Selective surface oxidation and segregation upon short term annealing of model alloys and industrial steel grades

Dissertation

zur
Erlangung des Grades
„Doktor der Naturwissenschaften“
an der Fakultät für Physik und Astronomie
der Ruhr-Universität Bochum

vorgelegt von

Srinivasan Swaminathan
geboren in Tiruvarur (Tamilnadu, India)

Bochum
2007
1. Gutachter: Prof. Dr. Andreas D. Wieck
2. Gutachter: Priv.-Doz. Dr. Michael Spiegel

Tag der Disputation: 11.12.2007
## Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>CONTENTS</td>
<td>I</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>III</td>
</tr>
<tr>
<td>LIST OF SYMBOLS</td>
<td>IV</td>
</tr>
<tr>
<td>CHAPTER 1 – INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>CHAPTER 2 – FUNDAMENTALS ON OXIDATION AND SEGREGATION</td>
<td>3</td>
</tr>
<tr>
<td>2.1. THERMODYNAMICS OF METAL-OXYGEN REACTIONS</td>
<td>3</td>
</tr>
<tr>
<td>2.2. KINETIC ASPECTS OF OXIDATION</td>
<td>9</td>
</tr>
<tr>
<td>2.3. EXTERNAL/INTERNAL SELECTIVE OXIDATION</td>
<td>15</td>
</tr>
<tr>
<td>2.4. SURFACE SEGREGATION</td>
<td>21</td>
</tr>
<tr>
<td>CHAPTER 3 – SELECTIVE SURFACE OXIDATION AND ITS INFLUENCE ON ZINC</td>
<td>27</td>
</tr>
<tr>
<td>WETTABILITY IN HOT-DIP GALVANIZING (HDG) PROCESS: BRIEF REVIEW</td>
<td>28</td>
</tr>
<tr>
<td>3.1. SURFACE CHEMISTRY AFTER RECRYSTALLIZATION ANNEALING</td>
<td>27</td>
</tr>
<tr>
<td>3.1.1. High strength steels</td>
<td>27</td>
</tr>
<tr>
<td>3.1.2. Model alloys</td>
<td>30</td>
</tr>
<tr>
<td>3.2. ZINC WETTABILITY</td>
<td>32</td>
</tr>
<tr>
<td>3.2.1. Contact angle measurement (Sessile drop method)</td>
<td>34</td>
</tr>
<tr>
<td>CHAPTER 4 – EXPERIMENTATION</td>
<td>37</td>
</tr>
<tr>
<td>4.1. MATERIALS</td>
<td>37</td>
</tr>
<tr>
<td>4.1.1. Model alloys</td>
<td>37</td>
</tr>
<tr>
<td>4.1.2. Industrial steel grades</td>
<td>37</td>
</tr>
<tr>
<td>4.2. EXPERIMENTAL SET UP</td>
<td>38</td>
</tr>
<tr>
<td>4.2.1. Infrared furnace</td>
<td>38</td>
</tr>
<tr>
<td>4.2.2. Liquid zinc spin coater</td>
<td>40</td>
</tr>
<tr>
<td>4.2.3. High temperature reactor</td>
<td>44</td>
</tr>
<tr>
<td>4.3. ANALYSIS METHODS</td>
<td>46</td>
</tr>
<tr>
<td>4.3.1. X-ray Photoelectron Spectroscopy (XPS)</td>
<td>46</td>
</tr>
<tr>
<td>4.3.2. Field Emission Scanning Electron Microscopy (FE-SEM)</td>
<td>47</td>
</tr>
<tr>
<td>4.3.3. Grazing Incidence X-Ray Diffraction (GI-XRD)</td>
<td>48</td>
</tr>
<tr>
<td>4.3.4. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)</td>
<td>48</td>
</tr>
<tr>
<td>4.3.5. Focused Ion Beam (FIB) micromachining</td>
<td>49</td>
</tr>
<tr>
<td>CHAPTER 5 – RESULTS AND DISCUSSIONS</td>
<td>50</td>
</tr>
<tr>
<td>5.1. ANNEALING STUDIES OF MODEL ALLOYS</td>
<td>50</td>
</tr>
<tr>
<td>5.1.1. Binary alloys (Fe-2Si, Fe-2Mn and Fe-0.8Cr)</td>
<td>50</td>
</tr>
<tr>
<td>5.1.2. Ternary alloys (Fe-2Mn-2Si, Fe-2Mn-0.8Cr and Fe-2Si-0.8Cr)</td>
<td>53</td>
</tr>
<tr>
<td>5.1.3. Quaternary alloy (Fe-2Mn-2Si-0.8Cr)</td>
<td>57</td>
</tr>
<tr>
<td>5.1.4. Discussions</td>
<td>62</td>
</tr>
<tr>
<td>5.1.5. Conclusions</td>
<td>69</td>
</tr>
<tr>
<td>5.2. EFFECT OF ALLOY COMPOSITION ON THE SELECTIVE OXIDIZATION OF TERNARY MODEL ALLOYS</td>
<td>70</td>
</tr>
<tr>
<td>5.2.1. Fe-Si-Cr ternary alloys (Fe-1Si-0.8Cr and Fe-2Si-0.8Cr)</td>
<td>70</td>
</tr>
<tr>
<td>5.2.2. Fe-Mn-Cr ternary alloys (Fe-1Mn-0.8Cr and Fe-2Mn-0.8Cr)</td>
<td>73</td>
</tr>
<tr>
<td>5.2.3. Discussions</td>
<td>75</td>
</tr>
<tr>
<td>5.2.4. Conclusions</td>
<td>76</td>
</tr>
<tr>
<td>5.3. ANNEALING STUDIES OF INDUSTRIAL STEELS</td>
<td>77</td>
</tr>
<tr>
<td>5.3.1. IF-1 steel</td>
<td>77</td>
</tr>
<tr>
<td>5.3.2. IF-2 steel</td>
<td>80</td>
</tr>
<tr>
<td>5.3.3. TS1000 steel</td>
<td>82</td>
</tr>
<tr>
<td>5.3.4. Discussions</td>
<td>85</td>
</tr>
<tr>
<td>5.3.5. Conclusions</td>
<td>87</td>
</tr>
</tbody>
</table>
5.4. **Effect of Dwelling Time on the Surface Coverage of Oxides in IF Steels and Quaternary Model Alloys**

5.4.1. Interstitial free (IF) steels ................................................................. 88
5.4.2. Quaternary model alloy ................................................................. 91
5.4.3. Discussions .................................................................................. 94
5.4.4. Conclusions .................................................................................. 96

5.5. **Wetting Studies: Hot-Dip Galvanizing Simulation of Model Alloys and Industrial Steel Grades** ........................................................................... 97

5.5.1. Quaternary model alloy ................................................................. 97
5.5.2. IF-1 steel ..................................................................................... 98
5.5.3. IF-2 steel ..................................................................................... 99
5.5.4. TS1000 steel ............................................................................... 100
5.5.5. Discussions ................................................................................ 100
5.5.6. Conclusions ............................................................................... 103

**CHAPTER 6 – SUMMARY** .............................................................................. 104

**REFERENCES** .................................................................................................. 108

**APPENDIX A: COMPARISON OF IN-SITU (HIGH TEMPERATURE REACTOR) AND EX-SITU (INFRARED FURNACE) ANNEALING** ........................................................................................................... 115

A.1. INTERSTITIAL FREE STEEL ................................................................. 115
A.1.1. In-situ and ex-situ annealing of IF-1 steel at low dew point -79 °C .... 115
A.1.2. Surface chemistry of IF-1 steel by in-situ annealing at different dew points ........................................................................... 117
A.2. BINARY MODEL ALLOY ...................................................................... 120
A.2.1. In-situ and ex-situ annealing of Fe-2Si binary alloy at dew point -40 °C .................................................. 120
A.3. CONCLUSIONS .................................................................................. 121

**APPENDIX B: STUDY OF INTERFACIAL LAYER FORMED DURING HOT-DIP GALVANIZING SIMULATION OF IF-1 STEEL BY LIQUID ZINC SPIN COATER** ................................................................. 122

**ACKNOWLEDGEMENTS** .............................................................................. 126

**LIST OF PUBLICATIONS** ............................................................................. 128

**CURRICULUM VITAE** ................................................................................ 129
List of abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Meaning</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE</td>
<td>Binding Energy</td>
</tr>
<tr>
<td>CP</td>
<td>Complex Phase</td>
</tr>
<tr>
<td>DP Steel</td>
<td>Dual Phase Steel</td>
</tr>
<tr>
<td>DP</td>
<td>Dew Point</td>
</tr>
<tr>
<td>EDX</td>
<td>Energy Dispersive X-Ray spectroscopy</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectroscopy for Chemical Analysis</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>Field Emission Scanning Electron Microscopy</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>GB</td>
<td>Grain Boundary</td>
</tr>
<tr>
<td>GI-XRD</td>
<td>Grazing Incidence X-Ray Diffraction</td>
</tr>
<tr>
<td>HDG</td>
<td>Hot Dip Galvanizing</td>
</tr>
<tr>
<td>HSS</td>
<td>High Strength Steels</td>
</tr>
<tr>
<td>HTR</td>
<td>High Temperature Reactor</td>
</tr>
<tr>
<td>IF</td>
<td>Interstitial Free</td>
</tr>
<tr>
<td>IR</td>
<td>Infra Red</td>
</tr>
<tr>
<td>LMIG</td>
<td>Liquid Metal Ion Gun</td>
</tr>
<tr>
<td>MPSE</td>
<td>Multi Purpose Secondary Electron</td>
</tr>
<tr>
<td>PID</td>
<td>Proportional-Integral-Derivative</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Ti-IF</td>
<td>Titanium-Interstitial Free</td>
</tr>
<tr>
<td>TiNb-IF</td>
<td>Titanium Niobium-Interstitial Free</td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>Time of Flight-Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>TRIP</td>
<td>Transformation Induced Plasticity</td>
</tr>
<tr>
<td>TS</td>
<td>Tensile Strength</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>ULC</td>
<td>Ultra Low Carbon</td>
</tr>
<tr>
<td>VP</td>
<td>Variable Pressure</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray Photoelectron Spectroscopy</td>
</tr>
<tr>
<td>YS</td>
<td>Yield Strength</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
</tbody>
</table>
## List of symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>Activation energy for the metal cations</td>
</tr>
<tr>
<td>a_Me</td>
<td>Activity of metal</td>
</tr>
<tr>
<td>a_Me,O</td>
<td>Activity of metal oxide</td>
</tr>
<tr>
<td>( \theta_i )</td>
<td>Angle taken on a simple planar surface composed entirely of surface component or chemical species i</td>
</tr>
<tr>
<td>( Z.e )</td>
<td>Charge of the emitted secondary ion</td>
</tr>
<tr>
<td>( \xi )</td>
<td>Depth of internal oxidation zone penetration</td>
</tr>
<tr>
<td>DP</td>
<td>Dew Point</td>
</tr>
<tr>
<td>D_o</td>
<td>Diffusivity of oxygen</td>
</tr>
<tr>
<td>D_B</td>
<td>Diffusivity of the solute B</td>
</tr>
<tr>
<td>( \gamma )</td>
<td>Dimensionless parameter (as a function of D_o)</td>
</tr>
<tr>
<td>L_0</td>
<td>Effective length of the spectrometer</td>
</tr>
<tr>
<td>( \theta_{eff} )</td>
<td>Effective or average contact angle</td>
</tr>
<tr>
<td>( \Delta H_A^0 )</td>
<td>Enthalpy of segregation</td>
</tr>
<tr>
<td>( \Delta S_A^0 )</td>
<td>Entropy of segregation</td>
</tr>
<tr>
<td>K</td>
<td>Equilibrium constant</td>
</tr>
<tr>
<td>( \Gamma )-Phase</td>
<td>Fe-Zn intermetallic with 18-31% Fe</td>
</tr>
<tr>
<td>( \zeta )-Phase</td>
<td>Fe-Zn intermetallic with 6-7% Fe</td>
</tr>
<tr>
<td>( \delta )-Phase</td>
<td>Fe-Zn intermetallic with 8-13% Fe</td>
</tr>
<tr>
<td>F</td>
<td>Field across the oxide film</td>
</tr>
<tr>
<td>( f_i )</td>
<td>Fraction by area of the surface made up of chemical species or component i</td>
</tr>
<tr>
<td>( \Delta RG )</td>
<td>Gibbs free energy for the reaction</td>
</tr>
<tr>
<td>( N_B^0 )</td>
<td>Initial solute B concentration</td>
</tr>
<tr>
<td>( \alpha )</td>
<td>Interaction energy term</td>
</tr>
<tr>
<td>( \gamma_{LG} )</td>
<td>Interfacial energy of liquid-gas system</td>
</tr>
<tr>
<td>( \gamma_{SG} )</td>
<td>Interfacial energy of solid-gas system</td>
</tr>
<tr>
<td>( \gamma_{SL} )</td>
<td>Interfacial energy of solid-liquid system</td>
</tr>
<tr>
<td><strong>Symbol</strong></td>
<td><strong>Description</strong></td>
</tr>
<tr>
<td>------------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>$k_{il}$</td>
<td>Inverse logarithmic rate constant</td>
</tr>
<tr>
<td>$E_k$</td>
<td>Kinetic energy</td>
</tr>
<tr>
<td>$k_l$</td>
<td>Linear rate constant</td>
</tr>
<tr>
<td>$k_{log}$</td>
<td>Logarithmic rate constant</td>
</tr>
<tr>
<td>$m$</td>
<td>Mass of the emitted secondary ion</td>
</tr>
<tr>
<td>$N_O^S$</td>
<td>Oxygen solubility</td>
</tr>
<tr>
<td>$k_p$</td>
<td>Parabolic rate constant</td>
</tr>
<tr>
<td>$p_o_2$</td>
<td>Partial pressure of oxygen</td>
</tr>
<tr>
<td>$p_{H_2O}$</td>
<td>Partial pressure of water vapour</td>
</tr>
<tr>
<td>$h$</td>
<td>Planck constant</td>
</tr>
<tr>
<td>$V$</td>
<td>Potential drop across the oxide film</td>
</tr>
<tr>
<td>$r$</td>
<td>Ratio of true to planar surface area</td>
</tr>
<tr>
<td>$\Gamma_A^{sat}$</td>
<td>Saturation coverage</td>
</tr>
<tr>
<td>$\phi_s$</td>
<td>Spectrometer work function</td>
</tr>
<tr>
<td>$K_{BO_v}$</td>
<td>Solubility product of oxide $BO_v$</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>Standard Gibbs free energy for the reaction</td>
</tr>
<tr>
<td>$\nu$</td>
<td>Stoichiometry parameter</td>
</tr>
<tr>
<td>$\Gamma_A$</td>
<td>Surface concentration of segregating species A</td>
</tr>
<tr>
<td>$\theta$</td>
<td>Surface coverage</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>Surface energy</td>
</tr>
<tr>
<td>$T$</td>
<td>Temperature</td>
</tr>
<tr>
<td>$a_A$</td>
<td>Thermodynamic activity of the segregating species A</td>
</tr>
<tr>
<td>$X$</td>
<td>Thickness of the oxide film</td>
</tr>
<tr>
<td>$t$</td>
<td>Time</td>
</tr>
<tr>
<td>$a$</td>
<td>Tunnelling (jump) distance for electron</td>
</tr>
<tr>
<td>$R$</td>
<td>Universal gas constant</td>
</tr>
<tr>
<td>$v$</td>
<td>Velocity of the emitted secondary ion</td>
</tr>
<tr>
<td>$\eta-Zn$</td>
<td>Zinc rich solid solution with 0.04%Fe</td>
</tr>
</tbody>
</table>
Chapter 1 – Introduction

High strength steels (interstitial free (IF), dual phase (DP), transformation-induced plasticity (TRIP), complex phase (CP), and martensitic steels) are of great interest for the automotive industry following the demand of producing lighter and stiffer car bodies. Therefore, most of the structural parts that compose the car body require very high strength materials with excellent formability. The alloying of steel grades with solution strengthening elements (Mn, Si, Al, Cr, etc.) satisfies the automotive industry’s need for steels with both higher strength and enhanced formability. The increased chemical complexity of the steels by addition of alloying elements causes significant problems in the hot-dip galvanizing (HDG) process.

Cold rolled high strength steels exhibit remaining stresses from the rolling process and, therefore, undergo recrystallization annealing before hot-dip galvanizing. The annealing process is conducted in a protective N₂-5%H₂ gas atmosphere (at a dew point of -30 °C) and during annealing, segregation and oxidation of minor alloying elements (Mn, Si, Al, Cr, etc.) occurs. The formed oxides are small islands and make the steel surface unsuitable for subsequent galvanizing, as these oxides deteriorate the wettability by liquid Zn. During further processing of the strips, the zinc coated surface exhibit defects (or bare spots) and in the worst case spallation occurs. Therefore, the surface state of the steel sheets i.e. surface chemistry after recrystallization annealing in the protective atmosphere, plays a key role in the quality of the surface finish.

As the composition of the steel grades is fixed, a modification of the surface chemistry is only possible by modifying the heat treatment parameters i.e. gas phase composition in order to influence the selective oxidation/segregation of harmful elements. Since the steel is a complex system of many alloying elements (i.e. multicomponent alloy), systematic investigations on the model alloys is needed for better understanding of oxide nucleation and segregation during annealing. Moreover, the compositions of the alloying elements in model alloys have to be chosen in accordance to composition of newly developed high strength steels.
The main objective of this work is to investigate the influence of the annealing conditions and the effect of alloying elements on the selective oxidation in model alloys and some industrial steel grades for comparison. Secondly, to investigate the influence of surface chemistry (i.e. type of oxides, thickness and its distribution/surface coverage) on the Zn wettability by simulating the hot-dip galvanizing process at laboratory scale.
Chapter 2 – Fundamentals on oxidation and segregation

2.1. Thermodynamics of metal-oxygen reactions

The chemical reaction of a metal (Me) with oxygen can be expressed as,

\[ \text{xMe} + \frac{y}{2} \text{O}_2 \leftrightarrow \text{Me}_x \text{O}_y \]  

(2.1)

The question of whether or not a reaction can occur is answered by the Gibbs Free Energy. In high temperature oxidation usually temperature and total pressure are constant and the driving force for the reaction is the Gibbs free energy.

For a chemical reaction, the Gibbs free energy \( \Delta_r G \) is given by,

\[ \Delta_r G = \Delta_r G^0 + RT \ln K \]  

(2.2)

Here, \( \Delta_r G^0 \) is the standard Gibbs free energy for the reaction.

The Gibbs free energy \( \Delta_r G \) gives information about the reaction direction. When the reaction is in equilibrium the value of \( \Delta_r G \) is zero, when \( \Delta_r G < 0 \) the reaction occurs in direction of the products and when \( \Delta_r G > 0 \) the reaction will occur in opposite direction. In equilibrium (i.e. \( \Delta_r G = 0 \)), the equation (2.2) becomes,

\[ \Delta_r G^0 = -RT \ln K \]  

(2.3)

The equilibrium constant \( K \) is the ratio of the activities of the products to reactants (law of mass action) and can be written as,

\[ K = \frac{a_{\text{Me}_x \text{O}_y}}{a^x_{\text{Me}} \cdot (p_{\text{O}_2})^{y/2}} \]  

(2.4)

Here \( a_{\text{Me}_x \text{O}_y} \), \( a^x_{\text{Me}} \) are the activities of metal oxide and metal, and \( p_{\text{O}_2} \) is the partial pressure of oxygen.

Taking into account that the activities of pure, condensed phases are one and replacing of equation (2.4) in (2.3) becomes,

\[ \Delta_r G^0 = RT \cdot \ln(p_{\text{O}_2})^{y/2} \]  

(2.5)

The equation (2.5) determines the minimum oxygen partial pressure (partial pressure of formation) to form the metal oxide. If the oxygen pressure exceeds this value at the
temperature in question, an oxide will form. The relation between standard Gibbs free energy and temperature used to predict equilibrium oxygen potentials is given by the Ellingham-Richardson diagram, shown in Fig. 2.1.

Fig. 2.1. Standard Gibbs free energy of formation of some selected oxides as a function of temperature (Ellingham-Richardson diagram) [BM83].

The scale on the right side of the diagram (Fig. 2.1) labelled ‘$p_{O_2}$’ is used to determine what partial pressure of oxygen will be in equilibrium with the metal and metal oxide at a given temperature. This may be directly obtained from the diagram by drawing a straight line from the origin marked ‘O’ (upper left corner of the diagram) through the free energy
line at the temperature of interest and reading the oxygen pressure from its intersection with the scale at the right side ‘\( p_{O_2} \)’.

In this present investigation, HSC program [HSC97] (Outokumpu Research, Finland) has been used to calculate the partial pressure of oxygen for the reactions of oxidation of elements of interest. The major oxidizing agent during annealing of steels is the dissociation equilibrium of water from the annealing atmosphere. A typical atmosphere used during the annealing of cold-rolled steel sheets is \( N_2-H_2 \). The adsorption of oxygen from the atmosphere, due to the dissociation equilibrium of \( H_2O \) can be written as,

\[
H_2 + \frac{1}{2} O_2 = H_2O
\]  \hspace{1cm} (2.6)

By applying the mass action law,

\[
K_1 = \frac{p_{H_2O}}{p_{H_2} \cdot p_{O_2}^{0.5}}
\]  \hspace{1cm} (2.7)

According to equation (2.3), the equilibrium constant \( K_1 \) can be related as follows,

\[
\Delta G^\theta = -RT\ln K_1
\]  \hspace{1cm} (2.8)

The partial pressure of \( H_2O \) in a gas is usually described by the dew point temperature (DP in °C). The dew point (DP) of the annealing atmosphere is the temperature at which the first droplet of liquid water or nucleus of ice appears, when this atmosphere is cooled down under conditions of constant partial pressure of water vapour. The water content basically determines the oxygen content of the atmosphere at any given temperature (equation 2.6) through chemical equilibrium between water vapour and gaseous oxygen and hydrogen. The relationship between \( p_{H_2O} \) and DP is available in many literatures [GGSW’94, HFL05]. The following formulas, which were adjusted by Huin et al. [HFL05] using experimental data provided by the Thermodata bank [The05], provide the saturation vapour pressure of water (\( p_{satH_2O} \)), in bar, at the temperature of the dew point (DP), in °C,
Chapter 2 – Fundamentals on oxidation and segregation

\[
\log_{10} p_{\text{sat} H_2O} = \begin{cases} 
  9.80 \text{ DP} / (273.15 + \text{DP}) - 2.22 & \text{if } \text{DP} \leq 0 \degree C \\
  7.58 \text{ DP} / (240 + \text{DP}) - 2.22 & \text{if } \text{DP} > 0 \degree C 
\end{cases} \tag{2.9}
\]

Then, the partial pressure of oxygen (pO2) in the annealing atmosphere given by the following formula [RAGR74],

\[
\frac{1}{2} \log_{10} p_{O_2} = 3.00 - \frac{13088}{T} + \log_{10}(p_{\text{sat} H_2O}/p_{H_2}) \tag{2.10}
\]

Since the industrial standard annealing atmosphere is 95%N2-5%H2 (in vol.%) and their total pressure is 1bar, then the partial pressure of hydrogen pH₂ = 0.05 bar. The calculated pO₂ for various dew points of the annealing atmosphere at 820 °C (used in this investigation) is listed in Table 2.1.

Table 2.1. Calculated equilibrium partial pressure of oxygen at 820 °C for various DP of the N₂-5%H₂ annealing atmosphere.

