Figure 6.25). However, internal oxidation of the 1.0% Si +5 °C dp steel was observed by TEM (Figure 6.54). The reason the predicted oxidation mode for Si does not agree with the experimental results is likely due to the multiple alloying elements in the experimental alloys. Multiple alloying elements require a higher oxygen partial pressure to promote internal oxidation.

		Prediction of internal or external oxidatio				
Alloy	Process atmosphere	Element	Ferrite matrix	Ferrite grain boundary	Austenite matrix	Austenite grain boundary
	-53 °C dn	Mn	External	External	Internal	
	-55 C up	Al	External		External	External
1.5% Al	-30 °C dn	Mn	Internal		Internal	LAternal
	-50°C up	Al	External		External	
	+5 °C dp	Mn	Internal		Internal	Internal
	is cup	Al	Internal		External	External
		Mn			Internal	
	-53 °C dp	Al	External		External	
		Si			External	External
		Mn	Internal		Internal	External
1.0% Al	-30 °C dp	Al	mternar		External	
		Si	External		Internal	
		Mn	Internal			Internal
	+5 °C dp	Al			Internal	External
		Si				
	-50 °C dp	Mn	External		Internal	
		Al			External	
		S1				External
1.00/ 01	-30 °C dp	Mn	Internal		Internal	
1.0% Si		Al	D 1		External	
		S1	External			T / 1
	+5 °C dp	Mn	T 1		T	Internal
		Al	Internal		Internal	External
		S1			T (1	
1.5% Si	-53 °C dp	Mn	External		Internal	
	-	SI Ma	Internal		External	External
	-30 °C dp	NIN C:	Thiernal External		Enternal	
	+5 °C dp	51 Ma	Internal		External	Internal
		IVIN C:			Internal	Internal External
		51				External

Table A.4: Predicted oxidation mode for experimental alloys

Appendix B: XPS binding energies compiled from the literature

Name	Mn 2p _{3/2}	$Mn \\ 2p_{1/2}$	Al 2p	Si 2p	Fe 2p _{3/2}	O 1s	Reference
Si				99.4		1	Finster 1988
SiO ₂				103.2		532.2	Finster 1988
SiO ₂				103.9		533.0	Finster 1988
Al ₂ O ₃			74.5			531.3	Strohmeier and Hercules 1984
MnO	641.7	653.3				530.2	Strohmeier and Hercules 1984
MnO ₂	642.6	654.2				529.7	Strohmeier and Hercules 1984
MnAl ₂ O ₄	641.6	653.4	74.5			531.3	Strohmeier and Hercules 1984
Mn ₂ SiO ₄				102.5			Casey et al. 1993
SiO ₂				103.2			Parezanović and Spiegel 2005
Mn ₂ SiO ₄	642.1			102.6			Parezanović and Spiegel 2005
Mn ₂ SiO ₄				103.3			Vanden Eynde et al. 2004
SiO ₂				104.5			Vanden Eynde et al. 2004
SiO ₂				103			Van De Putte et al. 2008
SiO _x				102			Van De Putte et al. 2008
Mn ₂ SiO ₄				101.4			Van De Putte et al. 2008
Fe _{1.1} O					709.5	529.9	Grosvenor et al. 2004
a-Fe ₂ O ₃					710.8	530.0	Grosvenor et al. 2004
Fe ₃ O ₄					Fe^{2+} :	530.2	Grosvenor et al. 2004
					709.0		
					Fe ³⁺ :		
					711.4	<u> </u>	
α-FeOOH		1			711.4		Grosvenor et al. 2004

Table B.1: XPS binding energies compiled from the literature

Appendix C: Effect of annealing time on selective oxidation

XPS depth profiles were used to study the effect of annealing time and temperature on the steel surface chemistry. The XPS depth profiles were collected for the as received surface, after reaching the IA temperature, following the 120 s hold at the IA temperature and after 30, 60, 90 and 120 s of the IBT hold at 465 °C. Depth profiles are shown for the four experimental alloys in Figure C.1 through Figure C.12 for oxygen and the alloying elements; Mn, Si and Al. It was determined that the majority of oxide growth occurred during the 120 s hold at the IA temperatures.



Figure C.1: XPS depth profiles for the 1.5% Al -53 °C dp steel, a) O, b) Mn and c) Al.



Figure C.2: XPS depth profiles for the 1.5% Al -30 °C dp steel, a) O, b) Mn and c) Al.



Figure C.3: XPS depth profiles for the 1.5% Al +5 °C dp steel, a) O, b) Mn and c) Al.



Figure C.4: XPS depth profiles for the 1.0% Al -53 $^{\circ}$ C dp steel, a) O, b) Mn, c) Al and d) Si.



Figure C.4 continued.



Figure C.5: XPS depth profiles for the 1.0% Al -30 $^{\circ}$ C dp steel, a) O, b) Mn, c) Al and d) Si.



Figure C.5 continued.



Figure C.6: XPS depth profiles for the 1.0% Al +5 °C dp steel, a) O, b) Mn, c) Al and d) Si.



Figure C.6 continued.



Figure C.7: XPS depth profiles for the 1.0% Si -50 °C dp steel, a) O, b) Mn, c) Al and d) Si.



Figure C.7 continued.



Figure C.8: XPS depth profiles for the 1.0% Si -30 °C dp steel, a) O, b) Mn, c) Al and d) Si.


Figure C.8 continued.



Figure C.9: XPS depth profiles for the 1.0% Si +5 $^{\circ}$ C dp steel, a) O, b) Mn, c) Al and d) Si.



Figure C.9 continued.



Figure C.10: XPS depth profiles for the 1.5% Si -53 °C dp steel, a) O, b) Mn and c) Si.



Figure C.11: XPS depth profiles for the 1.5% Si -30 °C dp steel, a) O, b) Mn and c) Si.



Figure C.12: XPS depth profiles for the 1.5% Si +5 °C dp steel, a) O, b) Mn and c) Si.