A study of oxides formed on hot-rolled steel strip

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Declaration

I, Xianglong Yu, declare that this thesis, submitted in fulfilment of the requirements for the award of Doctor of Philosophy, in the School of Mechanical, Materials and Mechatronic Engineering, University of Wollongong, Australia, is wholly my own work unless otherwise referenced or acknowledged. The document has not been submitted for qualifications at any other university or academic institution.

Xianglong Yu

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List of publications during the PhD course


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Abstract

Metallic oxide (scale) inevitably grows on the surface of hot-rolled strips due to thermal oxidation at elevated temperature and causes the surface quality of final products to deteriorate. The objective of the present work was to delve into the phase evolution mechanism of oxide scales during cooling and coiling after hot rolling and then propose a facile and controllable magnetite microstructure. The resulting innovative microstructure can then be applied to pickle-free steel with desired tribological properties in downstream metal processing.

A systematic experimental investigation and simulation analysis were conducted to explore the microstructural formation and properties of the oxide scale. The experimental techniques covered are high temperature microscope (HTM) for in situ observation of initial oxidation, hot rolling and accelerated cooling (HR-AC) for simulating hot rolling process, and a combination of the Gleeble 3500 and UMT2-tribometer in pin-on-disc configuration for tribological properties for subsequent applications. Some diffractometers and microscopies were also applied to identify and characterise the oxide scale. These ranged from a field emission guns-scanning electron microscope (FEG-SEM) with electron backscattered diffraction (EBSD), an atomic force microscope (AFM), a triple ion beam cutter (TIC), and a focused ion beam (FIB). Furthermore, the proposed enthalpy-based finite element method (FEM) technique and diffusion simulation based on the enabling mechanism were used to predict the precipitation of magnetite during continuous cooling.
The results obtained from in situ observations of oxidation by high temperature microscope indicated that grain boundary diffusion was the dominant transport mechanism which controlled the initial oxidation of microalloyed steel in a temperature range of 550 to 850 °C. The surface spallation failure of oxide scale occurred at the centre of grains of the microalloyed steel substrate during the oxidation initiation. The oxide scale grown on the coarse-grain steel substrate can cause adhesive properties to deteriorate when cooling to the room temperature. This grain refinement effect is more sensitive to the oxide scale formed at 550 °C than that formed at 600 °C. The tight oxide scale was proposed to elucidate effects of grain refinement in the steel substrate on high desired magnetite content and the integrity of the oxide scale.

The formation mechanism of the oxide scale was presented based on the results of HR-AC and the simulation analysis. The experimental results proved that the increase in the cooling rates from 10 to 100 °C/s leads to significant cracks of the oxide scale. The uniform surface morphologies and good adhesion properties of oxide scale can be achieved at a cooling rate of 20 °C/s and a thickness reduction below 12 %. Thermodynamic analysis provided compelling evidence that the nucleation rate of magnetite was higher than ferrite due to the high free energy of magnetite and the low thermal stability of the oxygen-rich wustite below the eutectoid temperature. An enthalpy-based algorithmic technique was presented based on some results from experimental and diffusion simulations. This approach enables an accurate prediction of magnetite precipitation.

Grain reconstruction of magnetite and hematite in tertiary oxide scale has been made via EBSD-EDS techniques. Accurate and quantitative data about the morphology and
crystallography of oxide scale were obtained at various thickness reductions (TRs) and cooling rates (CRs) after HR-AC experiments. The oxide scale consisting of a thin hematite outer layer and an inner duplex magnetite layer, develops a high proportion of low-angle and low-$\Sigma$ CSL boundaries, magnetite for $60^\circ/\langle 111\rangle$ ($\Sigma 3$), and hematite for $57.42^\circ/\langle 1\bar{2}10\rangle$ ($\Sigma 13b$) and $84.78^\circ/\langle 0\bar{1}10\rangle$ ($\Sigma 19c$). Grain refinement of magnetite (2–3 $\mu$m) at a TR of 28% can suppress the penetration of hematite into the oxide scale. Magnetite develops a strong $\theta$ fibre parallel to the oxide growth, which includes $\{100\}<001>$ and $\{001\}<110>$ texture components, resulting from the minimisation of surface energy for $\{100\}$ planes of magnetite. In contrast, $\{0001\}<10\bar{1}0>$ component dominates in hematite as the favored basal plane slip. The Hematite growth on $\theta$ fibre magnetite is $54.76^\circ$ titled from the $<001>$ crystal direction of magnetite.