<table>
<thead>
<tr>
<th>Dew point (DP in °C)</th>
<th>Calculated equilibrium partial pressure of oxygen at 820 °C [p_{O_2} in bar]</th>
</tr>
</thead>
<tbody>
<tr>
<td>-79</td>
<td>1.43 × 10^{-28}</td>
</tr>
<tr>
<td>-59</td>
<td>5.87 × 10^{-26}</td>
</tr>
<tr>
<td>-39</td>
<td>8.39 × 10^{-24}</td>
</tr>
<tr>
<td>-29</td>
<td>9.05 × 10^{-23}</td>
</tr>
<tr>
<td>0</td>
<td>1.89 × 10^{-20}</td>
</tr>
</tbody>
</table>

In Fig. 2.2, log pO₂ is plotted as function of temperature for oxidation reactions of Si, Mn, Cr and Fe. The dashed lines in this figure correspond to log pO₂ at DP ~ -30 °C, for the N₂-5%H₂ annealing atmosphere at 820 °C i.e. industrial annealing condition. It can be seen that the calculated partial pressure of oxygen in the industrial annealing condition is high enough to oxidize Si, Mn and Cr but not Fe. Oxides of Fe are reduced under this N₂-5%H₂ annealing condition.
Fig. 2.2. The calculated partial pressure of oxygen \( p_{O_2} \) as a function of temperature for oxidation reactions of Si, Mn, Cr and Fe.

The oxidation reaction of different elements of interest and its calculated equilibrium \( p_{O_2} \) at 820 °C is tabulated in Table 2.2. All the annealing conditions used in this present investigation (i.e. DP from -79 to 0 °C), is reducing for iron oxides. On the other hand, thermodynamical calculations show that, it’s practically impossible to reach the annealing conditions in which the oxidation of minor alloying elements like Al, Mn, Si etc. would be avoided. This can be clearly seen by comparing the table 2.1 and 2.2.
Table 2.2. Calculated equilibrium partial pressure of oxygen for oxidation reactions of different elements.

<table>
<thead>
<tr>
<th>Oxidation reactions</th>
<th>Equilibrium partial pressure of oxygen at 820 °C [ p_{O_2} \text{ in bar} ]</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \frac{4}{3} \text{Al} + \text{O}_2 = \frac{2}{3} \text{Al}_2\text{O}_3 )</td>
<td>( 4.46 \times 10^{-43} )</td>
</tr>
<tr>
<td>( \text{Ti} + \text{O}_2 = \text{TiO}_2 )</td>
<td>( 2.25 \times 10^{-36} )</td>
</tr>
<tr>
<td>( \text{Si} + \text{O}_2 = \text{SiO}_2 )</td>
<td>( 7.75 \times 10^{-35} )</td>
</tr>
<tr>
<td>( 2 \text{Mn} + \text{O}_2 = 2 \text{MnO} )</td>
<td>( 7.23 \times 10^{-30} )</td>
</tr>
<tr>
<td>( \frac{4}{3} \text{Cr} + \text{O}_2 = \frac{2}{3} \text{Cr}_2\text{O}_3 )</td>
<td>( 7.03 \times 10^{-28} )</td>
</tr>
<tr>
<td>( 2 \text{Fe} + \text{O}_2 = 2 \text{FeO} )</td>
<td>( 3.69 \times 10^{-19} )</td>
</tr>
<tr>
<td>( \frac{4}{3} \text{B} + \text{O}_2 = \frac{2}{3} \text{B}_2\text{O}_3 )</td>
<td>( 4.09 \times 10^{-32} )</td>
</tr>
<tr>
<td>( \frac{4}{5} \text{P} + \text{O}_2 = \frac{2}{5} \text{P}_2\text{O}_5 )</td>
<td>( 1.24 \times 10^{-30} )</td>
</tr>
<tr>
<td>( \frac{4}{5} \text{P} + \text{O}_2 = \frac{2}{5} \text{P}_2\text{O}_5 )</td>
<td>( 2.34 \times 10^{-19} )</td>
</tr>
</tbody>
</table>
2.2. Kinetic aspects of oxidation

Thermodynamical calculations help to predict the possible phases formed upon oxidation i.e. by calculating the equilibrium partial pressure of oxygen and the Gibbs Free Energy of formation one can determine the stability of oxides. However, in the very fast heating cycles considered here, the oxide growth is controlled by kinetics. The initial stages of metal-oxygen reaction involve the following steps:

(i) Adsorption of oxygen and surface reaction
(ii) Oxide nucleation
(iii) Lateral growth

At first, adsorption takes place before the oxygen partial pressure of oxide formation is reached. Being the active oxidizing species in the gas phase, oxygen molecules must approach the surface and become adsorbed there. Then, the adsorbed molecules split to form adsorbed oxygen which eventually attracts electrons from the lattice to become initially chemisorbed and finally incorporated into the lattice. This process can be represented as follows [BM83]:

\[
\begin{align*}
O_2(g) & \rightarrow O_2(ad) & 2O(ad) & \rightarrow 2O^2-(chem) \\
& & & 2e^{-}
\end{align*}
\]

(2.11)

Since the annealing atmosphere is a N$_2$-H$_2$ gas mixture, the oxidizing medium in our case is H$_2$/H$_2$O. In this case, the surface reactions may also be written as follows [Spi06]:

\[
\begin{align*}
H_2O(g) & \rightarrow H_2O (ad) & OH(ad) + H(ad) \\
& & \downarrow \quad H_2(g) \\
& & O(ad) + H(ad) \\
& & \quad \downarrow e^{-} \\
& & O^-(chem)
\end{align*}
\]

(2.12)
The surface coverage of adsorbed oxygen increases with increasing the partial pressure of oxygen. When a metal surface saturated with oxygen and further oxygen is supplied, oxide nuclei are formed on the surface. The oxide nuclei grow laterally to yield a continuous film on the surface. A model for such a growth process is shown in Fig. 2.3.

Fig. 2.3. Schematic model for the nucleation and growth of oxide on a metal surface. The oxide grows laterally until the surface is covered with a thin oxide film [Kof88].

Once the oxide nuclei are grown together, the surface oxides separate the metal from the gas phase. When a continuous film covers the surface, the reaction can proceed only through the solid-state diffusion of the reactants through the film. For thin films, the driving force for this transport of reactants may be due to electric fields in or across the film; for thick films or scales, it is determined by the chemical potential gradient across the scale. In reality, the reaction mechanism is complex and depends on a variety of factors such as pre-treatment and surface preparation, temperature, gas composition and pressure, and elapsed time of reaction. A classification of oxidation kinetics is shown in Fig. 2.4.
Chapter 2 – Fundamentals on oxidation and segregation

Adsorption and nucleation

Linear kinetics
Rate determining: Phase boundary reaction

Low temperature growth

In linear rate law, the oxidation of metals proceeds at a constant rate and may be described by,

\[ X = k_l t \quad (2.13) \]

Where \( X \) represent the thickness of the oxide film, \( t \) denotes the time and \( k_l \) represents the linear rate constant. In this case, the following phase boundary reactions are rate determining:

\[
\begin{align*}
M &= M^{2+} + 2e^- \quad \text{(metal/oxide)} \\
O_2 + 2e^- &= O^2- \quad \text{(oxide/gas)}
\end{align*}
\]

\( (2.14) \)

With time, oxide nuclei form on a metal surface, as shown in Fig. 2.3. Subsequently, an oxide film is formed on the surface and the kinetics of oxidation is controlled by diffusion in the layer, with a parabolic behaviour. The parabolic equation is given by,

\[ X^2 = 2k_p t \quad (2.15) \]

where \( k_p \) denotes the parabolic rate constant.

Fig. 2.4. Classification of different oxidation kinetics (linear, parabolic, logarithmic and inverse logarithmic).
The fundamental theoretical work on parabolic oxide scale growth (high temperature oxidation of metals) was done by Carl Wagner [Wag33]. The following are the assumptions made in Wagner’s theory.

1. The formed oxide scale is dense, well adhered to a metal surface and non-porous
2. Oxygen has only limited solubility in the metal
3. There are no space charge effects across the oxide and at the metal/oxide and oxide/gas interface
4. At each place in the scale as well as at the interfaces local thermodynamic equilibrium is established.

The basic assumption of the theory is that lattice diffusion of cations and/or anions associated with the transport of electrons through the dense scale are rate determining in the overall oxidation reaction. The schematics of the ionic migration process are shown in Fig. 2.5.

![Fig. 2.5. (a) Transport processes through a dense, singe-phase scale growing by lattice diffusion. Transport of reacting ions is rate determining.
(b) Transport processes in growing scale in terms of lattice and electronic defects, e.g. of metal vacancies and interstitial ions, electrons and electron holes [Kof88].](image)

The outward diffusion of cations and/or the inward diffusion of oxygen ions are responsible for the oxide growth. Which of these two processes, the outward or the inward diffusion, is rate determining, depends on the mobility of migrating ions in the system. The “driving force” for diffusion of ions is defined by a gradient of the chemical potential. A gradient of partial pressure of oxygen exists across the scale. From the partial pressure of oxygen in the
ambient atmosphere at the outer oxide surface, to the partial pressure of oxygen at the metal/oxide interface and the growth of the scale is parabolic with time for such a reaction mechanism. The most important outcome of Wagner’s analysis is the possibility to obtain complete information about the mechanism of the process (using the dependence of anion and cation conductivities on oxygen partial pressure and the dependence of diffusivities on oxygen partial pressure [BM83]). A number of investigations have been performed on oxides and it was shown that some oxides grow predominantly by inward diffusion of oxygen (SiO$_2$, Al$_2$O$_3$ and Cr$_2$O$_3$ in the most cases) and some by outward diffusion of cations (ZnO, MnO, FeO, Fe$_3$O$_4$, NiO, CoO).

At low temperatures and for very thin oxide films of thickness $X < 10$nm, an electric field across the film or space charges in the film caused by the chemisorption of oxygen on the oxide surface is considered. This theory is called Cabrera-Mott theory (inv. log/log rate law) [CM49].

Oxygen molecules dissociate and adsorb on the surface and thereby give rise to traps with an energy below the Fermi level of the metal. This gives a potential drop $V$ across the film and thereby a field $F = V/x$ is established in the oxide. Mott [Mot47] originally assumed that electron tunnelling through the film is rate determining and this yields to a direct logarithmic rate equation:

$$X = k_{\log} \log t + A \quad (2.16)$$

One of the basic assumption of the Cabrera-Mott theory is that the activation energy $W$ necessary for the cation to move is reduced by the strong field to $W-qaF/2$ where $q$ is the charge on the cation and $a$ is the jump distance by the way, this sounds like the Schottky-effect in semiconductors. But there, the energy of electrons is considered. If the transport of cations through the film is rate determining this assumption yields to the inverse logarithmic rate equation.

$$1/X = B - k_{\log} \log t \quad (2.17)$$
Although many theories need to describe the oxidation kinetics, in practical the oxidation reactions follow a combination of rate laws. For example, at high temperatures reactions may be interface controlled (linear) during initial stages and diffusion limited (parabolic) after extended oxidation. Schematic illustration of different oxidation regimes are presented in Fig. 2.6.

Fig. 2.6. Schematic illustration of the variation of $X$ (oxide thickness) or $\Delta m$ (mass change) with time for different reaction regimes.
2.3. External/internal selective oxidation

Basically, the term ‘selective oxidation’ refers to the preferred oxidation of the less noble elements in an alloy. Based on Wagner’s conditions, the selective oxidation can be classified into two types such as external oxidation and internal oxidation [Wag59]. It has been the subject of reviews by many researchers [Maa61, Rap65, Swi71, Mei71]. The phenomenon, i.e. occurrence of selective oxidation of alloying elements on the surface, is called external oxidation. The external selective oxidation is the basis for the design of engineering alloys (e.g. stainless steel) which contain a sufficiently high concentration of a solute (~18% Cr) to produce an external layer of a stable oxide (i.e. Cr$_2$O$_3$) which prevent oxidation of the parent metal, i.e. corrosion resistant.

In the present investigation (model alloys and industrial steels), Fe provides a matrix phase on which oxidation of minor alloyed less noble elements (Si, Mn, Cr etc.) take place. If the oxygen diffuses into an alloy and causes sub-surface precipitation of one or more alloying elements, then it is called internal oxidation. For simplicity, binary alloys A-B are considered in the following, where B is a dilute solute which forms a very stable oxide. The schematics of external and internal oxidation are shown in Fig. 2.7.

For the used annealing condition in this investigation, the metal A in the binary alloy A-B is noble and the solute B may form an oxide BO$_v$ i.e. the ambient ‘p$_{O_2}$’ is too low to oxidise A, but high enough to oxidise B. The overall reaction of the dissolution of oxygen as oxygen atoms may be written as
\[ \frac{v}{2} O_2 = vO \]  \hspace{1cm} (2.18)

Then, the subsequent reaction of the dissolved oxygen atoms with B atoms in the alloy can be as follows:

\[ B + vO = BO_v \]  \hspace{1cm} (2.19)

The necessary conditions for the formation of \( BO_v \) particles within the alloy phase are as follows [BM83]:

1) The \( \Delta G \) per mole \( O_2 \) of formation for the solute metal oxide \( BO_v \) must be more negative than the \( \Delta G \) of the formation for the base metal oxide.

2) The \( \Delta G \) for the reaction (2.19) must be negative. The required activity of dissolved oxygen at the reaction front must be accomplished through a sufficient solubility and diffusivity in the base metal.

3) The solute concentration in the alloy must be lower than the one required for the transition from internal to external oxidation.

4) The dissolution of oxygen into the alloy must not be prevented by the surface layer.

---

Fig. 2.8. Concentration profiles for an internal oxidation in the A-B binary alloy.
Wagner expressed the depth of internal oxidation zone penetration $\xi$ (in binary alloy A-B where B is a dilute solute which forms a very stable oxide) as follows,

$$\xi = 2\gamma(D_0t)^{1/2} \tag{2.20}$$

where $\gamma$ is a dimensionless parameter, $D_0$ is the diffusivity of oxygen and $t$ is the time.

There are two limiting cases (i.e. internal and external oxidation conditions) applied in this equation (2.20). The first limiting case is, when $\gamma >> 1$, it means that oxygen diffusion predominates the process, which is equivalent to Wagner’s internal oxidation condition, i.e. $D_0N^S_0 >> D_BN^0_B$ where $N^S_0$ is the oxygen solubility in A, $N^0_B$ is the initial solute B concentration and $D_0$, $D_B$ are the diffusivities of the oxygen and the solute B (in the matrix A), respectively. In Fig. 2.8, the case of selective internal oxidation of B in the binary alloy A-B is presented. Oxygen diffuses through the surface of the alloy into the bulk volume, reacting with B and precipitating oxide $BO\nu$. It can be seen that the oxygen flux varies (linearly) across the zone of internal oxidation. Here, the diffusivity-solubility product, $D_0N^S_0$ (permeability) for oxygen in the matrix metal is much higher than the permeability of solute B which leads to internal oxidation.

The value of the parameter $\gamma$ in this selective internal oxidation condition is as follows:

$$\gamma = \left( \frac{N^S_0}{2\nu N^0_B} \right)^{1/2} \tag{2.21}$$

where $N^S_0$ is the oxygen solubility in the metal at the surface, $\nu$ is the stoichiometry parameter of the oxide and $N^0_B$ is the solute concentration in the bulk alloy. Substituting the equation (2.21) in (2.20) yields [Kof88]

$$\xi = \left( \frac{2N^S_0 D_0}{\nu N^0_B t} \right)^{1/2} \tag{2.22}$$
Equation (2.21) indicates an inverse relationship between the zone thickness and the square root of the solute concentration. The consequence of this is that if the surface oxygen solubility and oxygen diffusivity are independent of the solute concentration (this is very likely for dilute solutions), the type of solute should not play a role or: a given amount of solute should produce the same thickness of the internal-oxidation zone [Dou95]. The validity of this relationship is confirmed by the work of Stott et al. who investigated various diluted nickel alloys (Ni-Al, Ni-Cr, Ni-Mn, Ni-Mo, Ni-V and Ni-W). They found the same thickness of the internal zone, for a particular solute concentration, in all cases, with an exception of Ni-Al alloy where the zone was thicker. The authors attributed this to the formation of rod-like precipitates of Al₂O₃ which were perpendicular to the alloy surface [SWWB’84].

Fig. 2.9. Concentration profiles for an external oxidation in the A-B binary alloy.

The second limiting case occurs with \( \gamma \ll 1 \), which is equivalent to Wagner’s external oxidation condition i.e. \( D_o N_o^S \ll D_B N_B^0 \) where \( N_o^S \) is the oxygen solubility in A, \( N_B^0 \) is the initial solute B concentration and \( D_o, D_B \) are the diffusivities of oxygen and solute B (in the matrix A), respectively. Fig. 2.9 represents the case of external scale formation by externally oxidized B. If the concentration of solute B is high enough and the outward
diffusion of B occurs contrary to the oxygen diffusion inwards, the enrichment of formed BO$_\nu$ oxides occurs. This decreases the oxygen diffusion into the alloy and an outer oxide layer forms. Here, the diffusivity-solubility product, $D_o N_{o}^s$ i.e. oxygen permeation in the matrix metal is significantly less than that of solute B ($D_B N_{B}^s$) which leads to external oxidation.

The value of the parameter $\gamma$ in this external selective oxidation condition is as follows,

$$\gamma = \left( \frac{N_{o}^s}{2\nu N_{B}^s} \right) \left( \frac{\pi D_o}{D_B} \right)^{1/2}$$

(2.23)

Unlike equation (2.21), this case is dependent on both $D_o$ and $D_B$, where $D_B$ is the diffusion coefficient of B in the alloy. Hence, an appreciable enrichment of B as BO$_\nu$ takes place due to the outward diffusion of B (Fig. 2.9).

In addition to the simple cases described above, Wagner’s model has been extended to take into account the presence of more than one element in solid solution in the metal [GYS94, HLLA’96, GN99]. Basically, the short term annealing conditions is a classical application where this model has to be considered between the two Wagner limiting cases. Although Wagner’s model contains all basic assumptions required, this classical model made several restricting hypotheses such as

1. Single alloying element is considered i.e. only binary alloy.
2. The model does not take into account the solubility products of the oxides.

Huin et al. extended the classical Wagner’s model to any element under any oxidizing conditions by introducing the solubility product of the oxides [HLLA’96]. The solubility product of BO$_\nu$ is given by

$$K_{BO\nu} = [c(B).c(O)^\nu]$$

(2.24)

where $c(B)$ is the critical solute concentration for the formation of BO$_\nu$. 
Apart from the solubility product of oxides, the interaction between the elements is taken into account in his extended model by assuming the competitive consumption of the available oxygen; however, this model is restricted to the isothermal case and to the formation of single oxides. The typical industrial annealing treatment is anisothermal, i.e. the temperature will increase linearly from room temperature to higher temperature, remains constant at higher temperature for some time and finally it is decreased by cooling back to room temperature (for more details, see the experimental section 4). In a multicomponent alloy formation of mixed oxides are occurs during heat treatments. For example, the formation of Mn-Si mixed oxides and Mn-Cr mixed oxides are found in the present investigation. Huin et al. carried out the further development of the model which can be applied for non-isothermal conditions and precipitation of mixed or ternary oxides [HFL05].
2.4. Surface segregation

In many different heat treatments and processes, steels are exposed to higher temperatures in either reducing (H₂-N₂) or oxidizing environments (air). In this processes an enrichment of the alloying elements are observed on the steel surface. Basically, the phenomena of enrichment of atoms from the (bulk) solid solution to surfaces, grain boundaries and interfaces are called segregation [GLV95]. Segregation has a strong impact on many processes such as surface oxide formation (surface segregation), adhesion of oxides on the metal surface (interface segregation) and embrittlement (grain boundary segregation) see Fig. 2.10.

![Schematics of the surface, grain boundary and interfacial segregation of a dissolved element (dark circles) in the metal matrix [GLV95].](image)

At elevated temperatures, most elements which can be dissolved in iron tend to enrich at surfaces, grain boundaries and interfaces. A distribution equilibrium is established at temperatures sufficiently high for the diffusion of these elements, which can be written as,

\[ \text{A (dissolved)} \leftrightarrow \text{A (segregated)} \quad (2.25) \]

According to Grabke et al., the driving forces for equilibrium segregation are:

1. Free bonds at the surface, saturated by interaction with the segregated atoms A.
2. The metal surface may be covered with a layer of atoms A which has a lower surface energy than the initial surface.
3. The release of atoms A from the bulk solution leads to a release of elastic energy, especially in the case of interstitial atoms, but also substitutional atoms larger than the iron atoms.

4. Most non-metal atoms become ionized upon segregation, e.g. in the segregated state they are negatively charged and larger than in solution.

The decrease in surface energy caused by equilibrium segregation is shown in Fig. 2.11 and can be expressed by Gibb’s law,

\[
\frac{dy}{d\ln a_A} = -RT \Gamma_A
\]

(2.26)

where \(a_A\) is the thermodynamic activity of the segregating species A, \(\Gamma_A\) is the surface concentration of segregating species A and \(\gamma\) is the surface energy.

![Fig. 2.11. Schematic of dependence of surface energy on the activity (Gibb’s law) of a segregating species.](image)

For a high activity \(a_A\), a saturation coverage \(\Gamma_A^{sat}\) is approached and the slope of \(\gamma\) versus \(\ln a_A\) becomes constant.

Since the surface segregation of species can be treated like adsorption of species from the gas phase, the surface coverage \(\theta\) in dependence on bulk concentration \(x_A\) and temperature can be given by the Langmuir-McLean isotherm. The degree of surface coverage \(\theta\) is expressed as:
\[ \theta = \frac{\Gamma_A}{\Gamma_{sat}} \quad \text{(2.27)} \]

Applying the Langmuir isotherm describing segregation to a limited number of sites with a constant Gibbs free energy \( \Delta G_A \), which is independent of coverage, then the degree of coverage with segregating species A is given by:

\[ \theta_A = \frac{K \cdot x_A}{1 + K \cdot x_A} \quad \text{(2.28)} \]

where \( x_A \) is the bulk concentration of the segregating species and K is the rate constant.

The relationship between the rate constant K and the standard Gibbs Free Energy of segregation \( \Delta G_A^0 \) is described as

\[ K = \exp\left(\frac{-\Delta G_A^0}{RT}\right) = \exp\left(\frac{\Delta S_A^0}{R}\right) \cdot \exp\left(\frac{-\Delta H_A^0}{RT}\right) \quad \text{(2.29)} \]

where \( \Delta H_A^0 \) is the enthalpy of segregation and \( \Delta S_A^0 \) is the entropy of segregation.

By combining the equations (2.28) and (2.29), the Langmuir-McLean equation [McL57] for segregation is obtained:

\[ \ln \frac{\theta}{1-\theta} = -\frac{\Delta H_A^0}{RT} + \frac{\Delta S_A^0}{R} + \ln x_A \quad \text{(2.30)} \]

The above equation (2.30) is used to derive the enthalpy and entropy of segregation of species A from measurement of \( \theta \) at a constant bulk concentration \( x_A \) of the segregated species in dependence on temperature (Fig. 2.12).
Fig. 2.12. (a) Schematics of the dependence of coverage on the concentration of a segregating species, (b) the thermodynamic evaluation at constant activities and (c) at constant coverages [GLV95].

Fig. 2.12a shows that with increasing activity (concentration) of segregating species in the bulk, as well as with decreasing temperature, the surface concentration (coverage) increases. As segregation is an exothermic phenomenon, it is favoured by a reduction in temperature, provided the temperature is in the range where diffusion in the solid state is sufficiently rapid. Grabke et al. claimed that the chemisorption is localized and there is no change in entropy upon segregation [GPTV77]. By applying this condition in Fig. 2.12b and 2.12c, the segregation enthalpy can be obtained from the slope of the straight lines.
In ternary and more complex systems, the thermodynamics of segregation is more complicated since there is the possibility that two or more species segregate and tend to occupy the same sites. The site competition between elements A and B can be described by the following equations,

\[
\begin{align*}
\frac{\theta_A}{1 - \theta_A - \theta_B} &= x_A \cdot \exp\left(-\frac{\Delta G_A}{RT}\right) \\
\frac{\theta_B}{1 - \theta_A - \theta_B} &= x_B \cdot \exp\left(-\frac{\Delta G_B}{RT}\right)
\end{align*}
\] (2.31)

Fig. 2.13. Site competition between Si and C in Fe-3%Si with 40 ppm C system (temperature dependence of the displacement equilibrium) [Gra89].

This site competition is decisive in the simultaneous segregation of non-metal elements and was observed for the system Fe-3%Si with 40 ppm C [Gra89]. The segregation enthalpy of Si on Fe ($\Delta H^0_{Si} = -48$ kJ/mol, where the negative sign indicates that the segregation is an exothermic process) is much lower than for carbon ($\Delta H^0_C = -85$ kJ/mol). This higher value of segregation enthalpy $\Delta H^0_C$ prevails the carbon segregation at lower temperatures.

Because of the strong repulsive interaction between C and Si, with increasing temperature C atoms are desegregated into the bulk and Si is able to segregate, and the free surface is occupied by segregated Si atoms. This site competition behaviour of Si and C is shown in Fig. 2.13
Grain boundary site competition was observed between N and S atoms [TG78, JBTB81], C and P atoms [ErG81, SOAK83] and P and N atoms [EG81]. In the work of Hua et al. the grain boundary segregation of P, B, C and Nb in Ultra Low Carbon (ULC) steel after the annealing was investigated [HGD98]. It was found that the presence of Nb, B and C in the alloy reduced P segregation on ferrite grain boundaries and that B was the most effective to reduce the P segregation compared to Nb and C.

Simultaneous segregation of elements A and B with strong chemical interaction leads to co-segregation. The process of co-segregation is also described by the Langmuir-McLean equation given below, with the introduction of an additional interaction energy term ($\alpha$) and assuming that there is no site competition.

$$
\frac{\theta_A}{1-\theta_A} = x_A \cdot \exp \left( -\frac{\Delta G_A - \alpha \cdot \theta_B}{R \cdot T} \right)
$$

$$
\frac{\theta_B}{1-\theta_B} = x_B \cdot \exp \left( -\frac{\Delta G_B - \alpha \cdot \theta_A}{R \cdot T} \right)
$$

(2.32)

In the present investigation, the strong chemical interaction between Mn and Si leads to co-segregation and form the Mn-Si mixed oxides [SS07]. In principle, co-segregation is the formation of a two-dimensional surface compound, stabilized over a wide range of thermodynamic conditions (temperature, bulk concentration) by epitaxy. With increased bulk concentration three-dimensional compounds like carbides, nitrides, etc. become stable and precipitation is expected [GLV95]. The formations of BN, CrN etc. are the good example of co-segregation.

Chemisorption of oxygen from the annealing atmosphere also induces the segregation of alloying elements. This type of segregation is called ‘chemisorption induced segregation’. For example, if the formation of pressure of Cr$_2$O$_3$ is not exceeded, the interaction of oxygen from the atmosphere and Cr from the bulk leads to chemisorption induced segregation, i.e. surface enrichments of O and Cr. For higher oxygen pressures there is a transition to ‘selective oxidation’.
Chapter 3 – Selective surface oxidation and its influence on zinc wettability in hot-dip galvanizing (HDG) process: Brief review

3.1. Surface chemistry after recrystallization annealing

3.1.1. High strength steels

The recrystallization annealing of high strength steels prior to hot-dip galvanizing leads to segregation and selective oxidation of minor alloying elements such as Al, Si, Mn, Cr etc., thus influencing the wetting behaviour with liquid zinc. Additions of these alloying elements are highly important, not only for their excellent strengthening effect but also for providing the required microstructure necessary for automotive applications. Numerous investigations concluded that the wettability rapidly decreases with the occurrence of external selective oxidation [VSL03, DZBM\textsuperscript{+04}, KSBV\textsuperscript{+04}, ECSC05]. These surface phenomena, i.e. segregation and selective surface oxidation depends on many factors such as the characteristics of the annealing cycle (temperature, gas composition, dew point, dwelling time) and the chemical nature of the elements involved, i.e. diffusion coefficients and their affinity to oxygen. The external oxidation of alloying elements creating higher strength in steels can lower the surface activity with respect to hot dip galvanizing and hence galvanizability of the steel is hampered as the wettability of these oxides with zinc is very poor [Gra95, ECSC05, BBS04, PS05, BMSW04]. Based on Wagner’s theory, the transition from external to internal oxidation is achievable by choosing the appropriate dew point in the annealing atmosphere [Wag59].

Olefjord et al. showed that the water content in the gas (i.e. dew point) would have to be extremely low if oxidation of reactive elements, such as Mn, Si, Al, V, Ti etc. should be avoided and that this is impossible in industrial galvanizing lines. The same authors found oxide islands of MnO, SiO\textsubscript{2}, TiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3} and V\textsubscript{2}O\textsubscript{3} on a cold-rolled steel surface after annealing at 850°C at DP -30 °C in 15%H\textsubscript{2}-N\textsubscript{2} gas atmospheres [OLJ80]. Iron was found in the metallic state. The most commonly used atmosphere is 5%H\textsubscript{2}-N\textsubscript{2} but also an increase up
to 15 %H\textsubscript{2} in the gas does not lead to reducing conditions for the mentioned alloying elements.

Guttmann et al. investigated the nature and location of the oxides formed on Ti-IF steel annealed at 820 °C (for 30 seconds) at DP -40 °C in N\textsubscript{2}-5%H\textsubscript{2} gas atmospheres by Transmission Electron Microscopy (TEM) \cite{GLAR95}. The TEM observation on carbon extraction replicas reveals the following:

1. Oxides of size 0.03-0.3 µm exist both at the grain boundaries (mainly MnSiO\textsubscript{3}) and in the surface layer above the grain interior (MnO, SiO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, Cr-rich oxides).
2. On the grain boundaries, Cr-rich spinels are found beneath coarse type MnSiO\textsubscript{3}.
3. More deeply buried in the grain boundaries beneath Cr-rich spinels, thin ribbons of another spinel (probably Al, Si, Fe (Cr, Mn) spinels) are observed.
4. In the vicinity of the surface above the grain interior, extremely fine Cr-rich spinels are found at the surface and also just underneath the surface region.

Many researchers reported about the influence of the dew point on the selective oxidation. Drillet et al. found that annealing of TiNb-IF steels at 810 °C at various dew points (also in 15%H\textsubscript{2}-N\textsubscript{2} gas atmosphere) showed the appearance of oxide islands of different chemistries, depending on the dew point of the annealing atmosphere \cite{DZBM01}. At a lower DP of -45 °C, Al\textsubscript{2}O\textsubscript{3} was found inside the grain boundaries (i.e. internal oxidation of Al) and Mn\textsubscript{3}SiO\textsubscript{4} had formed on the surface. Oxidation of Cr and the formation of (Mn, Cr)\textsubscript{3}O\textsubscript{4} occurred at DP = -15 °C. Above DP = 0 °C, the oxidation of P and the formation of Mn\textsubscript{3}(PO\textsubscript{4})\textsubscript{2} starts.

Investigations on the selective oxidation of high Si, Mn and Al steel grades (for e.g. Transformation Induced Plasticity (TRIP) steel) during recrystallization annealing was carried out by some researchers \cite{BC01, Min01, DZBM04, BMM07}. The conventional TRIP steels have ~1.5% Mn and 1.5% Si, in order to have excellent formability and strength. Moreover, increasing the Mn level from 2 to 5% increases the stability of the required austenite content but, on the other hand, a Mn level >2% is hampering the hot dip galvanizing process \cite{Min01}. Bordignon et al. investigated the surface oxidation of TRIP, dual phase (DP steel) and C-Mn steels in 20%H\textsubscript{2}-N\textsubscript{2} atmosphere with a dew point of -30 °C.
at 820 °C for 30 sec. These results indicated the presence of a rather homogenous layer of oxides on a TRIP steel alloyed with Si and Al in contrast to nodular oxides formed on the surfaces of DP and C-Mn steels [BC01].

Studies on the high Al (1.4%) steel grades showed the existence of a critical oxide thickness, about 6-8nm, above which the film becomes un-wettable. In that case it becomes difficult to determine what the most important parameter for a good wettability is: critical thickness allowing the dissolution in the Zn bath or nanoporosities in the oxide layer. With the high (1.28-2.0%) Si steel grade there is no evidence for the existence of such a critical thickness. Since the nucleation/growth kinetics is higher, the amorphous SiO₂ film is expected to reach earlier the critical thickness of un-wettability than the crystallized Al₂O₃ film, for the same annealing parameters [DZBM+04]. Furthermore, nowadays in TRIP steels, Si is replaced either completely or partially by addition of Al. The results show a tendency towards the internal oxidation of Al, with a greater degree of internal oxidation being shown for the higher oxygen potential (DP = -30 °C) annealing atmosphere. The 1.5%Al-TRIP steels showed good Zn wettability when using a DP = -30 °C with N₂-5%H₂ atmosphere and improved wettability when using a DP = -53 °C with a N₂-20%H₂ atmosphere. The decreased oxide thickness and the change in the distribution of oxides on the surface, showing a larger surface area that was free of oxide particles, contributed to the improved reactive wetting of the Al-TRIP steels at DP -53 °C [BMM07].

Parezanovic and Spiegel investigated the influence of non-metallic elements (B, S, P etc.) on the selective oxidation of alloying metals. It was shown that the interaction is strongly dependent on the partial pressure of oxygen in the atmosphere, diffusivities, surface segregation enthalpies and orientation [PS04]. It has been concluded that the austenitic grains (Dual Phase (DP) steel) favours the formation of BN more than ferritic grains (Interstitial Free (IF) steel). On DP500 steel annealed at a dew point of -60 °C, the formation of BN causes a ‘screening effect’ i.e. protects the surface from further oxidation. Also, the selective oxidation of P occurred at a dew point of 0 °C, suppressing the Si oxidation on the surface.

Preoxidation in air (or oxidizing atmosphere) prior to recrystallization annealing presents a promising tool for surface modification of steel sheets. Because during the preoxidation
process, mostly the formation of Fe-oxides occurs at the oxide/gas interface and less oxides of alloying elements are expected. Iron oxides can be reduced in the subsequent annealing cycle to metallic Fe, which is well wetted in the Zn bath. The influence of a preoxidation treatment on the external segregation of B on Ti-IF steel was investigated. Impressive B external segregation after recrystallization annealing was found on the outermost surface of the non-preoxidized specimen. For the preoxidized + annealed specimen no significant B enrichment was detected [ECSC05].

3.1.2. Model alloys

As these modern high strength steels present a complex system of many alloying elements, a number of investigations were performed on simplified model alloys. Experiments were carried out on the oxidation of binary alloys i.e. Fe with alloying elements like Mn, Si, Cr and Al in different atmospheres such as air, H2-N2, etc. Literature on the oxidation behaviour of Fe-Si and Fe-Mn alloys show that during annealing (at 750-820 °C) in N2-H2 gas atmosphere with various partial pressures of water vapour (i.e. different dew points) only SiO2 and MnO are stable on the surface [Tuc65, Atk82, YSY02, VSL02, PS04].

Parezanovic and Spiegel preoxidized various Fe-Si and Fe-Mn binary alloys in air at 700 °C. They found that even at very short times (≤ 60 seconds), very complex oxide layers are formed, i.e. fayalite (Fe2SiO4) in Fe-Si alloy and spinels (Fe, Mn)O in Fe-Mn alloy. They reported that the critical concentration of ~ 3% Si in Fe-Si alloys leads to the formation of a continuous layer of SiO2 on the surface. Preoxidation of Fe-Si alloys with low Si content (< 3 wt.%) are reducible to metallic Fe during recrystallization annealing at 820 °C in a N2-5%H2 gas atmosphere with a DP of -30 °C [PS04].

The surface chemistry of the binary alloys of Fe-0.5%Si, Fe-1.5%Mn annealed at different DP’s in pure N2 and N2-5%H2 gas atmospheres are compared by Vanden Eynde et al.. Annealing in a N2-H2 atmosphere leads to diffusion and oxidation of Si and Mn, moreover, the amount of external selective oxidation is decreasing with increasing water vapour content. Iron is fully metallic in the case of N2-5%H2 annealing, whereas an oxide component is detected in in the case of pure N2 annealing [VSL02]. Oxidation of Fe-3.15Si
(with 0.069Mn, 0.026Cr and 0.11Sn) alloy in 9.8 % H₂-Ar gas, with dew point of ~2 °C, at temperatures between 675-750 °C indicated an influence of annealing temperature on surface chemistry [SYYT’03]. At lower temperature only SiO₂ was found on the surface while at 750 °C formation of manganese silicate occurred. The existence of a 0.8-2.5 μm thick internal SiO₂ zone was confirmed as well. After exposing Fe-6.10 mol% Si alloy (with 0.079Mn and 0.055 Sn) to 25%H₂-N₂ atmosphere at various DP (-15 to 71 °C) at 850 °C for 300 sec, mostly SiO₂ was found on the surface for the lowest dew points [YSY02]. With increasing dew point, Mn-Si oxides were also detected in the layer of SiO₂ while at much higher dew points formation of Fe₂SiO₄ was observed.

Loison et al. studied the surface chemistry of Fe-1.58%Mn model alloys, annealed at 800 °C with dew points of -30 and -10 °C in N₂-5%H₂ gas atmosphere. The authors observed the presence of nodular Mn-oxides on the surface and especially at the grain boundaries rather than within the grains. Moreover, the oxide density is not uniform and clearly depends on the crystallographic grain orientation, which affects the diffusion of oxygen and manganese, as well as the nucleation and growth of oxide precipitates [LHLS’01]. At high dew points, facetting of the grains is locally detected, acting as oxide nucleation sites. Similarly, Fe-Mn alloys (Fe-0.6%Mn, Fe-1.5%Mn), annealed at 800 °C at a dew point of -30 °C in N₂-5%H₂ gas atmosphere have been investigated by Martinez et al.. They reported that the oxides form small crystallites which grow within the grains rather than a uniform layer [MCNS’02].

Sauerhammer et al. carried out investigations on high Mn content model alloys (Fe-20Mn, Fe-20Mn-3Si, Fe-20Mn-3Al and Fe-20Mn-3Si-3Al, all in wt.%), annealed at DP of -70 and -35 °C. They found that in the ternary alloys, an increase of the DP causes internal oxidation of Si and Al. In contrast, on the surface of Fe-20Mn-3Si-3Al (quaternary alloy) system after annealing at both DP’s, both Si and Al are found. It is most likely that mixed or spinel-type of oxides are present on the surface [SSS04].

Based on this brief literature survey, one must state that the segregation and the selective oxidation upon short term annealing of steels and model alloys are complicated. Fundamental investigations on the model alloys are helpful for a better understanding of high strength steels. More specifically, the alloying elements of model alloys and its
compositions have to be chosen with great care in order to analyze the situation with newly developed high strength steels. Studies concerning the ternary and quaternary model alloys are largely missing. In the present work, systematic investigations on the selective surface oxidation of binary, ternary and quaternary model alloys (Fe with combination of Si, Mn and Cr) are presented in detail.

3.2. Zinc wettability

After recrystallization annealing, steel sheets are hot-dip galvanized (HDG) in a Zn bath for corrosion protection. The adhesion of the Zn coating to the steel surface is one of the most important requirements in the HDG process. Generally, the bath composition used in HDG is Zn-0.2 wt.%Al. The Al is added to Zn bath to improve their adhesion as well as to improve corrosion resistance and brightness of the coatings. In the absence of Al, Fe-Zn intermetallic compounds are formed which are quite brittle and show no adhesion during further mechanical processing. With the addition of Al to the Zn bath, Fe-Al intermetallic phases, predominantly Fe$_2$Al$_5$ are formed, the so called inhibition layer. In this way, small amounts of Al suppress the formation of undesirable Fe-Zn intermetals. This phenomenon is called inhibition and offers a superior way to continuously galvanize steel sheets and produce a single $\eta$-Zn phase coating (Zn rich solid solution with less Fe (0.04%). So, the quality of the Zn coating strongly depends on the formation of an undistorted Fe$_2$Al$_5$ inhibition layer at the interface [MMM97, BL99, BC01, HCC01, DZBM'04, FP05].

The effect of a ‘stable’ inhibition barrier layer on Fe-Zn reaction kinetics during hot-dip galvanizing has been investigated by many researchers [GLAR’95, JM98]. The authors proposed that the kinetic destabilization of the steel/Fe$_2$Al$_5$ interface is mainly due to solid state diffusion of Zn through the interface which gives rise to outburst nucleation at the steel/Fe$_2$Al$_5$ interface. However, the formation of the Fe-Al interfacial/inhibition layer is hindered by poor wettability of oxides that are formed on the surface during the annealing process. The location of some of these oxide particles at substrate steel grain boundaries had led some investigators to conclude that oxide particles may cause the formation of Fe-Zn outburst [His89]. The proposed mechanism relies on the fact that the oxide particles
located at substrate steel grain boundaries can be reduced by Al in the Zn bath (i.e. aluminothermic reaction), thereby causing a local depletion of Al concentration in the bath in the vicinity of the newly formed oxide [KU73]. Because oxide particles are found to be concentrated at steel substrate grain boundaries, it has been proposed that the Al depletion near the substrate steel grain boundaries is significant, which may lead to localized Zn attack and the formation of Fe-Zn growths or outbursts at the grain boundary [His89]. On the other hand, due to the possibility of a reduction of thinner oxides by Al from the bath, low alloy grades show no problems during galvanizing. This reaction is improved by stirring of the Zn bath, but steels with 0.5 wt. % Cr or 1.2 wt. % Al or 1.4 wt. % Si in combination with 1.5 wt. % Mn show small defects in Zn coating after HDG [BC01]. Different oxides, such as Mn$_2$SiO$_4$, MnO and SiO$_2$, observed on IF steels after annealing at different dew points from –45 °C to +10 °C show no significant influence on wettability of the surfaces in a Zn bath [DZBM01]. A study of a liquid Zn attack on a uniform oxide layer on the surface of low C steel was carried out by Jordan and Marder [JM98]. They found that the inhibition effect of the oxide for liquid Zn was temporary, since cracks and other macrodefects in the oxide acted as a fast diffusion paths for Zn, localized Fe-Zn growth (outbursts) formed at the steel/coating interface.

During the galvanizing process, the growth of the inhibition layer starts at the grain boundaries of the underlying ferrite grain structure, proceeding laterally into the center of the grain surface with time. The reaction occurring at the steel/liquid zinc interface has been modeled in order to understand the galvanizing kinetics [GG05]. Komatsu et al. proposed the following mechanism for the formation of Fe-Al interfacial alloy layer during hot-dip galvanization in a Zn-0.15%Al bath [KAU01].

1. Initial reaction: The Fe-Zn intermetallics (ζ (6-7% Fe), Γ (18-31% Fe), δ (8-13% Fe)) and Fe$_2$Al$_5$ develop on the steel surface simultaneously.
2. The lower part of the Fe-Zn intermetallic in the vicinity of the steel surface transforms to the Γ phase by Fe diffusion
3. The Γ phase rapidly transforms to Fe$_2$Al$_5$ by Al diffusion from the neighbouring Fe$_2$Al$_5$ and the bath as given by the following equation: $\Gamma + Al \rightarrow Fe_2Al_5 + Zn$. When the Zn segregation to the Fe$_2$Al$_5$/Fe-Zn intermetallic interface is sufficient, Zn forms a thin liquid layer, which results in the separation.
4. While Zn segregation is not enough, the Fe-Zn intermetallics remain on Fe$_2$Al$_5$ and change to Fe$_2$Al$_5$ by diffusion of Al and Fe via the Al supersaturated Fe-Zn intermetallics.

Harvey and Mercer investigated the interfacial layer formation on commercially galvanized low C steel and observed a continuous inhibition layer composed of Fe$_2$Al$_5$ that ranged in thickness from 87 to 310 nm on coatings produced in a Zn bath containing 0.18% Al. In a Zn bath with 0.15% Al, a discontinuous Al-rich layer composed of either Fe$_2$Al$_5$ or an Fe-Al-Zn ternary compound with a thickness of 25 nm was observed [HM73]. Faderl et al. found a Fe$_{2.2}$Al$_{4.8}$Zn$_{0.8}$ interfacial layer on a commercial galvanized product [FMS95]. Lin and Meshii investigated the effect of steel substrate chemistry on the nature of the interfacial layers [LM95]. On IF steel, the interfacial layer was composed primarily of the Fe$_2$Al$_5$ phase with some pillar-like grains of Fe-Al-Zn ternary compound. On an extra low C steel (less than 0.01%) substrate, the authors observed only the Fe-Al-Zn ternary compound. Although the formation of an Fe$_2$Al$_5$ interfacial layer during galvanizing is the most widely accepted result, however, there also are reports that the interfacial layer is composed of Fe-Al-Zn ternary compounds, mixtures of Fe$_2$Al$_5$ and FeAl$_3$ [MMM97]. Hertveldt et al. reported that the morphology as well as the composition of the inhibition layer are strongly influenced by the HDG process parameters [HVC98].

Frenznick et al. showed the galvanizing of various binary model alloys (Fe-Si, Fe-Mn, Fe-Al) at low dew point < -60 °C [FSR04]. The results indicate that the wetting to dewetting transition occurs at about 3 wt.% of alloying elements for Fe-Si and Fe-Mn alloys. In the case of Fe-Al alloys, even a high Al content (5 wt.%) shows wettability, probably due to the good wettability of intermetallics.

3.2.1. Contact angle measurement (Sessile drop method)

Measuring the contact angle is a promising method to determine the wettability of liquid Zn on steels under laboratory conditions in order to predict the wetting behaviour in the industrial hot-dip galvanizing process (i.e. in continuous galvanizing lines). In this work,
the sessile drop method was used to measure and compare the wettability of the steels and model alloys by liquid Zn.

The sessile drop method is an optical contact angle technique used to estimate wetting properties of a localized region on the solid surface. The angle between the baseline of the drop and the tangent at the drop boundary is measured. Basically, the contact angle is defined as the angle between the liquid-gas (or vapour) and the solid-liquid interfaces of a solid-liquid-gas system i.e. an angle formed by this tangent line and the solid surface as shown in Fig. 3.1. For a good wetting surface, the measured contact angle ($\theta$) is less than $90^\circ$ (Fig. 3.1a) and if $\theta > 90^\circ$, then the surface is said to be bad wetting to the liquid Zn (Fig. 3.1b).

![Schematics of contact angle measurement](image)

(a) Good wetting ($\theta < 90^\circ$)

(b) Bad wetting ($\theta > 90^\circ$)

Fig. 3.1. Schematics of contact angle measurement. (cross section in measuring the optical profile of a sessile drop)

The Young-Dupre equation connects the contact angle with the local interfacial energies, [You05, Ada82]:

$$\cos(\theta) = \left( \frac{\gamma_{SG} - \gamma_{SL}}{\gamma_{LG}} \right)$$  \hspace{1cm} (3.1)
where $\gamma_{SG}$, $\gamma_{SL}$ and $\gamma_{LG}$ are interfacial energies of solid-gas, solid-liquid and liquid-gas system, respectively.

The Young-Dupre equation basically describes the force balance on the contact line and predicts the contact angle in terms of interfacial energy densities of the three interfaces of the system for an ideal, homogenous solid surface. In practice, wettability issues are more relevant to heterogeneous surfaces. The interfacial energy is then arising mainly from the chemistry of the different interfaces.

To describe this situation, Wenzel introduced an ‘average’ contact angle on a rough, chemically homogeneous substrate which is expressed in terms of the contact angle on a planar surface [Wen49]. Likewise, for smooth but chemically heterogeneous surfaces, the Cassie equation is used [Cas48].

Cassie equation: \[
\cos(\theta_{\text{eff}}) = \sum_i f_i \cos(\theta_i) \quad (3.2)
\]

Wenzel equation: \[
\cos(\theta_{\text{eff}}) = r \cos(\theta) \quad (3.3)
\]

where $\theta_{\text{eff}}$ is an effective or average contact angle on the heterogeneous surface, $\theta_i$ is the angle taken on a simple planar surface composed entirely of surface component or chemical species $i$ (i.e. alloying element oxides), $f_i$ is the fraction by area of the surface made up of $i$, and $r$ is the ratio of true to planar surface area.