To assess the technical feasibility of applying the proposed oxide scale, oxidation tests on the Gleeble 3500 and tribological tests in pin-on-disc configuration indicated that the free particles in the globular structure could act as a lubricant and help resist wear, whereas the compact particles in the lamellar microstructure may favour adhesive wear. The fine lamellar structure with a smooth contact interface resulted in a decrease in the coefficient of friction, whereas the coarse lamellar structure led to an increase.

The combination of various in situ techniques presented here provides the framework for any future investigation into the oxidation of other steel grades. The development of accelerated cooling has proved to be very effective and has made it possible to control the cooling rate by means of water flow. It is strongly recommended that these approaches are extended to study the phase transformation of other steel compositions.
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# Nomenclature

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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Accelerated Cooling</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>AGC</td>
<td>Automatic Gain Control</td>
</tr>
<tr>
<td>BC</td>
<td>Band Contrast</td>
</tr>
<tr>
<td>bcc</td>
<td>Body-Centred Cubic</td>
</tr>
<tr>
<td>BEI</td>
<td>Backscattered Electron Image</td>
</tr>
<tr>
<td>BSE</td>
<td>Back Scatter Electron</td>
</tr>
<tr>
<td>CCD</td>
<td>Charge-Coupled Device</td>
</tr>
<tr>
<td>CCP</td>
<td>Cubic Close-Packed</td>
</tr>
<tr>
<td>CCT</td>
<td>Continuous Cooling Transformation</td>
</tr>
<tr>
<td>CR</td>
<td>Cooling Rate</td>
</tr>
<tr>
<td>CSL</td>
<td>Coincident Site Lattice</td>
</tr>
<tr>
<td>CT</td>
<td>Coiling Temperature</td>
</tr>
<tr>
<td>DMC</td>
<td>Digital Micro-Circuit</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron Backscattered Diffraction</td>
</tr>
<tr>
<td>EBSPs</td>
<td>Electron backscatter diffraction patterns</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectroscopy</td>
</tr>
<tr>
<td>EM</td>
<td>Electron Microscope</td>
</tr>
<tr>
<td>ESEM</td>
<td>Environmental Scanning Electron Microscope</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-Centred Cubic</td>
</tr>
<tr>
<td>FEG</td>
<td>Field Emission Gun</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<td>--------------</td>
<td>-------------------------------------------</td>
</tr>
<tr>
<td>FEM</td>
<td>Finite Element Method</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused Ion Beam</td>
</tr>
<tr>
<td>FT</td>
<td>Finishing Temperature</td>
</tr>
<tr>
<td>HAGBs</td>
<td>High-Angle Grain Boundaries</td>
</tr>
<tr>
<td>HTXRD</td>
<td>High-Temperature X-Ray Diffraction</td>
</tr>
<tr>
<td>hcp</td>
<td>Hexagonal Close-Packed</td>
</tr>
<tr>
<td>HR</td>
<td>Hot Rolling</td>
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<tr>
<td>HSS</td>
<td>High Speed Steel</td>
</tr>
<tr>
<td>HTM</td>
<td>High Temperature Microscope</td>
</tr>
<tr>
<td>ICDD</td>
<td>International Centre of Diffraction Data</td>
</tr>
<tr>
<td>IF</td>
<td>Interstitial Free (steel)</td>
</tr>
<tr>
<td>IPF</td>
<td>Inverse Pole Figure</td>
</tr>
<tr>
<td>IQ</td>
<td>Image Quality</td>
</tr>
<tr>
<td>LAGBs</td>
<td>Low-Angle Grain Boundaries</td>
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<tr>
<td>LSCM</td>
<td>Laser Scanning Confocal Microscope</td>
</tr>
<tr>
<td>LV</td>
<td>Low Vacuum</td>
</tr>
<tr>
<td>ND</td>
<td>Normal Direction</td>
</tr>
<tr>
<td>ODF</td>
<td>Orientation Distribution Function</td>
</tr>
<tr>
<td>OM</td>
<td>Optical Microscope</td>
</tr>
<tr>
<td>PBR</td>
<td>Pilling-Bedworth ratio</td>
</tr>
<tr>
<td>PDF</td>
<td>Powder Diffraction File</td>
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<tr>
<td>PID</td>
<td>Proportional-Integral-Derivative</td>
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<tr>
<td>RD</td>
<td>Rolling Direction</td>
</tr>
<tr>
<td>ROT</td>
<td>Run-Out Table (cooling)</td>
</tr>
<tr>
<td>SE</td>
<td>Surface Energy</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
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<tr>
<td>--------------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>SEI</td>
<td>Secondary Electron Image</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
</tr>
<tr>
<td>TD</td>
<td>Traverse Direction</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermal Gravimetric Analysis</td>
</tr>
<tr>
<td>TKD</td>
<td>Transmission Kikuchi Diffraction</td>
</tr>
<tr>
<td>TIC</td>
<td>Triple Ion beam Cutter</td>
</tr>
<tr>
<td>TR</td>
<td>Thickness Reduction</td>
</tr>
<tr>
<td>UMT</td>
<td>Universal Mechanical Tester</td>
</tr>
<tr>
<td>WD</td>
<td>Working Distance</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
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</table>