In the present investigation, a complex surface chemistry of steels/model alloys has been observed due to segregation and selective oxidation upon annealing, which influences the Zn wettability considerably. In the Cassie equation, it’s clear that not only the surface coverage of various oxides but also the individual wettability of these oxides by liquid zinc define the overall contact angle. Therefore, investigation of the influence of surface chemistry (after recrystallization annealing) as well as thickness and surface coverage of oxides on the wettability of steel/model alloy is a fundamental demand to improve the hot-dip galvanizing of high strength steels.
Chapter 4 – Experimental

4.1. Materials

4.1.1. Model alloys

The binary, ternary and quarternary model alloys were melted and hot-rolled at the Max-Planck Institut für Eisenforschung (MPIE). The bulk composition of the model alloys is shown in Table 4.1. Vacuum melted alloys were hot-rolled at 1100 °C to a thickness of ~ 2 mm sheets and cut into the dimension of 10×15 mm pieces. Then, the samples were first polished with SiC paper (grit 80, 120, 240, 400, 600, 800, 1000, 2500 and 4000) and cleaned afterwards with ethanol. Following this, they were polished with diamond paste (first 3 µm, followed by 1 µm) to a mirror image. After polishing, the samples were ultrasonicated in ethanol for 10 min.

Table 4.1. Composition of the model alloys investigated.

<table>
<thead>
<tr>
<th>Model alloys</th>
<th>Compositions (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binary alloys</td>
<td>Fe-2Si, Fe-2Mn and Fe-0.8Cr</td>
</tr>
<tr>
<td>Ternary alloys</td>
<td>Fe-2Mn-2Si, Fe-2Mn-0.8Cr, Fe-2Si-0.8Cr, Fe-1Si-0.8Cr and Fe-1Mn-0.8Cr</td>
</tr>
<tr>
<td>Quarternary alloy</td>
<td>Fe-2Mn-2Si-0.8Cr</td>
</tr>
</tbody>
</table>

4.1.2. Industrial steel grades

We use high strength industrial steel grades such as two interstitial free (IF) steels namely IF-1, IF-2 and a tensile strength 1000 MPa steel (TS1000), which were procured from Salzgitter Mannesmann Forschung (SZMF). Table 4.2 gives the composition of those industrial steel grades. Cold-rolled steel sheets were cut into the dimension of 15×15 mm pieces. The samples were degreased and cleaned in an ultrasonic bath with ethanol. For the industrial relevant condition, the steel samples were examined in as-received condition and no grinding/polishing was performed.
Table 4.2. Composition of industrial steel grades investigated.

<table>
<thead>
<tr>
<th>Steels</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Al</th>
<th>Cr</th>
<th>Ti</th>
<th>S</th>
<th>P</th>
<th>N</th>
<th>B</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td>IF-1</td>
<td>0.006</td>
<td>0.137</td>
<td>0.022</td>
<td>0.058</td>
<td>0.029</td>
<td>0.106</td>
<td>0.004</td>
<td>0.009</td>
<td>0.004</td>
<td>-</td>
<td>0.004</td>
</tr>
<tr>
<td>IF-2</td>
<td>0.0032</td>
<td>0.148</td>
<td>0.045</td>
<td>0.046</td>
<td>0.033</td>
<td>0.086</td>
<td>0.010</td>
<td>0.011</td>
<td>0.004</td>
<td>0.0001</td>
<td>0.005</td>
</tr>
<tr>
<td>TS1000</td>
<td>0.191</td>
<td>1.808</td>
<td>0.423</td>
<td>0.017</td>
<td>0.116</td>
<td>0.009</td>
<td>-</td>
<td>0.059</td>
<td>0.0061</td>
<td>0.0002</td>
<td>0.177</td>
</tr>
</tbody>
</table>

4.2. Experimental set up

4.2.1. Infrared furnace

An Infrared (IR) furnace (Quad Ellipse Chamber, Model 5528-10, Radiant Energy Research Inc.) is used to conduct annealing experiments on model alloys. The annealing cycle is programmed as shown in Fig. 4.1a, the obtained annealing cycle during the experiment is shown in Fig. 4.1b.

Fig. 4.1. Annealing cycle (a) programmed and (b) obtained during experiment.

The IR radiant heating chamber consisted of four elliptical (polished) aluminium reflectors. It focuses the infrared energy supplied by halogen lamps with tungsten emitter onto a cylindrically shaped target area (Fig. 4.2). These lamps heat up and cool down nearly in response to power control signals. They reach 90% of full operating temperature within 3 seconds after a cold start. This feature offers a rapid heating rate. The radiant energy dissipates to ten percent within five seconds after power switch-off. The temperature of the
furnace was controlled using a Ni-CrNi thermocouple in contact with a quartz reaction tube while a Pt - PtRh thermocouple was in contact with the samples.

As stated earlier, the annealing was carried out in reduction atmosphere i.e. N₂-5%H₂ gas atmosphere. Injection of water vapor to the gas (i.e. dew point temperature) was obtained by passing the gas through oxalic acid mixtures (90% C₂H₂O₄·2H₂O (dihydrate) and...
10%$\text{C}_2\text{H}_2\text{O}_4$ (anhydrous)). The amount of water vapor in the gas is a function of temperature of the oxalic acid mixture [BL20], which is controlled by a thermostat (Lauda E200 Ecoline RE204). The exact amount of water vapor in the gas (i.e. dew point) was measured by using a Trace Moisture Analyzer (Model 8800A, Teledyne Analytical Instruments). The oxygen content was monitored by Trace and Percent Oxygen Transmitter (Model 3190A, Teledyne Analytical Instruments). A photograph of the IR furnace experimental set up is shown in Fig. 4.3.

The model alloys listed in Table 4.1 were annealed for 60 seconds at 820 °C in $\text{N}_2$-5%$\text{H}_2$ gas atmospheres with the different dew points -80 and -40 °C, respectively. The partial pressure of oxygen was calculated thermodynamically from the known p($\text{H}_2\text{O}$) (dew point temperature) and p($\text{H}_2$) (5 vol.% $\text{H}_2$ in the gas), according to the following reaction (4.1). The calculated p(O$_2$) for the dew points -80 and -40 °C are $\sim 1.43 \times 10^{-28}$ and $\sim 8.39 \times 10^{-24}$ bar, respectively.

$$\log p^{1/2}(\text{O}_2) = \frac{1}{K_r} \cdot \log \left( \frac{\text{p(H}_2\text{O)}}{\text{p(H}_2)} \right)$$  \hspace{1cm} (4.1)

where $K_r$ is the equilibrium constant defined by the mass action law at 820 °C for the reaction: $\text{H}_2 + \frac{1}{2} \text{O}_2 = \text{H}_2\text{O}$

### 4.2.2. Liquid zinc spin coater

Hot-dip galvanizing of industrial steel grades and model alloys was simulated (at laboratory scale) in an ‘in-house’ built liquid zinc spin coater, the equipment is shown in Fig. 4.4. The specimen is fixed on a heatable (up to 1100 °C) sample holder and its temperature is controlled by a k-type thermocouple connected to a PID controller. The sample holder has six electrical contacts at the back side and they are used in the following way: two contacts for heating and two for the thermocouples. The detailed schematic view of the sample holder is as shown in Fig. 4.5.
Fig. 4.4. ‘In-house’ built liquid zinc spin coater for simulating the hot-dip galvanization at laboratory scale.

Fig. 4.5. Schematics of rear and front view of the sample holder (Manual PTS, Version 3.00, Omnivac).

The specimen is introduced into a load lock, which is pumped and backfilled with a N\textsubscript{2}-5%H\textsubscript{2} gas atmosphere with a dew point of -79 °C. Afterwards, the specimen is transferred to the preparation chamber via the main chamber by a linear transfer. The sample receiving station in the preparation chamber is as shown in Fig. 4.6 and is provided with electrical contacts for heating and the set up for cooling.
In the preparation chamber, the specimen is annealed to 820 °C in N₂-5% H₂ gas atmospheres with different dew points (DP) which can be varied from low (DP = -79 °C) to high (DP = 0 °C). The dew point of the annealing atmosphere is controlled by a portable gas mixing system, shown in Fig. 4.7, which operates with the same principle as described in the section 4.2.1 (IR furnace set up). Since the main chamber of the spin coater has to be maintained with a very low DP (to avoid the oxidation of Zn), this gas mixing system is designed in such a way that it provides a very low DP atmosphere to the main chamber and at the same time various high DP atmospheres in the preparation chamber. The programmed and the obtained annealing cycle is shown in Fig. 4.8.
Chapter 4 – Experimental

Fig. 4.9. Zinc syringe and sample holder in position during wettability experiment.

Fig. 4.10. Programmed and obtained wetting (galvanizing) cycle.

After annealing, the specimen cools down to room temperature and the preparation chamber is pumped and backfilled with the low dew point atmosphere as maintained in the spin coater main chamber. Afterwards, the sample holder is transferred to a fixed rotatable stage in the main chamber and driven to a desired position (3 to 5 mm) under the zinc syringe as shown in Fig. 4.9. In the syringe, zinc is melted in a quartz glass capillary, embedded into a graphite body. The temperature of the melt (460 °C) is controlled by a PT100 platinum resistance thermometer and a PID controller. To simulate the galvanizing condition, the specimen, annealed at a specified dew point in the preparation chamber, is heated to 470 °C in the main chamber. The programmed and obtained galvanizing (wetting) cycle is as shown in Fig. 4.10. A zinc droplet is placed on the specimen and the wetting behaviour is monitored by a high speed camera (Sessile drop method). The contact angle is measured by a custom made analysis program. After a given reaction time, the spin coater starts to spin off most of the zinc drop, with a given rotation speed up to 2500 rpm. During this spinning process, nearly all residual liquid zinc is driven off the surface, leaving only the wetting zinc layer which opens the way to access the interface.

At each dew point, two specimens were annealed with a fairly equal condition in a preparation chamber for surface characterizations and wetting, respectively. With the UHV transfer vessel, the annealed specimen was transferred for surface analysis (XPS, FE-SEM) without contaminations due to laboratory atmosphere. It is important to notice that the
specimen surface chemistry as obtained during heat treatment in the preparation chamber does not change significantly upon re-heating prior to zinc coating.

4.2.3. High temperature reactor

The high temperature reactor (HTR) chamber, which is directly connected to the ultra high vacuum (UHV) cluster, is used only for the annealing of commercial steels and model alloys at different dew points. This equipment (shown in Fig. 4.11) allows the in-situ surface characterization by X-ray photoelectron spectroscopy (XPS) after annealing, without venting the vessel or exposing the specimen to air, in order to analyze the freshly annealed surface.

Fig. 4.11. High temperature reactor (connected with UHV cluster) for in-situ annealing experiments.

Annealing of interstitial free (IF-1) steel and the Fe-Si model alloy were conducted in the so-called ‘static’ mode where the whole chamber is flushed with the annealing atmosphere. Initially, the sample is introduced into a load lock, pumped and then transferred to the reactor chamber. Afterwards, the reactor chamber is backfilled with the annealing atmosphere (95%N₂-5%H₂) and kept under this condition for a time long enough to obtain a stable atmosphere with the required dew points (-79, -59 and -39 °C), controlled by a
portable gas mixture set up (inset figure of Fig. 4.11). Similar to the liquid zinc spin coater, heating of the sample was achieved by an integrated heater (CrNi spiral) in the sample holder. In order to compare the results of in-situ annealing with ex-situ annealing experiments, samples were heat treated in the two reactions under fairly equal annealing condition i.e. the same annealing cycle, gas flow rate etc. For the results see appendix A.

![Image](image_url)

(a) Without sample holder  
(b) With sample holder

Fig. 4.12. Sealing mechanism (window view) of the high temperature reactor.

This high temperature reactor chamber has also an option to operate in the so called ‘flow-through high pressure’ mode, where only the sample and parts of the sample holder are in contact with the reaction gas and the rest of the chamber is under UHV conditions (Manual HPR, Version 1.01, Omnivac). The special design of the reactor chamber allows this unique feature to separate the sample holder (in contact with the annealing atmosphere) inside the UHV. The sealing mechanism is shown in Fig. 4.12. The view through the window shows the upper and lower sealing funnels and the sample holder in the middle. The sealing mechanism is a reversed ‘conflat type’ seal, using special designed copper gaskets. The set screw at the top of the chamber is tightened to close and seal these two funnels. The gas \((N_2-5\%H_2)\) inlet is from the top side while gas outlet, electrical contacts (for heating) and thermocouple feedthrough are at the bottom of the chamber. Two assemblies of the lower and upper funnels with the sample holder (Fig. 4.12b) form the so called ‘high pressure chamber’ inside the UHV reactor chamber. The flow-through high pressure mode will come into action only after installing the separate rotary forevacuum pump to evacuate the high pressure chamber after the annealing treatment. This is an important step in order to minimize the pressure difference between high pressure chamber and the UHV reactor chamber.
4.3. Analysis methods

4.3.1. X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a widely used surface-sensitive technique for chemical analysis.

Surface analysis by XPS is accomplished by irradiating a sample with monoenergetic soft X-rays and analyzing the energy of the detected electrons. The incident photons (i.e. X-rays) interact with atoms in the surface regions, causing electrons to be emitted by the photoelectric effect. Although the penetration depth of the photons is of the order of micrometers, the emitted electrons originate from only the top few atomic layers (because the mean free path of electrons in solids is very small). The kinetic energy ($E_k$) of the emitted electrons are given by,

$$ E_k = h\nu - BE - \phi_s $$

(4.2)

where $h\nu$ is the energy of the photon, $BE$ is the binding energy of the atomic orbital from which the electron originates and $\phi_s$ is the spectrometer work function.

This binding energy is the energy difference between the initial and final states after the photoelectron has left the atom. Since each element has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements in the surface. From the binding energy and intensity of the photoelectron peak (or peak area), the elemental identity, chemical state, and quantity of an element are determined [BS93, MSSB95].

In this investigation, the bonding state of the elements i.e. the surface chemistry was determined using a Physical Electronics Quantum 2000 Scanning ESCA Microprobe. The sputter depth profiles were performed in XPS and sputtering was done with 2 keV $Ar^+$ ions. The sputter rate was calibrated by using an oxidized silicon wafer of known oxide thickness. In order to quantify the elemental depth profiles, CASA XPS software (with
appropriate sensitivity factor) was used. The elemental spectra were fitted with Gaussian-Lorentzian lines and Shirley background correction.

4.3.2. Field Emission Scanning Electron Microscopy (FE-SEM)

Scanning Electron Microscopy (SEM) is a high resolution surface imaging technique which is based on focusing a beam of electrons onto the surface of a sample and scanning of the beam across it in a “raster” or pattern of parallel lines. When an electron is incident on the surface, a number of phenomena occurs but most important for the microscope are the emission of secondary electrons with energies of a few tens of eV and re-emission or reflection of the high energy backscattered electrons from the primary beam. The signals that provide the greatest amount of information in SEM are the secondary electrons, backscattered electrons and X-rays. The intensity of the secondary electrons is very sensitive to the angle at which the incident electron beam strikes the surface, i.e. to topographical features on the sample. Also, the emitted X-rays have an energy characteristic of the parent element, detection and measurement of its energy permits elemental analysis of the selected area of the SEM image by means of Energy Dispersive X-Ray (EDX) spectroscopy.

Field Emission Scanning Electron Microscope (FE-SEM, LEO 1550 VP, GEMINI), equipped with EDX (Oxford) was used in this investigation to view the surface morphology. In the field emission (FE) SEM, a Schottky Field Emission cathode (an extremely thin and sharp tungsten needle) is employed. When the cathode is held at negative potential relative to the anode, the electric field at the tip is so strong that the potential barrier for the electrons decreases and they can “tunnel” directly through the barrier and leave the cathode. Because the electron beam produced by the FE source is about 1000 times smaller than in a classical SEM, the image quality is markedly better. Imaging is basically done by two detectors in-lens (placed behind the ‘lens’) and the MPSE. Pictures taken by the in-lens detector are more clear and hence high resolution than those taken by the MPSE detector due to the more focused electron beam behind the lens. EDX analyses (spectra and elemental mapping) were carried out with an attached Oxford EDX detector.
4.3.3. Grazing Incidence X-Ray Diffraction (GI-XRD)

Grazing Incidence X-ray Diffraction (GI-XRD) is used to study the phase composition on the surface of the sample. The incident X-ray is fixed at a very small angle with respect to the sample surface and the detector does 20 scan. In this investigation, the phase compositions on the surface of annealed quaternary model alloys were determined by GI-XRD using a Bruker AXS D8 Advance equipped with a Göbel mirror and Sol-X solid state detector (Li-drifted Si sensor). The measurements were carried out with an incidence angle of 1°. An important advantage of the Sol-X energy dispersive solid state detector are X-ray diffraction experiments on samples which emit fluorescence radiation, or experiments where extremely suppression of the background scattering is required.

4.3.4. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) uses a pulsed Ga\(^+\) or Cs\(^+\) primary ion beam (very short pulses of < 1 ns) to desorb and ionize species from a sample surface. The resulting secondary ions are accelerated into a mass spectrometer, where they are mass analyzed by measuring their time-of-flight from the sample surface to the detector. The actual desorption of material from the surface is caused by a "collision cascade" which is initiated by the primary ion impacting the sample surface. The emitted secondary ions (of mass m and charge Z.e) are extracted into the ToF analyzer by applying a high voltage potential (V\(_0\)) between the sample surface and the mass analyzer. The kinetic energy (E\(_K\)) of an ion is,

\[
E_K = \frac{1}{2} mv^2 = ZeV_0
\]  
(4.3)

The spectrometer (or secondary ion optics) consists of 3 electrostatic analyzers and a secondary ion detector (dual micro-channel plate detector). Since the primary ion beam is pulsed, the time t required for an ion to hit the detector plate is measured (so called Time-of-Flight ToF). If L\(_0\) is the effective length of the spectrometer, t is given by,

\[
t = L_0/v = L_0 \sqrt{m/2ZeV_0} = C \sqrt{m/Z} 
\]  
(4.4)
So, the secondary ions travel through the ToF analyzer with different velocities, depending on their mass to charge ratio. For each primary ion pulse, a full mass spectrum is obtained by measuring the arrival times of the secondary ions at the detector and performing a simple time to mass conversion. Apart from the mass spectrum acquisition, ToF-SIMS is capable of mass-imaging (by rastering a finely focused beam across the sample surface) and depth profiling.

For this investigation, elemental mappings (images) on the annealed quaternary model alloys were made by ToF-SIMS using PHI Trift II with a $^{69}$Ga Liquid Metal Ion Gun (LMIG) to visualize the distribution of individual species as a function of depth from the surface. The sputter rate was calibrated against a 100 nm SiO$_2$ grown on top of a Si wafer.

4.3.5. Focused Ion Beam (FIB) micromachining

A Focused Ion Beam (FIB) machine operates in a similar fashion as a scanning electron microscope with the exception that a beam of ions (usually Ga) replaces the beam of electrons. It is based on the principle of a strong electric field causing a thermally assisted field-emission of positively charged ions from a liquid metal ion source (LMIS) [VM07].

A FIB machine can be used for implantation, sputtering, deposition, micromachining and ion beam lithography. The two major classes of FIB systems are the low energy (10-30 keV) type with heavy ion species where momentum transfer and sputtering are important, and the higher energy (30-200 keV) type where electronic excitation and doping are the desired effects. 30 keV is about the apparative limit up to which the high voltage can be handled without insulating gas. Above 30 keV, the construction of a FIB is more complicated because there is the need to surround all high voltage parts by such inert gas in order to prevent sparks in the air or on insulating surfaces.

For the preliminary study on the Fe-Al interfacial layer, galvanized IF steel was micromachined using a FIB machine (ORSAY, Canion 31M plus) in the group of ‘Lehrstuhl für Angewandte Festkörperphysik’ at Ruhr-Universität Bochum. This system is a ‘dual beam’ FIB machine, consisting of both a FIB column and a SEM column, allowing micromachining and imaging in the same chamber.
Chapter 5 – Results and Discussions

5.1. Annealing studies of model alloys

This section describes the surface chemistry of binary, ternary and quarternary model alloys, annealed in an IR furnace for 60 secs at 820 °C in N₂-5%H₂ gas atmospheres with different dew points (DP) of -80 and -40 °C, respectively. The surface chemistry of an in-situ annealed quarternary model alloy (in the preparation chamber of liquid zinc spin coater) with DP = -29 and 0 °C is also presented.

5.1.1. Binary alloys (Fe-2Si, Fe-2Mn and Fe-0.8Cr)

![XPS core-level spectra of Si 2p3/2, Mn 2p3/2 and Cr 2p3/2 obtained on the binary model alloys annealed at a dew point of -80 °C.](image)

Fig. 5.1. The XPS core-level spectra of Si 2p3/2, Mn 2p3/2 and Cr 2p3/2 obtained on the binary model alloys annealed at a dew point of -80 °C.
The XPS core-level spectra of Si 2p$_{3/2}$, Mn 2p$_{3/2}$ and Cr 2p$_{3/2}$, obtained on the binary model alloys (Fe-2Si, Fe-2Mn and Fe-0.8Cr) annealed at a dew point of -80 °C are shown in Fig. 5.1. At this dew point of -80 °C, the calculated partial pressure of oxygen is $\sim 1.43 \times 10^{-28}$ bar and high enough to oxidise Si and Mn and at the very border for oxidation of Cr ($\sim 6.9 \times 10^{-28}$ bar) [HSC97]. The Si 2p$_{3/2}$ spectrum in Fig. 5.1a is fitted with one component at a binding energy of 104.6 eV corresponding to SiO$_2$ on the surface [PS04]. Only one component is present at 640.9 eV in the Mn 2p$_{3/2}$ spectrum (Fig. 5.1b), which corresponds to MnO [MSSB95]. On the surface of the Fe-0.8Cr alloy, the Cr 2p$_{3/2}$ spectrum (Fig. 5.1c) is fitted with one component at 576.5 eV, assigned to Cr$_2$O$_3$ [MSSB95].

Fig. 5.2. The XPS core-level spectra of Si 2p$_{3/2}$, Mn 2p$_{3/2}$ and Cr 2p$_{3/2}$ obtained on the binary model alloys annealed at a dew point of -40 °C.

Fig. 5.2 shows the XPS spectra of Si 2p$_{3/2}$, Mn 2p$_{3/2}$, and Cr 2p$_{3/2}$ of the binary alloys, annealed at dew point -40 °C. The Si 2p$_{3/2}$ spectrum (Fig. 5.2a) fits well with a single component at 104.3 eV i.e. to SiO$_2$. Two components are necessary to obtain a reasonable
fit for the Mn 2p<sub>3/2</sub> spectrum (Fig. 5.2b). The lowest binding energy component at 640.8 eV is assigned to MnO whereas the rest of the peak envelope is Mn<sub>3</sub>O<sub>4</sub> with a binding energy of 641.9 eV [PS04]. Increasing the dew point from -80 to -40 °C (p(O<sub>2</sub>) ~8.39 ×10<sup>-24</sup> bar) exceeds the partial pressure of oxygen for the formation of Mn<sub>3</sub>O<sub>4</sub> (~7.84 ×10<sup>-25</sup> bar). The Cr 2p<sub>3/2</sub> spectrum in Fig. 5.2c is fitted with one component at binding energy of 577.2 eV which is attributed to Cr<sub>2</sub>O<sub>3</sub> [SS94]. For the sake of simplicity, the oxygen core-level spectra are not shown here. However, their peak positions are corresponding to their respective oxides.

![Image](image1.png)

(a) Fe-2Si  
(b) Fe-2Mn  
(c) Fe-0.8Cr

Fig. 5.3. Surface morphology of the binary model alloys annealed at a dew point of -40 °C.

Fig. 5.3 shows the FE-SEM image of the binary alloys annealed at a dew point of -40 °C, visualizing that oxides of different size and morphology are formed on top of the grains and at the grain boundaries. On the surface of the Fe-2Si alloy (Fig. 5.3a), islands of SiO<sub>2</sub> are
visible. These islands are formed because the critical Si-concentration necessary for the formation of a continuous layer is about 3 wt.% [Tuc65], which is not reached here. The Mn and Cr oxides are decorated on and at the grain boundaries of Fe-2Mn (Fig. 5.3b) and Fe-0.8Cr (Fig. 5.3c) alloys, respectively. On the surface of every alloy annealed at every dew point, iron was detected also in the metallic state, showing a dominating metallic peak at 707.1 eV. But in some cases, an additional Fe-oxide peak appears at 711 eV (figure not shown). Though the annealing atmosphere is reducible for iron, the iron oxides on some specimens are formed by oxidation of the Fe during cooling because the stability of iron oxide increases with decreasing temperature. An ex-situ transport of specimens to XPS analysis could also cause Fe-oxidation.

5.1.2. Ternary alloys (Fe-2Mn-2Si, Fe-2Mn-0.8Cr and Fe-2Si-0.8Cr)

The high resolution XPS spectra of Si 2p 3/2, Mn 2p 3/2 and Cr 2p 3/2 obtained on the ternary alloys annealed at a dew point of -80 °C, are shown in the Fig. 5.4. The Si 2p 3/2 spectrum of Fe-2Mn-2Si alloy (Fig. 5.4a) can be fitted with two components. The higher intensity component is at 104.2 eV and attributed to SiO 2 [PS04]. The additional component at 102.1 eV confirms the presence of Mn-Si mixed oxides (MnSiO 3/Mn 2SiO 4) [VSL03, KS77]. The high intensity component of the Mn 2p 3/2 spectrum (Fig. 5.4b) at 642 eV of this alloy is supporting the formation of MnSiO 3/Mn 2SiO 4 [VSL03, BS93]. The weak component at 640.9 eV in Mn 2p 3/2 spectrum reveals the presence of MnO. On the surface of the oxidised Fe-2Mn-0.8Cr alloy, the fitted component at 640.9 eV in the Mn 2p 3/2 spectrum (Fig. 5.4c) belongs to MnO. The Cr 2p 3/2 peak position (Fig. 5.4d) at ~576 eV corresponds to Cr 2O 3 [MSSB95, SS94]. Surface analysis of the oxidised Fe-2Si-0.8Cr alloy shows the fitted peak position for silicon (Fig. 5.4e) at 103.2 eV, attributed to SiO 2 [MSSB95]. The Cr 2p 3/2 spectrum (Fig. 5.4f) of this alloy is fitted with two components; a higher intensity component at 577.1 eV refers to Cr 2O 3 and the second component at 574 eV to metallic Cr.
Fig. 5.4. The XPS core-level spectra of Si 2p\textsubscript{3/2}, Mn 2p\textsubscript{3/2} and Cr 2p\textsubscript{3/2}, obtained on the ternary model alloys annealed at a dew point of -80 °C.
Fig. 5.5. The XPS core-level spectra of Si 2p\(_{3/2}\), Mn 2p\(_{3/2}\) and Cr 2p\(_{3/2}\), obtained on the ternary model alloys annealed at a dew point of -40 °C.

Fig. 5.5 shows the XPS spectra of Si 2p\(_{3/2}\), Mn 2p\(_{3/2}\) and Cr 2p\(_{3/2}\) of the ternary alloys, annealed at a dew point of -40 °C. On the surface of the oxidised Fe-2Mn-2Si, only one component is present at 102.7 eV in the Si 2p\(_{3/2}\) spectrum (Fig. 5.5a) which is attributed to Mn-Si mixed oxides. The Mn 2p\(_{3/2}\) spectrum (Fig. 5.5b) is fitted with two components at
642.8 eV and 641.7 eV. Despite of their slight shift in the binding energies in both (Si 2p\textsubscript{3/2} and Mn 2p\textsubscript{3/2}) spectra, they can be assigned to MnSiO\textsubscript{3}/Mn\textsubscript{2}SiO\textsubscript{4} and MnO/Mn\textsubscript{3}O\textsubscript{4}, respectively. Analysing the surface of the Fe-2Mn-0.8Cr alloy, the Mn 2p\textsubscript{3/2} spectrum (Fig. 5.5c) is fitted with two components. A high intensity component at 641.9 eV belongs to Mn\textsubscript{3}O\textsubscript{4}, whereas the second component at 640.6 eV belongs to the Mn-Cr mixed oxides (MnCr\textsubscript{2}O\textsubscript{4}) [MSSB95]. The Cr 2p\textsubscript{3/2} peak position (Fig. 5.5d) is fitted with a component of position at 577 eV, assigned to Cr\textsubscript{2}O\textsubscript{3}. The fitted component position for silicon (Fig. 5.5e) on the surface of the Fe-2Si-0.8Cr alloy is at 103.9 eV and attributed to SiO\textsubscript{2}. The Cr 2p\textsubscript{3/2} spectrum (Fig. 5.5f) is fitted with a single component at an energy position of 577.9 eV, probably belonging to Cr-hydroxides. Despite this annealing condition is not favourable for any Cr-hydroxides, a monolayer may have been formed during cooling or due to contact with the laboratory atmosphere by ex-situ transport of the specimen for XPS analysis. However, in-depth observation on this alloy (corner plot in the Fig. 5.5f) gives evidence for the presence of Cr\textsubscript{2}O\textsubscript{3} along with metallic Cr in the near-surface region.

Different surface morphologies and its oxide distribution of the ternary alloys, annealed at a dew point of -40 °C are shown in Fig. 5.6. In the Fe-2Mn-2Si alloy, manganese silicates (Fig. 5.6a) spread all over the surface although they are not homogeneous in thickness and distribution. In Fig. 5.6b (Fe-2Mn-0.8Cr alloy), grain boundaries are enriched with oxide precipitates because they can act as a fast diffusion path.
Chapter 5 – Results and Discussions: Annealing studies of model alloys

5.1.3. Quarternary alloy (Fe-2Mn-2Si-0.8Cr)

Fig. 5.7 and 5.8 shows the XPS spectra of Si 2p, Mn 2p, and Cr 2p for the quarternary alloy (Fe-2Mn-2Si-0.8Cr), annealed at a dew point of -80 and -40 °C, respectively. The peak position of the Si 2p spectra (Fig. 5.7a and 5.8a) of both dew points clearly indicates the presence of Mn-Si mixed oxides, i.e. MnSiO$_3$/Mn$_2$SiO$_4$. For both dew points, the Mn 2p peak in the spectrum (Fig. 5.7b and 5.8b) can be fitted with two components. At the lower dew point, both components are located at 642 eV (MnSiO$_3$/Mn$_2$SiO$_4$) and 640.9 eV (MnO) respectively. At the higher dew point (as mentioned in the binary and ternary alloy sections), MnO/Mn$_3$O$_4$ is observed along with the Mn-Si mixed oxides. The Cr 2p peak position of the quarternary alloy, annealed at the...
lower dew point (Fig. 5.7c), belongs to metallic Cr. However, it can be fitted with a shoulder component at 576.7 eV, which corresponds to Cr$_2$O$_3$. Obviously, at the lower dew point of -80 °C, the partial pressure of oxygen is not high enough to oxidize Cr completely. At the higher dew point of -40 °C, the well pronounced Cr 2p$_{3/2}$ spectra (with fitted component at 577 eV in Fig. 5.8c) clearly confirms the presence of Cr$_2$O$_3$.

Fig. 5.7. The XPS core-level spectra of Si 2p$_{3/2}$, Mn 2p$_{3/2}$ and Cr 2p$_{3/2}$, obtained on the quaternary model alloy, annealed at a dew point of -80 °C.
Fig. 5.8. The XPS core-level spectra of Si 2p$\frac{3}{2}$, Mn 2p$\frac{3}{2}$ and Cr 2p$\frac{3}{2}$, obtained on the quartenary model alloy, annealed at a dew point of -40 °C.

The XPS depth profiles of the quartenary alloy, annealed at both dew points, are shown in the Figs. 5.9a and 5.9b. After annealing at the lower dew point, the oxide scale thickness is about 10 nm. At the higher dew point, the oxide scale thickness appears to be more than 32 nm. In this case, Si and Mn indicate the presence of Mn-Si mixed oxides throughout the depth profile and the existence of Cr-oxides is also confirmed in the entire profile. Interestingly, in-depth quantification shows that the amount of Cr$_2$O$_3$ increases with increasing depth at the higher dew point, obviously due to internal oxidation of Cr. On the other hand, Si and Mn oxides (as Mn-Silicate) are observed mainly on the surface and their concentration decreases in depth. The surface morphology of the quartenary alloy annealed at a dew point of -40 °C is shown in Fig. 5.9c.
Fig. 5.9. The XPS depth profiles ((a) DP -80 °C and (b) DP -40 °C)) and (c) surface morphology (at DP -40 °C) of the annealed quarternary model alloy.

An in-situ annealing of quarternary model alloy (Fe-2Mn-2Si-0.8Cr) at high dew points (-29 and 0 °C) is performed in the preparation chamber of the liquid zinc spin coater. The XPS core-level spectra of Mn 2p3/2, Si 2p3/2 and Cr 2p3/2, obtained after annealing at the high dew points of -29 and 0 °C, are shown in Fig. 5.10. The peak position in the Mn 2p3/2 spectra (Fig. 5.10a) is located at 642.3 eV and corresponds to MnSiO3/Mn2SiO4. Additionally, the Si 2p3/2 spectra (Fig. 5.10b) at binding energy of 102.3 eV clearly indicate the presence of Mn-Si mixed oxides formed at both annealing conditions. The Cr 2p3/2 peak positions (Fig. 5.10c) are at 577.1 eV, assigned to Cr2O3.
Chapter 5 – Results and Discussions: Annealing studies of model alloys

Fig. 5.10. The XPS core-level spectra obtained on the quaternary model alloy, annealed at the DP of -29 and 0 °C.

![Mn 2p3/2 and Si 2p3/2 spectra](a) and (b)

Fig. 5.11. The XPS depth profiles of the quaternary model alloy, annealed at the DP of -29 and 0 °C.

![Cr 2p3/2 spectra](c)

The quantification of XPS spectra (Fig. 5.11) reveals that the surface concentration of oxides decreases with increasing dew point from -29 to 0 °C, obviously due to internal
oxidation. Moreover, occurrence of internal oxidation or in other words less external oxidation at high dew point (Fig. 5.11b) leaves the surface with more metallic iron. Although the surface morphology looks similar in both cases (Fig. 5.12), high dew point annealing leads to the formation of less-selective oxides at the surface due to internal oxidation.

![Fig. 5.12. Surface morphology of the quarternary model alloy, annealed at the DP of -29 and 0 °C.](image)

(a) DP -29 °C  
(b) DP 0 °C

5.1.4. Discussions

The systematic annealing of model alloys has put some light on the oxidation and interaction of common alloying elements in high strength steels as a function of oxygen partial pressure, i.e. dew point (DP). Binary alloys Fe-0.8Cr and Fe-2Si, form monophase oxides Cr$_2$O$_3$ and SiO$_2$. In the Fe-Mn system an increasing dew point leads to the formation of Mn$_3$O$_4$ and MnO, MnO was found as the only component at lower DP. The quantification of the oxide forming elements on the surface of the binary alloys (Fig. 5.13a) shows that at low DP the enrichment of Si is much higher (due to its higher affinity to oxygen) compared to the concentrations of Mn and Cr. At higher DP, the concentration of Mn and Cr increases, due to the higher oxygen affinity.
Fig. 5.13. Surface concentration of annealed binary and ternary model alloys.

It is very clear that if Mn is alloyed with Si, MnSiO₃ as well as Mn₂SiO₄ is formed. The formation of mixed oxides is favourable for two reasons: First, the diffusion coefficients for Si and Mn in ferrite [D(Si) = 2.29×10⁻¹¹ cm²/sec and D(Mn) = 1.41×10⁻¹¹ cm²/sec] are nearly the same at ~820 °C [Oik82, HLLA⁺96] which causes their co-segregation and subsequent oxidation according to the following reactions (5.1) and (5.2),

\[
\text{MnO} + \text{SiO}_2 = \text{MnSiO}_3 \tag{5.1}
\]

\[
2\text{MnO} + \text{SiO}_2 = \text{Mn}_2\text{SiO}_4 \tag{5.2}
\]

Second, the values of the standard Gibb’s free energy ΔG⁰ and Gibb’s free energy ΔGr,P of the formation of MnSiO₃ and Mn₂SiO₄ a very negative, as calculated by using the formula (5.3) given below [NBS68].
\[ \Delta G_{T,P} = \Delta G^0 + RT \ln \left( \frac{p(H_2)}{p(H_2O)} \right) \]  

(5.3)

where \( \Delta G^0 = -303.3 - 21.3 \times 10^{-3}T \) (for \( MnSiO_3 \)) and \( \Delta G^0 = -412.8 - 39.0 \times 10^{-3}T \) (for \( Mn_2SiO_4 \)).

The free energy of \( MnSiO_3 \) formation at both dew points -80 and -40 °C are -1262.98 and -1312.86 kJ/mol respectively. For \( Mn_2SiO_4 \), these values are more negative and they are listed as follows, -1802.33 kJ/mol (for DP = -80 °C) and -1852.21 kJ/mol (for DP = -40 °C) respectively. The calculations of critical solute concentration of Mn and Si (Table 5.1) shows, that the formation of MnO and SiO2 is possible, i.e. \( Mn_{\text{real}} > Mn_{\text{critical}}; Si_{\text{real}} > Si_{\text{critical}} \) at a DP of -40 °C but not at a DP of -80 °C. Based on the extended Wagner’s model for internal oxidation proposed by Huin et al. [HLLA’96], the surface oxygen content (wt.%), the solubility products (\( K_{MnO}, K_{SiO2} \)) have been calculated at 820 °C for the dew points -40 and -80 °C, respectively. The solubility products (wt.%) and surface oxygen content (wt.%) are given by

\[ \log K_{SiO2} = \left[ -\frac{22010}{T} \right] + 4.0 \]  

(5.4)

\[ \log K_{MnO} = \left[ -\frac{10830}{T} \right] + 2.95 \]  

(5.5)

\[ \log O_s = \left[ -\frac{3690}{T} \right] + \log \left( \frac{p(H_2)}{p(H_2O)} \right) \]  

(5.6)

By using these formulas, the critical solute concentrations to form stable MnO and SiO2 have been obtained. The values are tabulated in Table 5.1. According to the calculations, MnO and SiO2 should not be stable at low dew point. Nevertheless, both oxides are found in our case on the surface. The reasons may be the oxides are formed during cooling as the critical solute concentration is decreasing with temperature (Table 5.2). And/or the actual surface concentration of Mn and Si will be higher compared to the bulk due to segregation processes.
Table 5.1. Calculated surface oxygen content, solubility product and critical solute concentrations for MnO and SiO$_2$ at the dew points of -80 and -40 °C.

<table>
<thead>
<tr>
<th>DP (°C)</th>
<th>Surface oxygen $O_s$ (wt.%)</th>
<th>Solubility product</th>
<th>Critical concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$K_{\text{MnO}}$</td>
<td>$K_{\text{SiO}_2}$</td>
</tr>
<tr>
<td>-80</td>
<td>$4.487 \times 10^{-9}$</td>
<td>$1.100 \times 10^{-7}$</td>
<td>0.102</td>
</tr>
<tr>
<td>-40</td>
<td>$1.084 \times 10^{-6}$</td>
<td>$7.291 \times 10^{-17}$</td>
<td>$1.100 \times 10^{-7}$</td>
</tr>
</tbody>
</table>

Table 5.2. Calculated solubility product and critical solute concentrations for various temperatures at a dew point of -80 °C.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Solubility product</th>
<th>Critical concentration (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{\text{MnO}}$</td>
<td>$K_{\text{SiO}_2}$</td>
</tr>
<tr>
<td>820</td>
<td>$1.100 \times 10^{-7}$</td>
<td>$7.291 \times 10^{-17}$</td>
</tr>
<tr>
<td>800</td>
<td>$7.191 \times 10^{-8}$</td>
<td>$3.072 \times 10^{-17}$</td>
</tr>
<tr>
<td>700</td>
<td>$6.599 \times 10^{-9}$</td>
<td>$2.395 \times 10^{-19}$</td>
</tr>
<tr>
<td>600</td>
<td>$3.504 \times 10^{-10}$</td>
<td>$6.139 \times 10^{-22}$</td>
</tr>
<tr>
<td>500</td>
<td>$8.703 \times 10^{-12}$</td>
<td>$3.361 \times 10^{-25}$</td>
</tr>
</tbody>
</table>

The quantification of elements on the surface of Fe-2Mn-2Si alloy is shown in Fig. 5.13b. In comparison with the binary Fe-2Mn alloy, Mn is enriched at low DP due to its affinity to Si to form Mn-Si-mixed oxides. This is the classical case for chemisorption induced co-segregation, which is even more pronounced at a DP of -40 °C. In the case of Fe-2Si-0.8Cr ternary alloy, the binary oxides SiO$_2$ and Cr$_2$O$_3$ are present at both dew points, since no mixed oxides of Si and Cr are formed. It is interesting to see from fig. 5.13d that the surface silicon concentration is much less at DP = -80 °C as in the binary Fe-2Si and the ternary Fe-2Mn-2Si alloy. It is also interesting to note that in contrast to the binary alloy Fe-0.8Cr; also metallic Cr was detected at low DP. This incomplete oxidation of Cr may be attributed to kinetic factors in the sense that surface oxygen is consumed basically by oxidation of silicon. The less amount of silicon is a result of a share of available oxygen atoms between Cr and Si, whereas not all the chromium can be oxidised. On the surface of the Fe-2Mn-0.8Cr alloy, there is no significant enrichment of Mn and Cr at low DP (Fig. 5.13c). At a DP of -40 °C, Mn-Cr mixed oxides are formed as given below:

$$\text{MnO} + \text{Cr}_2\text{O}_3 = \text{MnCr}_2\text{O}_4$$  \hspace{1cm} (5.7)
According to the phase stability diagram in FactSage™ data base, the Mn-Cr mixed oxides (i.e. MnCr$_2$O$_4$) are more stable at higher dew point, because the oxidation of manganese is more pronounced. Consequently, at a DP of -80 °C, only binary oxides MnO and Cr$_2$O$_3$ are formed.

Upon oxidation of the Fe-2Mn-2Si-0.8Cr alloy, mainly Mn-silicates are formed (at all dew points) as ternary oxides showing that the affinity between Si and Mn is obviously higher than between Mn and Cr. By closely observing the Cr peak positions, it clearly shows the formation of only Cr$_2$O$_3$ in the entire profile, leading to the conclusion that there is no interaction of Cr with Mn in the quarternary system. For explaining the influence of Si and Mn on the oxidation of Cr at DP = -40 °C, in-depth distributions of Cr-oxide are plotted in Fig. 5.14. It shows that when Mn alloyed with Cr, they co-segregate as both elements are having almost equal affinity to oxygen. There is a slight tendency for internal oxidation of chromium in Fe-0.8Cr and Fe-2Mn-0.8Cr alloy since the chromium concentration increases slightly with increasing depth. When Si is alloyed with Cr, the distribution of Cr decreases almost linearly from the surface to the oxidation front, i.e. suppressing the in-depth Cr-oxidation by decreasing the surface oxygen potential upon oxidation of silicon which, in turn, leads to more external oxidation of Cr. When Si and Mn alloyed together with Cr in the quarternary alloy, the Cr concentration is increasing with increasing depth, showing a clear trend for its internal oxidation. This can be explained on the basis of permeability
calculations for oxygen ($D_{OOS}$) and solute species ($D_{AAB}$, here $A_B = 2\%$Mn, 2\%Si and 0.8\%Cr) by using the equations given in extended Wagner’s model proposed by Huin et al [HLLA‘96]. Internal oxidation is possible only if $D_{OOS} >> D_{AAB}$ where $D_O$ and $D_A$ are diffusion coefficient of oxygen and the respective solute species. The surface oxygen concentration and solute (A) bulk concentration are represented as $O_S$ and $A_B$ respectively. The calculated inward oxygen permeability and the outward solute (Mn, Si and Cr) permeability are listed in table 5.3 and 5.4.

Table 5.3. Calculated inward oxygen permeability for different dew points.

<table>
<thead>
<tr>
<th>Dew point (°C)</th>
<th>Inward oxygen permeability ($D_{OOS}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-80</td>
<td>$1.65 \times 10^{-15}$</td>
</tr>
<tr>
<td>-40</td>
<td>$3.98 \times 10^{-13}$</td>
</tr>
<tr>
<td>-29</td>
<td>$1.31 \times 10^{-12}$</td>
</tr>
<tr>
<td>0</td>
<td>$1.89 \times 10^{-11}$</td>
</tr>
</tbody>
</table>

Table 5.4. Calculated outward permeability of the alloying elements Mn, Si and Cr.

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Bulk composition (wt.%)</th>
<th>Outward permeability ($D_{AAB}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>2.0</td>
<td>$2.827 \times 10^{-11}$</td>
</tr>
<tr>
<td>Si</td>
<td>2.0</td>
<td>$4.588 \times 10^{-11}$</td>
</tr>
<tr>
<td>Cr</td>
<td>0.8</td>
<td>$5.16 \times 10^{-12}$</td>
</tr>
</tbody>
</table>

At a dew point of -40 °C, the calculated inward oxygen permeability and outward Cr permeability is on the very border for chromium external/internal oxidation. By increasing the dew point, i.e. an increase of surface oxygen content in the annealing atmosphere leads to the higher inward oxygen permeability. It is quite obvious that oxygen diffuses deeper during annealing at high dew point since the oxygen free surface adsorption rate is directly related to the partial pressure of oxygen in the annealing atmosphere. The formation of Mn-Si mixed oxides at a DP of -40 °C prevails thus hindering the interaction of Mn with Cr and, therefore, suppressing its segregation to the surface and consequently internal oxidation of Cr occurs.

The table 5.3 and 5.4 clearly shows that the calculated permeabilites at a DP of -29 °C fulfill the condition for internal oxidation of Cr and at the very border for Si and Mn. Also,
as per the calculation, further increase of DP to 0 °C tends to internal oxidation of all alloying elements considered here. But the competition between alloying elements for the available oxygen in the annealing atmosphere and the formation of ternary/mixed oxides are not considered in the above permeability calculations. This may be the reason for having a slight external oxidation of alloying elements even after annealing at very high dew point. However, the obtained depth profile at the DP of -29 and 0 °C clearly reveals the trend for the internal oxidation of Cr. At very high DP = 0 °C, surface concentration of Si and Mn oxides decreases significantly and is the evidence for transition to internal oxidation.

The surface chemistry of the model alloys (binary, ternary and quarternary system) annealed at the different dew points of -80 and -40 °C are summarized in Table 5.5.

Table 5.5. The surface chemistry of model alloys annealed at dew points -80 and -40 °C.

<table>
<thead>
<tr>
<th>Model alloys</th>
<th>Surface chemistry</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DP -80 °C</td>
</tr>
<tr>
<td>Fe-2% Si</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Fe-2% Mn</td>
<td>MnO</td>
</tr>
<tr>
<td>Fe-0.8% Cr</td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td>Fe-2% Mn-2% Si</td>
<td>MnO, SiO₂, MnSiO₃/Mn₂SiO₄</td>
</tr>
<tr>
<td>Fe-2% Mn-0.8% Cr</td>
<td>MnO, Cr₂O₃</td>
</tr>
<tr>
<td>Fe-2% Si-0.8% Cr</td>
<td>SiO₂, Cr₂O₃, Cr</td>
</tr>
<tr>
<td>Fe-2% Mn-2% Si- 0.8% Cr</td>
<td>MnSiO₃/Mn₂SiO₄, MnO, Cr₂O₃, Cr</td>
</tr>
</tbody>
</table>
5.1.5. Conclusions

1. Increasing the dew point from -80 °C to -40 °C generally leads to more pronounced surface oxidation.

2. In the binary alloys only binary oxides are formed i.e. SiO$_2$ (Fe-2Si) and Cr$_2$O$_3$ (Fe-0.8Cr) independent on the dew point. In the case of Fe-Mn, MnO is formed at lower DP and additional Mn$_3$O$_4$ at higher DP.