### Algebraic symbols

- **$A$**: constant parameter
- **$c$**: heat capacity
- **$c_{in}$**: specific heat after phase change
- **$c_p$**: specific heat
- **$c_w$**: specific heat before phase change
- **$D$**: density of oxide scale; diffusion coefficient
- **$D_{eff}$**: effective-diffusivity coefficient of the species
- **$D_{GB}$**: diffusion coefficient along the grain boundaries
- **$D_L$**: diffusion coefficient in the lattice
- **$d$**: density of metal substrate; average grain diameter
- **$\text{div}(\ )$**: divergence operator
\( f \) volume fraction of interfaces

\( G \) Gibbs free energy or function

\( \Delta G \) change in Gibbs free energy

\( \Delta G' \) change of reaction in Gibbs free energy

\( \Delta G_v \) standard change of reaction in Gibbs free energy

\( \text{grade}(\ ) \) gradient operator

\( H \) enthalpy

\( H(T) \) volumetric enthalpy

\( h_{w1} \) heat convection coefficient

\( h_{w2} \) film coefficient

\( i \) specific enthalpy

\( K \) constant parameter; stiffness matrix

\( k_0 \) rate constant

\( k_1 \) linear rate constant

\( k_p \) parabolic rate constant

\( L \) latent heat

\( M \) molecular weight

\( m \) atomic weight of metal

\( n \) atoms number of metal in oxide scale; outward unit normal to boundary surface

\( N_v \) steady-state nucleation rate of the individual phases

\( q : \) heat flux

\( \dot{q} \) heat transfer rate

\( \bar{q}(x) \) normal heat flux

\( Q \) activation energy
\( Q(x) \) source of internal heat generation.

\( \tilde{P} \) equivalent nodal load matrix

\( P_i \) Planck constant

\( R \) gas constant

\( R_a \) arithmetic average of surface roughness

\( R_{ku} \) kurtosis

\( R_{max} \) maximum height of unevenness

\( R_q \) root mean squared of surface roughness

\( R_{sk} \) skewness

\( Re \) Reynolds number

\( \Delta t \) interval of time step

\( T \) temperature

\( \tilde{\tau} \) nodal temperature vector and

\( T_{ext} \) temperature of the cooling water

\( T_v \) temperature of phase change

\( T_{w1} \) temperature of the vapour film

\( T_{w2} \) temperature of the cooling water

\( t \) time; thickness

\( w \) width of the impingement zone

\( x \) oxide scale thickness; distance to the exit; coordinate

\( y \) thickness coordinates of oxide scale

\( z \) width coordinates of oxide scale

\( \alpha(T) \) nonlinear function of temperature
\( \gamma \) heat convection coefficient; surface energy
\( \delta \) grain-boundary width
\( \varepsilon \) emissivity of the material; elastic strain energy
\( \theta \) difference of the temperature
\( \kappa, \kappa(T), \lambda_w \) thermal conductivity
\( \mu \) relaxation parameter; frictional coefficient
\( \mu_f \) dynamic viscosity
\( \rho, \Delta \rho \) density and its difference
\( \sigma, k \) Stefan-Boltzmann constant
\( \tau(H) \) temperature function of enthalpy relationship
\( v \) velocity of the jet; rolling speed