3. By presence of Si and Mn in the system (Fe-Mn-Si), the formation of MnSiO$_3$/Mn$_2$SiO$_4$ takes place on the surface at all dew points.

4. When Mn and Cr are present in the alloy (Fe-Mn-Cr), they show also chemical interaction by forming MnCr$_2$O$_4$ at a DP of -40 °C, apart from their own oxides Mn$_3$O$_4$ and Cr$_2$O$_3$. In Fe-Si-Cr alloy, Si and Cr are forming their binary oxides, i.e. SiO$_2$ and Cr$_2$O$_3$ at every DP without any interaction between them.

5. In the quarternary system (Mn with Si and Cr), Mn interacts only with Si by forming manganese silicates, although Mn showed its interaction with Cr in the ternary system. Obviously, Mn has higher affinity to Si than to Cr. Annealing at higher dew points (i.e. increasing the oxygen partial pressure in the annealing atmosphere) shows a trend for internal oxidation of Cr with increasing in-depth distribution of Cr-oxides.
5.2. Effect of alloy composition on the selective oxidation of ternary model alloys

In this section, the effect of Si and Mn concentration on the selective oxidation of Cr in different Fe-Si-Cr and Fe-Mn-Cr alloys are discussed. Oxidation behaviour of in-situ annealed Fe-1Si-0.8Cr, Fe-2Si-0.8Cr, Fe-1Mn-0.8Cr and Fe-2Mn-0.8Cr (with different dew points -80, -40 and -29 °C) are presented and analyzed in detail.

5.2.1. Fe-Si-Cr ternary alloys (Fe-1Si-0.8Cr and Fe-2Si-0.8Cr)

Fig. 5.15. The XPS core-level spectra obtained on the surface of Fe-1Si-0.8Cr alloy annealed at the DP of -80, -40 and -29 °C.

The XPS core-level spectra of Si 2p\textsubscript{3/2} and Cr 2p\textsubscript{3/2} obtained on the surface of Fe-1Si-0.8Cr alloy annealed at the different dew points (DP) -80, -40 and -29 °C, are shown in Fig. 5.15. They reveal clear differences depending on the DP of the annealing atmosphere. The Si 2p\textsubscript{3/2} spectra (Fig. 5.15a) is located at ~103.8 eV and assigned to SiO\textsubscript{2} [MSSB95]. Despite of a slight shift in the measured spectra at low DP = -80 °C, it corresponds to SiO\textsubscript{2} only. The Cr 2p\textsubscript{3/2} spectra of this alloy obtained at a DP of -80 °C (inset figure of Fig. 5.15b) is fitted with two components; the higher binding energy component at 576.8 eV refers to Cr\textsubscript{2}O\textsubscript{3} and the lower binding energy at 574.6 eV to metallic Cr [MSSB95]. It is important to note that the calculated partial pressure of oxygen at very low DP -80 °C (1.4×10\textsuperscript{-28} bar) is at the very border for oxidation of Cr (6.9×10\textsuperscript{-28} bar) [HSC97]. Annealing at the DP of -40 and -29 °C is enough to oxidize Cr completely, which is confirmed by noting the Cr 2p\textsubscript{3/2}
spectra at 576.9 eV. Although Cr oxidizes externally, the weak signal of Cr at a DP of -29 °C implies the change of Cr oxidation mode from external to internal.

Fig. 5.16. The XPS core-level spectra (at various depths) obtained on the Fe-2%Si-0.8%Cr alloy annealed at a DP of -29 °C.

Annealing the Fe-2%Si-0.8%Cr alloy at all dew points used here shows a surface chemistry similar to Fe-1%Si-0.8%Cr, i.e. the formation of binary oxides (SiO$_2$, Cr$_2$O$_3$). The remarkable difference appears after annealing at the DP of -40 and -29 °C, showing the effect of partial oxidation of Si on Cr oxidation. Fig. 5.16 shows the XPS core-level spectra of Si 2p$_{3/2}$ and Cr 2p$_{3/2}$ (at various depths) obtained on the Fe-2%Si-0.8%Cr alloy annealed at a DP of -29 °C. By looking into the Si 2p$_{3/2}$ spectra (Fig. 5.16a) of this alloy, only SiO$_2$ is observed on the surface. At the sub-surface region (i.e. after 3 nm sputtering), metallic Si peak appears along with dominating oxide peak. With increasing the sputter depth to 19 nm, the spectra clearly shows an increasing contribution of the metallics. The obtained Cr 2p$_{3/2}$ spectra (Fig. 5.16b) clearly visualize a widening of the metallic Cr shoulder (along with dominating oxide peak) by increasing the sputter depth. The Cr 2p$_{3/2}$ spectra measured after 19 nm sputtering (inset figure of Fig. 5.16b) is fitted with two components. The higher intensity component is at 576.5 eV and attributed to Cr$_2$O$_3$. The additional component at 574.4 eV confirms the presence of metallic Cr.

The XPS depth profiles of both Fe-Si-Cr alloys annealed at a DP of -29 °C are shown in Fig. 5.17. In comparison with Fe-1%Si-0.8%Cr sputter profile (Fig. 5.17a), a higher amount of Cr was observed on Fe-2%Si-0.8%Cr alloy (Fig. 5.17b), moreover, the former one shows
the tendency of internal oxidation of Cr at this DP = -29 °C (i.e. slight increase of Cr concentration with increase of depth).

Fig. 5.17. The XPS depth profiles of both Fe-Si-Cr alloy annealed at a DP of -29 °C.

Fig. 5.18 shows the surface morphology of both the Fe-Si-Cr alloys annealed at a DP of -29 °C. The black patches of Si oxides are found on the surface of Fe-1%Si-0.8%Cr alloy (Fig. 5.18a) and in Fe-2%Si-0.8%Cr alloy (Fig. 5.18b), the coverage of nano-islands are observed throughout the surface.

Fig. 5.18. Surface morphology of the Fe-Si-Cr alloys annealed at a DP of -29 °C.
5.2.2. Fe-Mn-Cr ternary alloys (Fe-1Mn-0.8Cr and Fe-2Mn-0.8Cr)

Annealing of both Fe-Mn-Cr alloys (Fe-1%Mn-0.8%Cr, Fe-2%Mn-0.8%Cr) at low DP -80 °C forms a very small amount of their binary oxides (MnO, Cr2O3) on the surface. At the DP of -40 and -29 °C, formation of Mn-Cr mixed oxides was observed and moreover, increasing the dew point increases the external surface oxidation in this case.

Fig. 5.19. The XPS core-level spectra obtained on the surface of Fe-1Mn-0.8Cr alloy annealed at a DP of -29 °C.

Fig. 5.19 shows the high resolution XPS spectra of Mn 2p3/2 and Cr 2p3/2, obtained on the surface of Fe-1%Mn-0.8%Cr alloy annealed at a DP of -29 °C. The measured Mn 2p3/2 spectra (Fig. 5.19a) at DP -29 °C is fitted with two components, the higher binding energy component at 641.6 eV is assigned to MnO/Mn3O4 whereas the rest of the peak envelope is MnCr2O4 with a binding energy of 640.4 eV [MSSB95]. The Cr 2p3/2 spectra (Fig. 5.19b) is fitted with a single component of position at 576.7 eV refers to Cr2O3.

In-depth observation of XPS core-level spectra (Mn 2p3/2, Cr 2p3/2) obtained on the Fe-2%Mn-0.8%Cr alloy annealed at a DP of -29 °C are shown in Fig. 5.20. The presence of MnCr2O4 along with MnO/Mn3O4 in the entire profile confirms the Mn-Cr interaction. Two components are necessary to obtain a reasonable fit for the Mn 2p3/2 spectrum obtained after 19nm sputtering from the surface (inset figure of Fig. 5.20a). The respective components are, at 641.8 eV and 640.6 eV, the former one belongs to MnO/Mn3O4 and the later to Mn-Cr mixed oxides. In the entire profile, the Cr peak position (Fig. 5.20b) is at 576.4 eV confirming the presence of Cr2O3.
Chapter 5 – Results and Discussions: Effect of alloy composition on the selective oxidation

Fig. 5.20. The XPS core-level spectra (at various depths) obtained on the Fe-2Mn-0.8Cr alloy annealed at a DP of -29 °C.

Fig. 5.21. (a) Surface concentration of Fe-Mn-Cr alloys and (b) Surface morphology of Fe-2Mn-0.8Cr alloy annealed at a DP of -29 °C.

The surface quantification of the oxide forming elements of Fe-Mn-Cr alloys annealed at a DP of -29 °C is shown in Fig. 5.21a. The surface concentration of Mn and Cr increases with their bulk concentration in the alloy. The FE-SEM image of Fe-2%Mn-0.8%Cr alloy annealed at a DP of -29 °C (Fig. 5.21b) showing the population density of oxide nuclei on the surface.
5.2.3. Discussions

At all DP, both Fe-Si-Cr alloys form monophase oxides SiO$_2$ and Cr$_2$O$_3$. The detection of metallic Cr after annealing at low DP may be attributed to kinetic factors in the sense that surface oxygen is consumed basically by oxidation of Si. One may also argue that the partial pressure of oxygen at low DP is at the very border for oxidation of Cr, thus causing the incomplete oxidation. But earlier investigation on Fe-0.8%Cr alloy annealed at this DP shows clearly the complete oxidation of Cr [SS07] and proves that the above argument is false.

Annealing of Fe-1%Si-0.8%Cr alloy at a DP of -40 °C, the surface shows maximum external oxidation of Si and Cr. Further increase of DP to -29 °C in this alloy notably decreases the external oxidation of Cr. Increasing the DP increases the oxygen partial pressure, so the permeability of oxygen into the alloy increases thus decreases the external oxidation or promoting internal oxidation. In contrast to the above case, annealing of Fe-2%Si-0.8%Cr alloy at a DP of -29 °C shows the higher concentration of Cr on the surface i.e. external oxides. Most notably, partial oxidation of Si and Cr was observed at the sub-surface region. This profound difference in the oxidation kinetics is due to the higher Si concentration in this alloy. More specifically, Si decreases the surface oxygen concentration, thus promoting more external oxidation of Cr. This case is similar to the occurrence of quasi-sudden oxidation on the surface of high strength steels due to a decrease of surface oxygen potential by boron [DZBM01]. Furthermore, the oxygen competition between Si and Cr in Fe-2%Si-0.8%Cr alloy ends up with partial oxidation of these elements in the near-surface region. It is interesting to note the effect of Si on Cr oxidation even though there is no sign of Si-Cr interaction in this case.

In the Fe-Mn-Cr alloy, annealing at increased DP (i.e. -40 and -29 °C) not only forms their binary oxides, but also the ternary MnCr$_2$O$_4$ oxides. The interactions between Mn and Cr oxides are well in agreement with earlier studies [DZBM01, WCC07] and follow the route of solid-state reactions given below.
MnO + Cr₂O₃ = MnCr₂O₄
(or)
½ Mn + Cr + O₂ = ½ MnCr₂O₄  \hspace{1cm} (5.8)

Despite of the Mn-Cr strong interaction, the concentration of Cr on the surface is less in Fe-Mn-Cr alloys when compared with Fe-Si-Cr alloys. Obviously, the Mn oxide formation is dominating considerably in this case. However, throughout the analyzed depth (till 19nm), the formation of MnCr₂O₄ was found along with Mn oxides. Increasing the Mn concentration to 2% in the bulk does not significantly influence on the oxidation mode of Cr.

5.2.4. Conclusions

1. Annealing at the lower DP of -80 °C, only binary oxides were observed in all cases and increasing the DP to -40 °C generally leads to more pronounced surface oxidation.

2. In Fe-1%Si-0.8%Cr alloy, high DP (-29 °C) annealing showed the transition from external selective oxidation of Cr to internal. Increasing the bulk Si content in this alloy i.e. Fe-2%Si-0.8%Cr alloy, is suppressing the surface oxygen potential which results in an increase of external oxidation of Cr. The oxygen competition between the alloying elements implies the partial oxidation of Si and Cr in the sub-surface region.

3. At the DP of -40 and -29 °C, the Fe-Mn-Cr alloys show the chemical interaction by forming MnCr₂O₄ along with their binary oxides (MnO/Mn₃O₄ and Cr₂O₃). In spite of Mn-Cr interaction, doubling the Mn concentration does not induce any change in the oxidation mode of Cr.
5.3. Annealing studies of industrial steels

This section explains the influence of dew point (-79, -29 and 0 °C) on the surface chemistry of industrial steel grades after recrystallization annealing prior to hot-dip galvanizing. Standard grade interstitial free steels (namely IF-1, IF-2) and experimental grade TS1000 (tensile strength 1000 MPa) steel are annealed in the liquid zinc spin coater. For the surface analyses (XPS and FE-SEM), the annealed steel specimens are transferred by UHV transfer vessel in order to avoid contaminations by air.

5.3.1. IF-1 steel

The XPS core-level spectra of Al 2p3/2, Cr 2p3/2, Si 2p3/2, Mn 2p3/2, P 2p and S 2p obtained on the surface of IF-1 steel specimen annealed at the dew points (DP) of -79, -29 and 0 °C are shown in Fig. 5.22. At very low DP -79 °C, the calculated partial pressure of oxygen is \(1.43 \times 10^{-28}\) bar and high enough to oxidize Al, Si and Mn and at the limit for oxidation of Cr \((6.9 \times 10^{-28}\) bar) [HSC97]. The Al peak signal is detectable only at a DP of -79 °C indicating that at higher dew points the transition from external to internal oxidation takes place. This tendency was observed by looking at the Al 2p3/2 spectra (Fig. 5.22a), with its peak position at 75.4 eV corresponding to Al2O3 [BC01]. The external oxidation of Cr (Fig. 5.22b) started at a DP of -29 °C and its peak position at 577 eV is assigned to Cr2O3 [SS07, MSSB95]. The weak Cr 2p3/2 spectrum at the higher DP of 0 °C is due to the external/internal oxidation transition. The Si 2p3/2 spectra (Fig. 5.22c) at binding energy of 102.4 eV confirm the presence of MnSiO3/Mn2SiO4 [SS07, VSL03]. The Si oxidizes externally at the DP of -79 and -29 °C, but the weak signal of Si at a DP of 0 °C suggests a change in the oxidation mechanism from external to internal. For the DP’s -79 and -29 °C, the Mn 2p3/2 spectra (corner figure in Fig. 5.22d) at binding energy of 642.1 eV supports the formation of MnSiO3/Mn2SiO4, as a classical example for chemisorption induced co-segregation of Mn and Si [SS07, BS93]. This is also verifying the results from the model alloy experiments. The Mn 2p3/2 spectrum obtained at a DP of 0 °C is fitted with two components, the higher binding energy component at 643.3 eV is assigned to Mn3(PO4)2 whereas the rest of the peak envelope is MnSiO3/Mn2SiO4 with a binding energy of 642 eV [BC01]. Segregation of P starts at high DP of 0 °C and additionally confirms the formation
of Mn-P oxides by observing the P 2p spectrum (Fig. 5.22e) at 134.2 eV. The segregation of S is also found in all cases and its binding energy at 162.7 eV (Fig. 5.22f) is attributed to MnS [MSSB95].

Fig. 5.22. The XPS core-level spectra of Al 2p\textsubscript{3/2}, Cr 2p\textsubscript{3/2}, Si 2p\textsubscript{3/2}, Mn 2p\textsubscript{3/2}, P 2p and S 2p obtained on the surface of IF-1 steel annealed at different dew points.
Fig. 5.23 shows the FE-SEM image of the IF-1 steel annealed at different dew points, showing oxides of different size and morphology within the grain and at the grain boundaries. The ‘cubic morphology’ TiN was found on the surface of IF-1 steel annealed at a DP of -79 °C (Fig. 5.23a) and is well confirmed by EDX (Fig. 5.23b). It can be noticed that at DP = -29 °C, very tiny oxides are formed (Fig. 5.23c) and most often aligned in the cold rolling direction. Secondly tiny oxides are preferably formed on the grain boundaries as this act like short circuits for their diffusion to the surface. A very strong ‘surface facetting’ is exhibited during annealing at a DP of 0 °C, by a strong oxygen adsorption on the surface (Fig. 5.23d). The edges of these faces are preferential sites for nucleation of oxides.

(a) DP -79 °C  
(b) DP -79 °C (EDX for TiN)

(c) DP -29 °C  
(d) DP 0 °C

Fig. 5.23. Surface morphology of IF-1 steel annealed at different dew points and EDX spectrum (Fig. 5.23b) of TiN formed on the surface at a DP of -79 °C.
5.3.2. IF-2 steel

Fig. 5.24. The XPS core-level spectra of Al 2p$_{3/2}$, Cr 2p$_{3/2}$, Si 2p$_{3/2}$, Mn 2p$_{3/2}$, P 2p, and B 1s obtained on the surface of IF-2 steel annealed at different dew points.

In comparison with IF-1, the IF-2 steel has a higher amount of Si, Mn and Cr in addition to 1ppm of B. The XPS core-level spectra of Al 2p$_{3/2}$, Cr 2p$_{3/2}$, Si 2p$_{3/2}$, Mn 2p$_{3/2}$, P 2p and B 1s obtained on the surface of IF-2 steel specimen annealed at different dew points (DP) are shown in Fig. 5.24. At the lower DP of -79 °C, external selective oxidation of Al, Si and
Mn occurs and, as expected, no Cr was found on the surface. The Al 2p$_{3/2}$ spectrum (Fig. 5.24a) detected at 75.5 eV is attributed to Al$_2$O$_3$. For the DP’s -29 and 0 °C, the Cr 2p$_{3/2}$ spectra (Fig. 5.24b) obtained at 577 eV corresponds to Cr$_2$O$_3$. As the IF-2 steel has twice the amount of Si compared to the IF-1 steel, excess SiO$_2$ (Si 2p$_{3/2}$ spectra (Fig. 5.24c) at binding energy of 103.2 eV [MSSB95]) was found on the surface in addition to MnSiO$_3$/Mn$_2$SiO$_4$. The formation of Mn-Si mixed oxide is confirmed by the position of the Mn peak at 642.3 eV (corner figure in Fig. 5.24d). In order to show the presence of manganese phosphate at DP = 0 °C (Fig. 5.24d), two components are necessary to obtain a reasonable fit in the Mn 2p$_{3/2}$ spectrum, their corresponding binding energies are as follows; 643.1 eV and 642 eV, respectively. The former one belongs to Mn$_3$(PO$_4$)$_2$ and the latter to the Mn-Si mixed oxides. Additionally, the P 2p spectrum (Fig. 5.24e) for the specimen annealed at a DP of 0 °C confirms the presence of Mn-P mixed oxides. Small amounts of boron are also present on the specimen surface annealed at a DP of 0 °C, identified by the weak B 1s signal at 192.5 eV (Fig. 5.24f), which refers to B as B$_2$O$_3$ [MSSB95].

Fig. 5.25 shows the FE-SEM image of the IF-2 steel annealed at different dew points, coarse islands of oxides are formed inside the grains as well as on the grain boundaries (Fig. 5.25a) reflecting their prominent role as easy diffusion paths. Similar to the IF-1 steel, TiN particles are detected on the surface (Fig. 5.25b). At high DP of 0 °C, the Mn$_3$(PO$_4$)$_2$ is found on the grain boundaries (Fig. 5.25c) and confirmed by EDX analyses (Fig. 5.25d).
Chapter 5 – Results and Discussions: Annealing studies of industrial steels

Fig. 5.25. Surface morphology of the IF-2 steel annealed at different dew points and EDX spectrum (Fig. 5.25d) of Mn₃(PO₄)₂ formed on the surface at DP 0 °C.

5.3.3. TS1000 steel

In comparison with both IF steels, the experimental grade TS1000 steel has the highest amount of Mn, Si, Cr and V. The XPS core-level spectra of Mn 2p₃/₂, Cr 2p₃/₂ and V 2p₃/₂ obtained on the surface of TS1000 specimen annealed at the dew points (DP) of -29 and 0 °C are shown in Fig. 5.26.
As expected, the co-segregation of Mn and Si leads to the formation of MnSiO$_3$/Mn$_2$SiO$_4$ at both DP, well in agreement with the Mn-Si interaction found on the quarternary model alloy and the IF steels. In addition to this, MnO was also observed on the surface (Fig. 5.26a), because the Mn/Si ratio (in wt.%) is > 4 due to the high amount of bulk Mn concentration. The external oxidation of Cr (Fig. 5.26b) takes place at a DP of -29 °C, but at high DP of 0 °C, only a weak signal of Cr was detected due to its internal oxidation tendency, as observed also for the model alloy and the IF-steel grades. Selective oxidation of V occurs at DP = -29 °C, and can be seen clearly in V 2p$_{3/2}$ core-level spectra, shown in Fig. 5.26c. The used annealing condition exceeds the equilibrium partial pressure of oxygen for the formation of V$_2$O$_3$ ($1.24 \times 10^{-30}$ bar) [HSC97]. The V signal was not detected anymore after annealing at high DP of 0 °C (inset figure of Fig. 5.26c), most probably due to its internal oxidation.
Fig. 5.27. The XPS core-level spectra of B 1s and P 2p obtained on the TS1000 steel annealed at the DP of -29 and 0 °C.

Only at DP = -29 °C, segregation of B (as B$_2$O$_3$) was detected (Fig. 5.27a) by a weak signal with XPS measurements. Segregation of P occurs at DP 0 °C (Fig. 5.27b) by forming Mn$_3$(PO$_4$)$_2$. In general, at DP -29 °C, the surface is mainly covered with Si, Mn and Cr oxides and most probably the internal oxidation of these elements at high DP 0 °C favours the segregation of P to form manganese phosphate.

Fig. 5.28. Surface morphology of the TS1000 steel annealed at the DP of -29 and 0 °C.
Chapter 5 – Results and Discussions: Annealing studies of industrial steels

5.3.4. Discussions

At a DP of -79 °C, the inward oxygen permeability is low and external oxidation of Al, Mn and Si occurs. By increasing the DP from -79 to -29 °C, the permeability of oxygen is higher and oxygen diffuses deeper into the alloy which favours internal oxidation of Al on all the steel grades (IF-1, IF-2 and TS1000) studied here. At DP = -29 °C, the partial pressure of oxygen (~9.05×10^{-23} bar) exceeds the equilibrium partial pressure for oxidation of Cr and hence Cr₂O₃ is formed on the surface. In all the steels, the chemisorption induced co-segregation of Mn and Si leads to the formation of MnSiO₃/Mn₂SiO₄ at all dew points, well in agreement with the Mn-Si interaction observed on model alloys [SS07]. Increase of DP to 0 °C shows the internal oxidation effect on Cr and Si i.e. the transition from external
to internal oxidation. The segregation of P starts at DP = 0 °C in all steels investigated here, showing a strong interaction with Mn, thereby the oxidation of Si and Cr is shifted from external to internal at this high dew point. This might be open the way for the strong Mn-P interaction to form Mn$_3$(PO$_4$)$_2$. Thermodynamically, the formation of manganese phosphate is favourable by the following reactions,

$$\frac{6}{5} \text{MnO} + \frac{4}{5} \text{P} + \text{O}_2 = \frac{2}{5} \text{Mn}_3(\text{PO}_4)_2$$ \hspace{1cm} (5.9)

$$\frac{3}{4} \text{Mn} + \frac{1}{2} \text{P} + \text{O}_2 = \frac{1}{4} \text{Mn}_3(\text{PO}_4)_2$$ \hspace{1cm} (5.10)

The partial pressure of oxygen for the above two reactions are $5.24 \times 10^{-27}$ and $4.43 \times 10^{-28}$ bar, respectively [HSC97]. The high dew point 0 °C ($p(\text{O}_2) \sim 1.89 \times 10^{-20}$ bar) exceeds the partial pressure of oxygen for the formation of Mn$_3$(PO$_4$)$_2$. Moreover, the phosphorus diffusion coefficient in ferrite at ~820 °C is high [$D(\text{P}) = 5.9 \times 10^{-8}$ cm$^2$/s] and might also be causing the co-segregation with Mn and subsequent oxidation, despite of strong Mn-Si interaction. Segregation of B may cause quasi-sudden oxidation at the surface i.e. decrease of surface oxygen potential, leading to an external oxidation of other elements [FP05]. This could be the reason for having small amounts of external oxidation of Si and Cr on the surface of IF-2 annealed at DP = 0 °C. In addition to the minor role of 1ppm boron in the IF-2 steel, slightly higher amount of alloying elements than present in the IF-1 steel grades makes the noteworthy difference as a consequence of external oxidation of Si and Cr at high DP of 0 °C. On the surface of TS1000 steel, V$_2$O$_3$ was observed only at a DP of -29 °C as this steel has a high amount of vanadium. The boron content in this steel is 2 ppm which leads to the formation of B$_2$O$_3$ on the surface at this dew point. At high dew point of 0 °C, the formation of manganese phosphate was more favoured as observed on both IF steels.
5.3.5. Conclusions

1. By increasing the dew point from -79 to -29 °C, internal oxidation of Al was observed on the surface of the industrial steel grades (standard IF-1, IF-2 and experimental TS1000 steel) investigated here. On the surface of both IF steels, significant Mn-Si interaction was found at DP = -29 °C, and despite of low B concentration in the IF-2 steel, B₂O₃ was also detected on the surface. Increasing the DP to 0 °C leads to the formation of less-selective oxides at the surface and also induces the internal oxidation of Cr. The occurrence of P selective oxidation at high DP leads to the formation of Mn-phosphate preferentially at the grain boundaries.

2. The tensile strength 1000 MPa steel (with higher amount of Mn and Si contents) annealed at a DP of -29 °C leads to an increase in the Mn-Si oxide density at the surface. Apart from this, formation of Cr₂O₃, V₂O₃ and weakly segregated non-metallic element B (as B₂O₃) are found on the surface. Increasing the dew point in the annealing atmosphere (i.e. to DP 0 °C) profoundly alters the surface chemistry by the formation of Mn₅(PO₄)₂ and also internal oxidation of Cr.
5.4. Effect of dwelling time on the surface coverage of oxides in IF steels and quaternary model alloys

What happens to the surface coverage by oxides if dwelling time (1 min) in the standard annealing cycle be increased? Two things may happen: either the oxides formed during standard annealing grow further (i.e. growing bigger in size) or new nuclei are formed instead. This section is basically to understand the influence of dwelling time on the nucleation of oxides during recrystallization annealing of IF steels (IF-1, IF-2) and quaternary model alloy.

5.4.1. Interstitial free (IF) steels

Fig. 5.30. Surface morphology of the IF-1 steel annealed at a low DP of -79 °C with different dwelling time.
Fig. 5.30 shows the surface morphology of IF-1 steel annealed at a low DP of -79 °C with different dwelling time 1, 5 and 10 minutes, respectively. Increasing the dwelling time in the annealing cycle increases the population density of oxides. This can be clearly seen on the specimen annealed for 10min (Fig. 5.30c). However, one can also notice in Fig. 5.30b that apart from the more oxide nucleation increase of dwelling time increases the size of oxides as well.

Fig. 5.31. The XPS core-level spectra obtained on the IF-1 steel annealed at a low DP of -79 °C with different dwelling time.

It is also important to notice that increase of dwelling time does not change the surface chemistry. This can be clearly seen in the obtained XPS spectra shown in Fig. 5.31. Oxides of Al, Si and Mn were confirmed by identifying the XPS spectra peak positions (as explained in detail in section 5.3) and moreover, there was no sign of Cr even on the surface annealed for 10 min dwelling time. At this low DP, the surface oxygen content is
rather low and leads to growth of tiny aluminium oxide particles along with manganese silicates.

Similar to IF-1 steel, in the case of IF-2 steel also increased surface coverage of oxides was observed with increase of dwelling time and is shown in Fig. 5.32. There is no change in surface chemistry was observed with increase of dwelling time. The external oxidation of aluminium is the most dominating at a low DP of -79 °C and this seems to be increasing with increase of dwelling time, as shown in the Al 2p$_{3/2}$ XPS spectra (Fig. 5.33a). The XPS depth profile obtained on the IF-2 steel specimen annealed for 10 min is shown in Fig. 5.33b, implies an oxide thickness of around 20-30 nm much higher than for the specimen annealed for 1 min (6-9 nm).

Fig. 5.32. Surface morphology of the IF-2 steel annealed at a low DP of -79 °C with different dwelling time.
Chapter 5 – Results and Discussions: Effect of dwelling time on the surface coverage

5.4.2. Quarternary model alloy

The quarternary Fe-2Mn-2Si-0.8Cr alloy specimens were annealed at 820 °C in N₂-5%H₂ gas atmospheres of DP = -40 °C with dwelling time of 1 and 5 min, respectively. The obtained surface morphology is shown in Fig. 5.34. By increasing the dwelling time to 5 min, the flower-like crystalline shaped oxides are increasing in size. Moreover, the surface coverage of oxides seems to be much higher after longer annealing time.

![Fig. 5.34. Surface morphology of the quarternary model alloy annealed at a DP of -40 °C with different dwelling time.](image-url)

(a) 1min  
(b) 5min
Chapter 5 – Results and Discussions: Effect of dwelling time on the surface coverage

Fig. 5.35. GI-XRD spectra obtained on the quarternary model alloy annealed at a DP of -40 °C with different dwelling time.

The GI-XRD spectra (with an angle of 1°) obtained on the quarternary model alloy annealed with different dwelling time 1 and 5 min is shown in Fig. 5.35. The peak positions confirm the presence of Mn-Si mixed oxides together with Cr-oxides. As observed on the IF steels, there is no change in surface chemistry.

Fig. 5.36. Depth profile obtained on the quarternary model alloy annealed at a DP of -40 °C with 5 min dwelling time.

Fig. 5.36 shows the XPS depth profile obtained on the quarternary alloy specimen annealed for 5 min. As shown in the plot, the concentrations of Mn-Si oxides were high on the surface and decreasing linearly with increasing sputter depth whereas Cr oxide concentration is increasing with depth showing the trend for internal oxidation of Cr. After 100 nm of sputtering, the concentrations of Si and Mn (as Mn-Si mixed oxides) are increasing again, which is similar to Cr. This effect leads to the question of two stage
oxidation front in the quarternary model alloy. ToF-SIMS mapping of Si was carried out on the specimens annealed for 1 min and 5 min, the results are shown in Fig. 5.37 and 5.38.

![ToF-SIMS Si mapping](image)

(a) On the surface  
(b) After 100 nm sputtering  
(c) After 200 nm sputtering  
(d) After 500 nm sputtering

Fig. 5.37. ToF-SIMS Si mapping on the quarternary model alloy annealed at a DP of -40 °C with 1 min dwelling time.

The maps show clearly that Si (as Mn-Si mixed oxides) is enriched on the surface. After 100 nm sputtering, the intensity is at minimum, increasing again after 200 nm. The Si-rich zone can be seen even after 500nm sputtering.

Fig. 5.38 shows the obtained Si mapping of the quarternary alloy specimen annealed for 5 min. As expected, an enrichment of Si is observed on the surface. The mapping after 100 nm sputtering (Fig. 5.38b) indicates the decrease of Si-intensity, but in comparison with the specimen annealed for 1min (Fig. 5.37b) its concentration is high. Further sputtering (i.e. sputter depth of 200 nm and 500 nm) confirms an increase of the Si
concentration in depth. However, the extended oxidation front (i.e. two stages of oxidation front) is more pronounced on the specimen annealed for 5 min.

![Fig. 5.38. ToF-SIMS Si-mapping on the quaternary model alloy annealed at a DP of -40 °C with 5 min dwelling time.](image)

**5.4.3. Discussions**

It is very clear that annealing of IF steels at a very low DP of -79 °C lead to external oxidation of Al, Mn and Si. Surface coverage of these oxides increases with increase of dwelling time in two ways. Firstly further growth of initially formed oxides (i.e. growing bigger in their size) and secondly, opens the way for new nucleation of oxides as increased dwelling time in the annealing process has sufficient time for the alloying elements to diffuse/segregate to the surface.
Annealing of quaternary Fe-2Mn-2Si-0.8Cr alloy at DP = -40 °C leads to external oxidation of Mn and Si, and also shows the trend for internal oxidation of Cr. At a DP of -40 °C, the outward solute permeability of Mn and Si is higher than the inward oxygen permeability, hence external oxidation occurs. Outward Cr permeability is the border to satisfy the internal oxidation condition. With increase of dwelling time in the standard annealing cycle, an extended oxidation front i.e. pronounced external/internal oxidation of Mn, Si and Cr is observed. Based on the Wagner’s theory, the oxide zone thickness can be written as follows [Kof88],

\[ \xi \propto \sqrt{t} \]  

(5.11)

where \( t \) is the dwelling time of the annealing cycle.

It can be clearly evidenced by the above equation that increasing the dwelling time \( t \), the oxidation zone thickness (\( \xi \)) increases. This may be the reason for having external/internal oxidation of Mn, Si and Cr in the quaternary model alloy annealed at DP -40 °C with increased dwelling time. Secondly further oxidation of alloying elements can occur during cooling as the solubility product of the oxides decreases with temperature. The schematics of an external/internal oxidation of Mn and Si, the tendency of internal oxidation of Cr is as shown in the Fig. 39. Apart from the thermodynamical calculations, in this case, the oxidation kinetics is very complex as one has to consider the oxygen competition between the alloying elements and also the formation of ternary or mixed oxides (i.e. co-segregation of Mn and Si).

![Fig. 5.39. Schematics of external/internal oxidation of Mn, Si and Cr in quaternary model alloy annealed at a DP of -40 °C.](image-url)
5.4.4. Conclusions

1. On the IF steels, increasing the dwelling time in the standard annealing cycle gradually increases the surface coverage of oxides.

2. In general, annealing of the quaternary Fe-2Mn-2Si-0.8Cr alloy at a DP of -40 °C with increased dwelling time (5 min) shows an extended oxidation front. More specifically, the higher concentration of Mn-Si oxides was observed on the surface. With increase of depth, their concentration decreases linearly and after a certain depth (i.e. 100 nm) again the oxide rich zone was observed. In the case of Cr, the tendency of internal oxidation was observed in the sub-surface region as this annealing condition is the border for internal oxidation of Cr.
5.5. Wetting studies: Hot-dip galvanizing simulation of model alloys and industrial steel grades

The surface chemistry and zinc wettability are correlated by simulating the hot-dip galvanizing process at laboratory scale with an ‘in-house’ built liquid zinc spin coater. In the earlier sections, the surface chemistry of model alloys and industrial steel grades after annealing at different dew points are discussed. The present section focusing on the results of zinc wetting experiments conducted on the quarternary model alloy and the steel grades (IF-1, IF-2 and TS1000). The zinc wettability is determined by using sessile drop contact angle measurement. The influences of annealing conditions (i.e. dew point, dwelling time) on the wetting kinetics are discussed in this section.

5.5.1. Quarternary model alloy

![Initial 3sec](a) DP -29 °C

![Initial 3sec](b) DP 0 °C

Fig. 5.40. The zinc drop placed on the quarternary model alloy annealed at the dew point of -29 and 0 °C.

Fig. 5.40 shows the Zn wettability (initial and after 3sec) on the surface of the quarternary model alloy annealed at the DP of -29 and 0 °C, respectively. It can be clearly observed that the initial contact angle is in the wetting regime, i.e. $\theta_{\text{initial}} < 90^\circ$. The measured contact
angle of liquid zinc (after 3 seconds) for the dew point -29 °C and 0 °C are 42.6° and 39.4°, respectively.

5.5.2. IF-1 steel

Fig. 5.41 shows the wetting behaviour of zinc on the surface of IF-1 steel annealed at the dew points of -79, -29 and 0 °C, respectively. The wettability at an initial stage and after 3 secs is shown in Fig. 5.41a and 5.41b, respectively. The wetting behaviour clearly visualizes that the contact angle is less than 90° (i.e. wetting regime) at all dew points.

(a) Initial

(b) After 3 seconds

Fig. 5.41. The zinc drop placed on the surface of IF-1 steel annealed at the dew points of -79, -29 and 0 °C.

The Zn wettability tests are performed on the IF-1 steel specimens annealed at a dew point of -79 °C with different dwelling time 5 min and 10 min. It is important to note that the dwelling time is 1 min for the standard annealing cycle. Although the specimens are in wetting regime (i.e. initial contact angle is <90°) in all cases a slight increase of contact angle with increase of dwelling time is observed (Fig. 5.42).
Chapter 5 – Results and Discussions: HDG simulation of model alloys and steels

Fig. 5.42. Initial Zn wettability on the surface of IF-1 steel annealed at dew point -79 °C with different dwelling time.

5.5.2. IF-2 steel

Fig. 5.43. The zinc drop placed on the surface of IF-2 steel annealed at the dew points of -79, -29 and 0 °C.

The zinc wettability of the IF-2 steel surface annealed at different dew points is shown in Fig. 5.43. The contact angle measurement from the initial stage (Fig. 5.43a) and the wetting after 3 secs (Fig. 5.43b) reveals that specimen annealed at all DP’s used here are in wetting regime.
5.5.3. TS1000 steel

Fig. 5.44. The zinc drop placed on the TS1000 steel annealed at the dew point of -29 and 0 °C.

The wettability of Zn on the surface of TS1000 steel annealed at the DP of -29 and 0 °C is shown in Fig. 5.44. Non-wetting behaviour was observed on the surface of this steel annealed at DP = -29 °C (Fig. 5.44a), i.e. $\theta_{\text{initial}} > 90^\circ$. In this case, the measured contact angle of zinc drop after 3 seconds is 133.2°. On the other hand, it is seen from Fig. 5.44b that the TS1000 steel annealed at a DP of 0 °C shows good wetting and the measured contact angle of Zn after 3 seconds is 77.5°.

5.5.4. Discussions

In the quarternary model alloy annealed at the DP of -29 and 0 °C, in spite of the presence of Mn-Si mixed oxides and Cr$_2$O$_3$ on the surface, the initial contact angle exhibited in the wetting regime, i.e. $\theta_{\text{initial}} < 90^\circ$ (Fig. 5.40). It is interesting to note that spreading of liquid zinc is comparatively faster on the surface annealed at DP = 0 °C than on the surface annealed at DP = -29 °C. Obviously, increasing the DP from -29 to 0 °C decreases the external oxidation of Mn and Si, also causing the internal oxidation of Cr, thus improving the wetting.
The wettability tests have shown that both IF steel annealed at the dew points of -79, -29 and 0 °C are in the wetting regime i.e. the initial contact angle is < 90°. As shown in Fig. 5.41 and Fig. 5.43, the wetting kinetics is comparatively high on the surface annealed at very low DP of -79 °C. Due to lower surface oxygen content at this dew point, the surface is mainly covered with tiny aluminium oxide particles along with manganese silicates and, moreover, the XPS sputter profile (figure not shown here) reveals the oxide thickness of ~ 6-9 nm. These thin oxides are reduced very quickly by the small amount of Al in the Zn drop or even bridged by the zinc coating [FP05, KMM07]. The measured contact angle of the zinc drop on the surface of both IF-1 and IF-2 steel annealed at different dew points are shown in Fig. 5.45, indicating that the contact angle is decreasing significantly with time for all DP. It is interesting to note that at DP = -79 °C the measured contact angle on IF-2 is slightly smaller than on IF-1 steel as the concentration of Al₂O₃ is much higher (Fig. 5.46) on the surface of IF-1. Although the surface annealed at DP = -29 °C, is in the wetting regime, the kinetics of wetting is quite slow. Obviously, the kinetics of the aluminothermic reaction and the formation of the inhibition layer in this case is strongly hindered by the Mn-Si oxides. The surface annealed at a high DP of 0 °C shows good reactive wetting as in this case the transition to internal oxidation of Si and Cr is observed due to the higher oxygen permeability and, therefore, the amount of Mn-Si oxide on the surface is decreased. It must be noted that manganese phosphate is the dominating compound on the surface of IF steels annealed at a DP of 0 °C. Even though small amounts of B₂O₃ are present on the surface of IF-2 steel at this DP, no wetting problems are observed.

Fig. 5.45. The measured contact angles of Zn drop on the surface of IF steels annealed at different dew points.
Fig. 5.46. Surface concentration of both IF steels annealed at a DP of -79 °C.

Basically, increasing the dwelling time (1 min) in the standard annealing cycle does not change the surface chemistry but increases the surface coverages by oxides. It has been reported in the section 5.4. On the surface of IF-1 steel annealed at a DP of -79 °C with increased dwelling time (5 min and 10 min), the Zn wettability observation (Fig. 5.41) shows that the slight increase in the contact angle, which is due to increase of surface coverage by oxides as the effect of dwelling time. However the initial contact angle is < 90° i.e. the specimens are in the wetting regime. Obviously, not only the surface chemistry can influence the wetting speed but also the surface coverage of oxides. Increase of dwelling time leads to the same effect on the IF-2 steel also.

On the surface of TS1000 steel annealed at a DP of -79 °C, the Zn wettability experiments reveals non-wetting behaviour. Due to higher amounts of alloying elements (Mn, Si, Cr and V) in this steel, the maximum external selective oxidation occurred at a DP of -29 °C. Apart from the Mn-Si mixed oxides and Cr$_2$O$_3$ (which are usually found on the model alloys), the formed V$_2$O$_3$, MnO and a small amount of B$_2$O$_3$ might be hampering the zinc wetting comparison to model alloys and IF steels. At high DP = 0 °C, the formation of Mn-phosphate takes place while the oxidation of other elements moves to internal (e.g. for V$_2$O$_3$ in this case) or atleast decreases the contributions of other alloying element oxides (Mn-Si mixed oxides, Cr$_2$O$_3$) on the surface. It seems that the formed Mn-phosphate is likely to be responsible for enhancing the surface wettability from non-wetting to wetting regime.
5.5.5. Conclusions

1. The sessile drop contact angle measurements clearly visualize the kinetics of reactive wettability of zinc as a function of dew point. The visualization of wetting behaviour reveals that the surface chemistry, oxide distribution (i.e. surface coverage) and its thickness are the factors affecting the wetting speed.

2. For both the DP -29 and 0 °C, the formation of MnSiO$_3$/Mn$_2$SiO$_4$ and Cr$_2$O$_3$ takes place on the surface of the quaternary model alloy and, nevertheless, the alloy exhibits a measured contact angle of < 90°. Annealing at the higher dew point (DP = 0 °C), is beneficial in significantly decreasing the external oxidation, thus enhancing the kinetics of reactive wetting.

3. On the surface of IF steels, the wettability reaction is more favourable at a low DP of -79 °C as the formed oxides are very thin (mainly Al$_2$O$_3$). At DP = -29 °C, low wetting speed is due to delay in kinetics of an aluminothermia reduction of significant thicker oxides (Mn-Si mixed oxides and Cr$_2$O$_3$). Internal oxidation of alloying elements at very high DP 0 °C, enhance the zinc wetting on the surface. Increasing the dwelling time in the annealing cycle gradually increases the surface coverage of oxides. Despite of slight increase in the contact angle, all annealing conditions stand in the wetting regime in zinc wettability tests.

4. The TS1000 steel (with higher amount of Mn and Si contents) annealed at a DP of -29 °C leads to an increase in the Mn-Si oxide density at the surface. Apart from this, the formation of Cr$_2$O$_3$, V$_2$O$_3$ and weakly segregated non-metallic element B, hampers the zinc wetting on the surface. Increasing the dew point in the annealing atmosphere (i.e. DP = 0 °C) profoundly alters the surface chemistry, segregation of P and formation of Mn$_3$(PO$_4$)$_2$ as well as internal oxidation of Cr, thus facilitating zinc wettability.
Chapter 6 – Summary

High strength steels for automotive industry undergo recrystallization annealing before hot-dip galvanizing. Segregation and selective surface oxidation of the alloying elements (Al, Si, Mn, Cr etc.) makes the steel surface unsuitable for subsequent galvanizing as the wettability of these oxides with zinc is poor. In order to understand the surface phenomena during annealing of multicomponent alloy (i.e. steel), systematic approach on model alloys is needed.

In this work, influence of annealing conditions and the effect of alloying elements on the selective oxidation in model alloys and some industrial steel grades were investigated. The model alloys of binary (Fe-2Si, Fe-2Mn and Fe-0.8Cr), ternary (Fe-2Mn-2Si, Fe-2Mn-0.8Cr and Fe-2Si-0.8Cr) and quaternary (Fe-2Mn-2Si-0.8Cr) systems were studied. In addition to that, ternary alloys of Fe-1Si-0.8Cr and Fe-1Mn-0.8Cr were also examined to understand the influence of alloying element composition on the selective oxidation. The compositions of the alloying elements in model alloys (all in wt.%) have been chosen in accordance to composition of newly developed high strength steels. In the case of steels, standard grade interstitial free (IF) steels namely IF-1, IF-2 and experimental grade tensile strength 1000 MPa steel (TS1000) were investigated. All specimens were annealed at 820 °C in N₂-5%H₂ gas atmospheres with the wide range of dew points (DP) (i.e. -80 to 0 °C). The surface chemistry after annealing and its wettability with liquid zinc have been correlated as a function of dew points by simulating the hot-dip galvanizing process at laboratory scale.

On investigated model alloys, increasing the dew point from -80 to -40 °C generally leads to more pronounced surface oxidation. In the binary alloys only binary oxides are formed i.e. SiO₂ (Fe-2Si) and Cr₂O₃ (Fe-0.8Cr) independent on the dew point. In the case of Fe-Mn alloy, MnO is formed at low DP and additional Mn₃O₄ at higher DP. By presence of Si and Mn in the system (Fe-2Mn-2Si alloy), the formation of MnSiO₃/Mn₂SiO₄ takes place on the surface at both dew points. When Mn and Cr are present in the alloy (i.e. Fe-2Mn-0.8Cr), they show also chemical interaction by forming MnCr₂O₄ at DP = -40 °C, apart from their own oxides Mn₃O₄ and Cr₂O₃. In Fe-2Si-0.8Cr alloy, Si and Cr are forming their binary oxides i.e. SiO₂ and Cr₂O₃ at every DP without any interaction between them. In the
quaternary system (Mn with Si and Cr), Mn interacts only with Si by forming manganese silicates, although Mn showed its interaction with Cr in the ternary system. Obviously, Mn has higher affinity to Si than to Cr. Annealing at the higher dew points (-40, -29 and 0 °C) i.e. increasing the oxygen partial pressure in the annealing atmosphere showing the trend for internal oxidation of Cr. At DP = 0 °C, the surface concentration of Si and Mn oxides decreases significantly i.e. transition to internal oxidation.

The ternary alloys of Fe-Si-Cr and Fe-Mn-Cr were focussed in order to understand the effect of Si and Mn bulk concentration on the selective oxidation of Cr. In Fe-1Si-0.8Cr alloy, high DP (-29 °C) annealing showed the transition from external selective oxidation of Cr to internal. Although there is no sign of Si-Cr interaction, increasing the bulk Si content in this alloy i.e. Fe-2Si-0.8Cr alloy, suppressing the surface oxygen potential which results the increases of external oxidation of Cr. The oxygen competition between the alloying elements implies the partial oxidation of Si and Cr in the sub-surface region. At the DP of -40 and -29 °C, the Fe-Mn-Cr alloys show the chemical interaction by forming MnCr$_2$O$_4$ along with their binary oxides (MnO/Mn$_3$O$_4$ and Cr$_2$O$_3$). In spite of Mn-Cr interaction, doubling the Mn concentration does not induce any change in the oxidation mode of Cr.