Additional superscripts

\( fb \) steady film
\( s \) saturated vapour
\( (i) \) last iteration
Chapter 1

Introduction

1.1 Background

The oxidation of metal surfaces being processed at elevated temperature is inevitable and it causes the surface quality of final products to deteriorate [1–3]. The oxide scale formed on low carbon steels generally consists of a typical three-layered microstructure with a thin outer layer of hematite (Fe$_2$O$_3$), an intermediate layer of magnetite (Fe$_3$O$_4$), and an inner layer of wustite (Fe$_{1-x}$O, 1-x=0.84–0.95) adjacent to the steel substrate [4, 5]. This three-layered microstructure remains until a eutectoid point of the Fe-O phase equilibrium diagram [6] is reached if oxygen is available at a temperature of 570 °C [7, 8]. When the temperature drops below 570 °C, the wustite phase becomes unstable and will decompose into eutectoid products of magnetite and ferrite [9–11]. Through this eutectoid transformation, the desired morphology and composition of oxide scale could be obtained by controlling the cooling conditions during subsequent operations and selecting different grades of steels [12]. Several studies [13] have indicated that a multilayered oxide scale is needed to form appreciable amounts of magnetite particles which can then be used as natural lubricant additives to reduce friction and wear during cold steel rolling. This provides a great incentive to develop a novel structural layer of oxide scale to achieve a hot-rolled strip that is free of acid pickling.
Now the dream of the 1980s of pickle-free steel [14, 15] seems to be taking shape on the horizon. Inspired by the self-cleaning surface of a lotus leaf, metal oxide nanoparticles are expected to open up a new idea in developing advanced functional materials with biometric microstructures which enhance the industry of metal forming. Indeed, with the development of new experimental and computational techniques, progress has recently been made to investigate the oxidation of microalloyed steels [16–18] and the eutectoid transformation of oxide scale [19, 20]. The magnetite nanoparticles within the oxide scale formed on commercially produced steel strips could be the product of decomposed wustite and could enhance the adherence properties of oxide scale. Few studies to date have focused on the specific formation of oxide scale on hot-rolled steel strip which can be applied to cold rolling without acid pickling. The facile and controlled microstructures of the desired magnetite and its deformable and tribological properties have not yet been fully explored, which is a significant research gap.

1.2 Objective and methodology

The aim of the present work is to examine the microstructural evolution of oxide scale that form during cooling and coiling after hot rolling, and then to propose a tight magnetite microstructure, which will enhance pickle-free hot-rolled steel strip by selecting of the appropriate process parameters. To characterise the oxide scale, experimental techniques such as high temperature microscope (HTM) for an initial oxidation (< 30 s), Gleeble 3500 for short term oxidation (960 s), a hot rolling mill combined with accelerated cooling (HR-AC) system for simulating hot rolling, and the UMT2-tribometer in pin-on-disc schematics for the tribological properties for subsequent application were covered. Some diffractometers and microscopies such as
electron backscattered diffraction (EBSD), atomic force microscope (AFM) and focused ion beam (FIB) were also used to identify and characterise the oxide scale. Moreover, numerical simulation techniques such as the developed enthalpy-based finite element method (FEM) were also used to predict the precipitation of magnetite during continuous cooling.

1.3 Outline of the thesis

This thesis contains (apart from this introductory chapter (Chapter 1)), literature review (Chapter 2), methodology (Chapter 3), four separate experimental studies and numerical simulations (Chapters 4 to 7), and conclusions (Chapter 8). A schematic diagram of the structure of this thesis is shown in Fig. 1.1. Chapter 2 provides information on the current understanding of the oxidation of steels and summarises the experimental techniques used to investigate oxide scale. Chapter 3 introduces the experimental instruments and analytical methodology used to generate a specific oxide scale and to analyse its physical and mechanical properties. In Chapter 4, the initial oxidation test in HTM is specifically devoted to isothermal mechanism of microalloyed steel, and to characterise the interface between oxide scale and steel substrate using various microscopies. Chapter 5 brings us closer to the industrial site through HR-AC system and EBSD investigation. It attempts to reveal the effects of processing parameters on the oxidation of microalloyed steel, such as the thickness reduction (TR), the cooling rates (CRs), the finishing temperature (FT) and the coiling temperature (CT), to establish the relationship between the microstructure and microtexture of oxide scale and process parameters. In Chapter 6 the relevant numerical simulations are carried out to predict the microstructure of oxide scale. Chapter 7 investigates the tribological
properties of the generated oxide scale to determine the technically and economically feasible conditions required for pickle-free steel on commercial hot-rolled strip. The conclusion and an outlook sketching possible future opportunities are presented in Chapter 8.

Fig. 1.1 A schematic diagram of the thesis outline.
Chapter 2

Literature review

This chapter is a review of the current understanding of the growth of oxide scale in terms of the phase transformation that takes place. These include thermodynamics and kinetics, the development of oxide scale formed on steel alloys at high temperature and continuous cooling, the precipitation of magnetite and the behaviour of oxide scale on hot-coiled steel, and the role that decomposed wustite plays on the tribological properties of oxide scale as they apply for cold rolling. A more extensive effort was also made to summarise the experimental techniques used to investigate oxide scale.

2.1 Thermodynamics and kinetics

2.1.1 Free energy-temperature diagram

The change in Gibbs free energy, $\Delta G$, is the driving energy for metal-oxygen reactions associated with the formation of oxide and also the indicator of where that reaction may go. Oxidation will only occur in the direction that lowers the Gibbs free energy. Graphical data for the standard Gibbs free energy of the formation of oxides versus temperature (Fig. 2.1 [21, 22]) can be used to predict the conditions under which a metal is reduced or a metal oxide is oxidised [23, 24].
Fig. 2.1 Ellingham/Richardson diagram showing the Gibbs free energy of formation for oxides selected as a function of temperature, together with the corresponding equilibrium $P_{O_2}$ and $H_2/H_2O$ and $CO/CO_2$ ratios. The blue and green lines are relevant to equilibrium $P_{O_2}$ at a certain temperature [21, 22].

From the diagram we can estimate the equilibrium values of partial oxygen pressure, as well as the $CO/CO_2$ and $H_2/H_2O$ ratios in contact with metals and their oxides, by
drawing straight lines through the points labelled O, H, and C, respectively, and through the point on the metal/metal oxide line at the temperature of interest, while extrapolating to the scales of CO/CO₂, H₂/H₂O and \(P_{O_2}\) [3, 21]. For instance, at ambient temperature the iron oxide scale verifiably consists of two sub-layers (green circle) with magnetite next to the metal and hematite as a topmost sub-layer in contact with the atmosphere at temperatures below 570 °C, and three sub-layers (blue circle) with wustite next to the metal, then magnetite as an intermediate sub-layer and the topmost sub-layer of hematite at temperatures above 570 °C [2, 25].

### 2.1.2 Mechanism of oxidation

The formation of a multiphase oxide described above is due to iron having divalent and trivalent ions (Fe²⁺ and Fe³⁺). This means the complete oxidation of iron can be divided into three main steps [2], where iron oxidises to the lowest valence ion Fe²⁺ and forms the first sub-layer of wustite (FeO) next to the metal. Then some of Fe²⁺ ions oxidise further to Fe³⁺ and contain both valence iron ions as the intermediate sub-layer of magnetite (Fe₃O₄). Under conditions of sufficient oxygen the outer sub-layer of hematite (Fe₂O₃) only consists of the highest valence iron ion Fe³⁺. Fig. 2.2 [26] shows the simplified scheme for the diffusion-controlled growth of multilayered scales on pure iron above 570 °C. Whereas, at temperatures below 570 °C, the wustite phase is unstable and the oxidation of iron directly results in magnetite [2, 3, 25], as indicated from the iron-oxygen phase diagram in Fig. 2.3 [6].
Fig. 2.2 Schematic illustration of the diffusion-controlled oxidation of pure iron to form a three-layered scale of FeO, Fe₃O₄ and Fe₂O₃ in an oxygen gas environment above 570 °C, while showing the diffusion steps and interfacial reactions [26].

![Schematic illustration of the diffusion-controlled oxidation of pure iron to form a three-layered scale of FeO, Fe₃O₄ and Fe₂O₃ in an oxygen gas environment above 570 °C, while showing the diffusion steps and interfacial reactions.]