The influence of the annealing condition (i.e. dew point of the annealing atmosphere) on the surface chemistry of industrial steel grades was investigated. By increasing the dew point from -79 to -29 °C, internal oxidation of Al was observed on the surface of the industrial steel grades (IF-1, IF-2 and TS1000 steel) studied here. On the surface of both IF steels, significant Mn-Si interaction was found at a DP of -29 °C, and despite of low B concentration in the IF-2 steel, B$_2$O$_3$ was also detected on the surface. Increasing the DP to 0 °C leads to the formation of less-selective oxides at the surface and also induces the internal oxidation of Cr. The occurrence of P selective oxidation at high DP leads to the formation of Mn-phosphate preferentially at the grain boundaries. The tensile strength 1000 MPa steel (with higher amount of Mn and Si contents) annealed at a DP of -29 °C, leads to an increase in the Mn-Si oxide density at the surface. Apart from this, formation of Cr$_2$O$_3$, V$_2$O$_3$ and weakly segregated non-metallic element B (as B$_2$O$_3$) are found on the surface. Increasing the dew point in the annealing atmosphere (i.e. DP = 0 °C) profoundly alters the surface chemistry by the formation of Mn$_3$(PO$_4$)$_2$ and also internal oxidation of Cr.
Effects of dwelling time of the annealing process on the surface coverage of oxides have been studied. On the IF steels, increasing the dwelling time in the standard annealing cycle gradually increases the surface coverage of oxides. In general, annealing of the quarternary Fe-2Mn-2Si-0.8Cr alloy at a DP of -40 °C, with increased dwelling time (5 min) shows an extended oxidation front. More specifically, the higher concentration of Mn-Si oxides was observed on the surface. With increase of depth, their concentration decreases linearly and after a certain depth (i.e. 100 nm) again the oxide rich zone was observed. In the case of Cr, the tendency of internal oxidation was observed in the sub-surface region as this annealing condition is the border for internal oxidation of Cr.

Laboratory scale hot-dip galvanizing simulation of model alloy and industrial steel grades, establish the relationship between surface chemistry and zinc wettability (sessile drop contact angle measurement). The sessile drop contact angle measurements clearly visualize the kinetics of reactive wettability of zinc as a function of dew point. The visualization of wetting behaviour reveals that the surface chemistry, oxide distribution (i.e. surface coverage) and its thickness are the factors affecting the wetting speed. For both the DP of -29 and 0 °C, the formation of MnSiO₃/Mn₂SiO₄ and Cr₂O₃ takes place on the surface of the quarternary model alloy and, nevertheless, the alloy exhibits a measured contact angle of < 90°. Annealing at high dew point (DP = 0 °C), is beneficial in significantly decreasing the external oxidation, thus enhancing the kinetics of reactive wetting. On the surface of IF steels, the wettability reaction is more favourable at a low DP of -79 °C, as the formed oxides are very thin (mainly Al₂O₃). At DP = -29 °C, low wetting speed is due to delay in kinetics of an aluminothermia reduction of significant thicker oxides (Mn-Si mixed oxides and Cr₂O₃). Internal oxidation of alloying elements at very high DP 0 °C, enhance the zinc wetting on the surface. Increasing the dwelling time in the annealing cycle gradually increases the surface coverage of oxides. Despite of slight increase in the contact angle, all annealing conditions stand in the wetting regime in zinc wettability tests. Annealing of TS1000 steel at a DP of -29 °C leads to an increase in the Mn-Si oxide density at the surface. In addition to this, the formation of Cr₂O₃, V₂O₃ and B₂O₃, hampers the zinc wetting on the surface. Annealing at high DP of 0 °C, favours the transition from external to internal oxidation of Cr, V etc. thereby initiating the segregation of P at this dew point. Occurrence of internal oxidation of alloying elements and also the formation of Mn₃(PO₄)₂ at a DP of 0 °C facilitating the zinc wettability. Basically, simulating hot-dip galvanizing
condition to the experimental grade tensile strength 1000 MPa steel (TS1000) and the quarternary model alloy Fe-2Mn-2Si-0.8Cr opens the way to pinpoint the wettability problems in newly developing high strength steels.
References


References


[Gra89] H. J. Grabke, Surface and grain boundary segregation on and in iron and steels, ISIJ Int. 29 No. 7 (1989) 529.


References


[You05] T. Young, An essay on the cohesion of fluids, Phil. Trans R. Soc. London 95 (1805) 65.

Appendix A: Comparison of in-situ (High temperature reactor) and ex-situ (Infrared furnace) annealing

A.1. Interstitial Free steel
A.1.1. In-situ and ex-situ annealing of IF-1 steel at low dew point -79 °C
This section compares the results of in-situ and ex-situ annealing experiments at very low dew point -79 °C. An infrared furnace was employed for ex-situ annealing and a high temperature reactor HTR (connected with UHV cluster) for in-situ annealing. Annealing conditions (gas atmosphere, flow rate and dew points) are maintained same in both cases. The specimens annealed in IR furnace were transported into XPS for surface analysis through air. In the case of specimen annealed in the reactor chamber was directly transported into XPS (see Fig. 4.11 in chapter 4) without exposing to air (in-situ surface analysis).

Fig. A.1. The XPS analysis of IF-1 steel surfaces: In-situ and Ex-situ annealing at a low dew point of -79 °C
After annealing at a DP of -79 °C, the surface condition of the specimens were first characterized by XPS and then followed to SEM. The peak positions of Si 2p\(_{3/2}\), Al 2p\(_{3/2}\), Mn 2p\(_{3/2}\) and S 2p are shown in the Fig. A.1. External selective oxidation of Al and Mn are observed in both in-situ as well as in ex-situ annealing experiments. They are present at the surface and their concentrations decreases in depth. In ex-situ annealed specimen, peak position of Si 2p 102.6 eV and corresponds to Al\(_2\)SiO\(_5\) [MSSB95]. The weak Si 2p signal is detected on in-situ annealed specimen and is corresponding to SiO\(_2\) [MSSB95]. The Al 2p peak positions 74.8 eV (in ex-situ) and 75.5 eV (in in-situ) indicates the presence of Al\(_2\)SiO\(_5\) and Al\(_2\)O\(_3\) respectively [MSSB95, HISM94]. Segregation of S is observed in both experiments, but in ex-situ annealing, S 2p peak is observed only after 2 nm of sputtering. The absence of S 2p signal at the surface may be due to ‘screening effect’ of other element and also due to the ex-situ transport. The energy position of S 2p peak is at 162.5 eV and corresponds to MnS [MSSB95]. The presence of both MnS and Mn-oxides are confirmed by identifying Mn 2p peak position.

Fig. A.2. The XPS depth profiles of IF-1 steel after annealing at a low dew point of -79 °C.

It is quite obvious that C contamination will be much lower on in-situ annealed specimen. XPS depth profile of both cases is shown in the Fig. A.2. It is clearly showing that oxides are present only until 8nm in depth.
Appendix A: In-situ Vs. Ex-situ annealing

Fig. A.3. The FE-SEM image of IF-1 steel after annealing at a low dew point of -79 °C.

The surface morphology of both in-situ annealed and ex-situ annealed IF-1 steel surfaces are shown in the Fig. A.3. As shown in the above figures, the oxides are not formed like continuous layer; instead they formed as an island of different sizes (50 to 200 nm) and shapes. Also the distribution of the oxides differs on both surfaces.

A.1.2. Surface chemistry of IF-1 steel by in-situ annealing at different dew points

This part describes the results of in-situ annealed IF-1 steel specimens (in HTR) at different dew points -79, -59 and -39 °C, respectively. The XPS peak positions of Al 2p3/2, Si 2p3/2, Cr 2p3/2 and S 2p (for various dew points) are shown in the Fig. A.4. By increasing the dew point increase of water vapour content in the annealing gas atmosphere (N2 with 5% H2) and, therefore, increasing the partial pressure of oxygen on the sample surface. This shifts the oxidation mechanism from external to internal. At higher dew point -39 °C, the partial pressure of oxygen is $8.39 \times 10^{-24}$ bar. This is sufficient amount for oxidising Al, Si, Mn and Cr. The oxygen permeability D_oOs into the steel is increased compared to lower dew points. This means that the oxidation of elements with very high affinity to oxygen takes place already below the surface, as soon as the amount of oxygen is enough for exceeding the solubility product of the oxide in question. This is obtained for Al, which is not detected on the surface any more at higher DP (Fig. A.4) indicates the internal oxidation of Al. At the dew points of -79 and -59 °C, clearly the external oxidation of Al is observed on the surface. By increasing the dew point, a slight increase in the Si 2p3/2 signal is observed.
The energy position of Si 2p$_{3/2}$ peak is at 103.3 eV which corresponds to SiO$_2$. The external oxidation of Cr is detected only at higher dew point -39 °C. It is interesting to note that Cr is not detected even at -59 °C, though the partial pressure of oxygen is high enough to oxidise Cr. It may be due to the more external oxidation of Al observed at this dew point. Also the quantity of Al is more in this case. At -39 °C, the surface is covered mostly with Cr and Mn oxides. At this dew point the presence of MnSiO$_3$ is also confirmed by observing the Mn 2p peak position about 642 eV [BS93, CPS93]. Sulphur is extremely surface active and strongly segregates to the surface due to its higher segregation enthalpy of -190 kJ/mol [Gra89] and the S 2p peak at 162.5 eV corresponds to MnS [MSSB95].

Fig. A.4. The XPS analysis of IF-1 steel surfaces after in-situ annealing at the different dew points of -79 °C, -59 °C and -39 °C.
Appendix A: In-situ Vs. Ex-situ annealing

![XPS depth profiles of IF-1 steel after in-situ annealing at different dew points](image1)

Fig. A.5. The XPS depth profiles of IF-1 steel after in-situ annealing at different dew points.

The depth profile for the dew points -59 °C and -39 °C are shown in the Fig. A.5. Presence of Mn and Cr are observed until 30 nm in depth. In this case no Al was observed due to internal oxidation. It is important to note that quantity of metallic Fe is more at higher dew point. Fig. A.6 shows the FE-SEM image of the IF-1 steel surfaces annealed at the DP of -59 °C and -39 °C, visualizing that the oxides of different size and morphology are formed inside the grain and at the grain boundaries. At a dew point of -39 °C, the oxides are decorating the grain boundaries, as the grain boundaries are easy paths for diffusion. These oxides are much smaller in size compared to the one observed at lower dew point of -79 °C.

![FE-SEM image of IF-1 steel after in-situ annealing](image2)

Fig. A.6. The FE-SEM image of IF-1 steel after in-situ annealing.
A.2. Binary model alloy

A.2.1. In-situ and ex-situ annealing of Fe-2Si binary alloy at dew point -40 °C

Fig. A.7. The XPS analysis of binary Fe-2Si model alloys: In-situ and ex-situ annealing at dew point of -40 °C.

The XPS core-level spectra of Fe-2Si binary alloy (Fe 2p₃/₂, Si 2p₃/₂) annealed at DP -40 °C in in-situ and ex-situ annealing methods are shown in Fig. A.7. In both cases, the Si 2p₃/₂ spectra clearly indicates the presence of SiO₂. Though the annealing atmosphere is reducible for iron, the iron oxides are identified (Fig. A.7b) on the surface of Fe-2Si alloy annealed in IR furnace. These Fe-oxides might be formed during cooling as the stability of it increases with decreasing temperature. Moreover, an ex-situ transport of specimen to XPS analysis could also cause Fe-oxidation. In-situ XPS analysis of the specimen reveals the presence of metallic Fe on the surface as shown in Fig. A.7a. The surface morphology of Fe-2Si alloy annealed at DP -40 °C (in both cases) clearly visualize the islands of SiO₂.
A.3. Conclusions

In-situ and ex-situ annealing of IF-1 steel annealed at 820 °C in N\textsubscript{2}-5%H\textsubscript{2} protective atmosphere with dew point of -79 °C leads to external oxidation of Al, Mn and Si. The less amount of Si on in-situ annealing reveals that the partial pressure of oxygen might be slightly less than in the ex-situ annealing experiments. This means that achieving local equilibrium on the surface is more favourable in the in-situ reactor chamber. The selective oxidation mechanisms are strongly influenced by the dew point of the annealing atmosphere. Increasing the dew point shifts the oxidation mode from external to internal. This phenomenon is observed for Al at dew point of -39 °C. At higher dew point the steel surface is covered with Mn and Cr oxides as well as MnSiO\textsubscript{3}, MnS is also observed on the surface. On Fe-2Si binary alloy, in both cases the surface chemistry is same. In-situ annealing is highly useful in such way to avoid the contamination due to air and it helps to prevent the re-oxidation to some extent.
Appendix B: Study of interfacial layer formed during hot-dip galvanizing simulation of IF-1 steel by liquid zinc spin coater

This part is basically to show the accessibility of Fe-Al interfacial layer formed during hot-dip galvanizing of IF-1 steel by liquid zinc spin coater. For the interface study, both recrystallization and galvanizing temperature cycles were carried out in the main chamber of the spin coater. The IF-1 steel specimen was annealed to 820 °C in N\textsubscript{2}-5%H\textsubscript{2} gas atmospheres with a DP of -79 °C. After 1 min dwelling, the specimen was allowed to cool down to 470 °C and then, directly the galvanizing process was conducted, i.e. 0.2wt.% Al bearing Zn droplet was placed on the surface. After 2 to 3 seconds, the spin coater starts with a rotation speed of 2500 rpm. During the fast spinning process nearly all residual liquid zinc is driven off from the surface and opens the way to access the interface (without further physical/chemical treatments).

In general, it is agreed that the inhibition of Fe-Zn reactions during hot-dip galvanizing is due to the formation of a thin Fe-Al rich layer at the Fe-Zn interface. A small amount of Al (0.2 wt.%) in the liquid Zn bath inhibits the Fe/Zn reactions, offers a superior way to galvanize steel sheets and produce a Zn coating on the surface. Fig. B.1a shows that the morphology of the interface is composed primarily of Fe-Al phase and also covered with ‘pillar-like’ Zn overlays. The EDX spectra 1 (Fig. B.1b) confirms the presence of colonies of Fe-Al rich interfacial layer and the spectra 2 in Fig. B.1c identifies large Zn pillars on the Fe-Al phase. Although the above results shows the possibility of accessing the interface by using spin coating technique, on the other hand completely get-rid off the residual Zn seems to be not in practical. Komatsu et al. proposed that the formation of Fe\textsubscript{2}Al\textsubscript{5} interface layer and Fe-Zn intermetallic are simultaneous in the early stage of galvanizing reactions [KAU01]. This may also be the reason for having some Zn/Fe-Zn intermetallic crystals on the top of the Fe-Al phase after spinning process.
Appendix B: Study of Fe-Al interfacial layer formed during HDG simulation

Fig. B.1. (a) FE-SEM image of Fe-Al interface layer obtained on the IF-1 steel annealed and galvanized at DP of -79 °C by liquid zinc spin coater, (b) and (c) EDX analysis of Fe-Al phase and Zn pillars, respectively.

In order to demonstrate the steel/Zn interface clearly, obtained interfacial layer was micromachined (to the depth of ~1-2µm) by using 30kV Ga⁺ ions in ORSAY Canion 31M Plus Focussed Ion Beam (FIB) unit. Fig. B.2 shows the morphology of micromachined interface captured with different (In-lens and MPSE) detectors in FE-SEM. The area which is machined by FIB represents the substrate (i.e. steel) and the surrounding (of the machined area) shows the formed Fe-Al interfacial layer which is partially covered with Zn pillar-like crystals. The randomly distributed Zn outbursts are mainly due of fast spinning process. An EDX-mapping was also performed in the micromachined area to clearly distinguish the substrate (steel)/Fe-Al interfacial layer/Zn outbursts (Fig. B.3).
Appendix B: Study of Fe-Al interfacial layer formed during HDG simulation

Fig. B.2. FE-SEM image of micro-machined steel/Zn interface of IF-1 steel by FIB.

Fig. B.3. EDX-mapping of micro-machined steel/Zn interface of IF-1 steel.
The contrast of the micro-machined area is much higher in Fe-mapping (Fig. B.3b), indicating the steel substrate. EDX mapping showed in Fig. B.3b (for Fe) and 3c (for Al), clearly confirms the formed Fe-Al interfacial layer and the remaining areas were occupied with Zn overlays. Faderl et al. reported that the interfacial layer is composed of Fe-Al-Zn ternary compounds [FMS95]. There are also reports that the interfacial layer is a mixture of Fe$_2$Al$_5$ and FeAl$_3$ [MMM97, BL99]. However, the obtained EDX-mapping confirms that the interfacial layer consists of only the Fe-Al phase. This preliminary investigation is insufficient to say something about the exact chemistry/stoichiometry of it.

As a conclusion, an attempt to access the steel/zinc interface (i.e. Fe-Al inhibition layer) of standard IF steel by using an ‘in-house’ built liquid zinc spin coater was successful and the initial study confirms that the interfacial layer mainly consists of a Fe$_x$Al$_y$ phase. It has to be pointed out that the spin coating technique generates the scope of accessibility of Fe-Al inhibition layer without any laborious steps such as chemical or mechanical treatment. Preliminary study shows that interfacial layer is composed of Fe-Al phase.
Acknowledgements

The work described in this thesis was carried out at the Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf in connection with ‘International Max-Planck Research School for Surface and Interface Engineering in Advanced Materials’ (IMPRS-SurMat) curriculum.

First of all, I would like to thank my boss at MPIE Priv.-Doz. Dr. Michael Spiegel who introduced me into the world of ‘High Temperature Reactions’. I am very much grateful for his understanding and support with enlightening words which guided me to do things to the best of my abilities. His scientific advises and numerous discussions during the last three years significantly contributed to the progress of my work. Without his support, this thesis would have not been accomplished.

I am very much thankful to my supervisor at RUB Prof. Dr. Andreas D. Wieck for time-to-time discussions about the project progress which helped me towards the best solutions in this work. I express my sincere gratitude for his willingness to help and the encouragement to access his focused ion beam equipment for this project.

I wish to thank Prof. Dr. Martin Stratmann and Prof. Dr. Gunther Eggeler (Spokesmen-SurMat) for providing an opportunity to pursue my doctoral study in this Max-Planck Research School. I also gratefully acknowledge the financial support from IMPRS-SurMat and Salzgitter Mannesmann Forschung GmbH for this project. Special thanks to Dr. Angela Büttner (Administrative Director-SurMat) for her great help in all the official issues. Thanks also for organizing the basic level German course at our institute; it was really helpful for me and more enjoyable too. Many thanks to Dr. Christoph Somsen, who assisted a lot during the registration process at Ruhr-Universität Bochum. I had a pleasure to interact more closely with Dr. Thomas Koll and Mr. Michael Pohl (SZMF) during the project meetings. Thanks for their constructive discussions and support throughout the project. Thanks also to Dr. Thorsten Reier and Prof. Dr. Matthias Niemeyer (SZMF) who have been actively interested in this work.

I would like to thank all my present and former colleagues, Postdocs and all other Ph.D students for contributing to such an inspiring and pleasant atmosphere. I am deeply thanking Dr. Birgit Pöter who motivated me a lot throughout my Ph.D program and also for her great help in all the possible way. I am most grateful for her help in finding the apartment; especially she signed ‘der Mietvertrag’ for me as the house-owner didn’t believe on foreign students. I really impressed by her friendship.
I am obliged to Dr. Ivana Parezanovic and Dr. Björn Sauerhammer for their guidance during the early stages of this project. Special thanks to Ivana for her fruitful discussions about this project and also for her great friendly nature. I also thank to Dr. Tatiana Liapina and Dr. Andrey Lyapin for the numerous informative discussions we had. I should say that I had loads of fun and great laughs in their friendly company. I would like to thank Dr. Amar Yadav, Dr. Henrik Astemann, Dr. Boris Hüning, Mr. Sergiy Borodin, Mrs. Cezarina Cela Mardare and Mr. Markus Schmitt for their kindness and interesting conversations. Thanks to Mrs. Else Müller-Lorentz for the operating instructions about electron microscope. Many thanks go to Mrs. Cornelia Arckel (Dept. Secretary) for her all sorts of help during these years. Great thanks to Mr. Olaf Eichler (System Admin.) for ready to give me a hand with all my computer problems. Thanks to Mr. Dirk Vogel and Mr. Eberhard Heinen for their hints during the initial build-up period of the project. I would also like to acknowledge the help of IT department (Mr. Ron McCormack), Electronics workshop (Mr. Bernd Schönberger), and Mechanical workshop (Mr. Ralf Selbach), Materials technology (Mr. Michael Kulse). I am most grateful to Mr. Rolf Wernhardt (RUB) for his kind help with the focused ion beam equipment.

I wish to express my thanks to Dr. R. Kanagadurai (RSGC, Thanjavur) for his unwavering moral support throughout my study. Heart thanks to my friend Pandiyan (PNU, S.Korea) and Dr. Booma for their great support during the most difficult timings. Special thanks to all my friends in India for their constant encouragement. Few lines are not really enough to express my feelings about their importance in my life.

I am deeply thanking to all my Indian friends in Germany for their support especially at the difficult stages. Great thanks to Mini (RUB) for her cheerfulness, I acknowledge her for helping me in the thesis submission formalities. Special thanks to Lakshman for his great help in all the way, it had been a pleasure to sharing a home with him. I would like to thank Aparna (RUB) for her support in the difficult timings. I will never forget the fantastic times spent together with them.

Finally I wish to conclude by thanking my parents and my sister’s family for their love, endless support and unshakeable confidence on me. The word ‘Amma-Appa’ (Mom-Dad) itself is the greatest source of inspiration to me and I strongly believe that their blessings carried me to finish this work.

Just in case, if I miss anyone, this may apply: Thank you to whom it concerns!
List of publications

Thermodynamic and kinetic aspects on the selective surface oxidation of binary, ternary and quarternary model alloys  
Srinivasan Swaminathan, Michael Spiegel  

Hot-dip galvanizing simulation of interstitial free steel by liquid zinc spin coater: Influence of dew point on surface chemistry and wettability  
Srinivasan Swaminathan, Thomas Koll, Michael Pohl, Andreas D. Wieck, Michael Spiegel  
Steel Res. Int. 79 (2008) No.1

Effect of alloy composition on the selective oxidation of ternary Fe-Si-Cr, Fe-Mn-Cr model alloys  
Srinivasan Swaminathan, Michael Spiegel  
(Orally presented at the 12th European Conference on Applications of Surface and Interface Analysis (ECASIA’07), Brussels-Flagey, Belgium, September 9-14, 2007)

Hot-dip galvanizing simulation of model alloys and industrial steel grades: Correlation between surface chemistry and wettability  
Srinivasan Swaminathan, Thomas Koll, Michael Pohl, Michael Spiegel  
Galvatech proceedings (2007).  
(This paper will be orally presented in Galvatech’07, Osaka, Japan, 18-23 November 2007)

Influence of Si, Mn and Cr on the selective oxidation of model alloys  
Srinivasan Swaminathan, Michael Spiegel  
EUROCORR’06 proceedings (2006).  
(Orally presented at the EUROCORR’06, Maastricht, Netherland, 25-28 September 2006)
Curriculum Vitae

Name: Srinivasan Swaminathan

Date and Place of Birth: 27.07.1979, Tiruvarur (Tamilnadu, India)

Nationality: Indian

Education:

1994 Secondary education, V. S. Boys Higher Secondary School, Tiruvarur

1996 Higher secondary education, V. S. Boys Higher Secondary School, Tiruvarur

1999 B.Sc (Physics), Thiru. Vi. Ka. Govt. Arts. College (affiliated to Bharathidasan University), Tiruvarur

2001 M.Sc (Physics), Rajah Serfoji Govt. College (affiliated to Bharathidasan University), Thanjavur

Thesis title: Analysis of thermoluminescence glow curves of alkali halides

Since 15.06.2004 IMPRS-SurMat Scholar, High Temperature Reactions Group (Head: Priv.-Doz. Dr. Michael Spiegel), Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf

Registered as a Ph.D Student at Fakultät für Physik und Astronomie, Lehrstuhl für Angewandte Festkörperphysik (Prof. Dr. Andreas D. Wieck), Ruhr-Universität, Bochum

Research experience:

2001-04 Project Associate, Dept. of Physics, Indian Institute of Technology Madras

Theme: Transparent conductive oxide (TCO) thin films for space applications