Fig. 2.3 The iron-oxygen equilibrium phase diagram [6].
Chapter 2 Literature review

The diffusion-controlled oxidation of pure iron holds for the diffusion of iron cations and/or oxygen anions in the reaction-product oxide scales [2, 25, 26], as shown schematically in Fig. 2.2. The slowest rate at which these ions migrate through the substrate to the outer oxide surface is the rate-limiting step during oxidation in terms of Wagner’s theory [27]. The diffusion of cations and/or oxygen anions generally depends on the crystallographic structure of generated oxides [3]. Wustite is the highly non-stoichiometric iron-deficient phase with a defective NaCl structure detailed in Section 2.2.1. The high content of vacancies [28] in the lattice enables the reactants to be a high mobile (Fig. 2.4 [22, 29]). The composition of magnetite has a much smaller degree of non-stoichiometry than wustite so that at ambient temperature its non-stoichiometry tends towards a small oxygen-excess and the mobility of the reactants in the magnetite lattice is much slower than in wustite [30, 31]. However, the diffusion of the reactants in the hematite lattice is extremely slow (Fig. 2.4), and thus the inward diffusion of oxygen dominates the growth of the oxide scale [32, 33].

![Arrhenius diagram for iron and oxygen self-diffusion][22, 29]

**Fig. 2.4** Arrhenius diagram for iron and oxygen self-diffusion [22, 29]
The growth of oxides is also relevant to the integrity of the oxide scale [34, 35]. The overall reaction rate in the latter stages of oxidation depends on whether the oxide scale remains continuous and protective as it grows, or whether it contains cracks and pores and is relatively nonprotective [36–38]. This situation, in turn, depends on whether the volume of the reaction product is more or less than the volume of metal from which the product forms [39, 40]. The growth misfit between the oxide and steel is given by the Pilling-Bedworth ratio (PBR) [41, 42], \( \frac{M_d}{nM} \), where \( M \) is the molecular weight, \( D \) is the density of oxide scale, \( m \) and \( d \) are the atomic weight and density of metal, respectively, and \( n \) is the number of metal atoms in a molecular formula of scale substance (\( n=3 \) for Fe\(_3\)O\(_4\)) [43]. If PBR>1, a protective oxide scale is predicted to form, whereas when this ratio is less than unity, the oxide scale is formed in tension and tends to be nonprotective. The PBR for iron/wustite is 1.78 [42], so compressive stresses are present in the wustite layer [44, 45], which is the predominant phase in the early stages of isothermal oxidation above 700 °C [25, 26]. Moreover, PBR is usually used to explain the variation of internal stress due to the growth stress which facilitates the loss of adhesion and further affects the morphologies and growth rate of scale, that causes blistering, wedge and crack defects [15, 46]. This situation will be addressed further in Section 2.3.4.

2.1.3. Growth kinetics of oxide scale

During the simplified treatment of the diffusion-controlled oxidation introduced above, the three main equations that express the oxidation rates are (1) the linear, (2) the parabolic, and (3) the logarithmic [2, 28, 43, 47, 48].
For the linear equation [49, 50], the rate of oxidation is constant,

\[
\frac{dx}{dt} = k_1 \text{ and } x = k_1 t
\]  

(2.1)

where \(k_1\) is the linear rate constant, \(x\) is the thickness of oxide scale, and \(t\) is the oxidation time. This linear equation is obeyed during the initial stage of oxidation [51] whenever the rate of oxygen arriving at the surface of the oxide scale is constant because the oxygen diffusion in the thin oxide scale is the rate-limiting step which contributes to a rate controlled by the properties of the gas, including the temperatures and partial pressure of oxygen in the atmosphere [52, 53].

With the parabolic equation [47, 54, 55], the diffusion of ions or cations vacancies through the oxide scale is the rate-limiting step and therefore the oxidation rate is inversely proportional to the thickness of the oxide scale [56, 57]:

\[
\frac{dx}{dt} = k_p x \text{ and } x^2 = 2k_p t
\]  

(2.2)

where \(k_p\) denotes the parabolic rate constant that is expected to obey Arrhenius’s relationship [58, 59]. This equation holds for protective oxide scales that correspond to PBR>1 and is applicable to the oxidation of many metals at elevated temperatures. Despite the rapid initial reactions, the longer term oxidation rate of iron under isothermal conditions is quite steady following the parabolic rate law within the range of 250 to 1200 °C [60, 61]. When oxidation occurs at low temperatures, metals forming a protective oxide scale follow the logarithmic or inverse logarithmic equations below 200 °C [62, 63].
These rate constants mentioned above are expected to obey the Arrhenius equation [58, 59].

\[ k_p = k_0 \cdot e^{-Q/RT} \]  

(2.3)

where \( k_0 \) is a constant, \( Q \) is the activation energy, \( R \) is the universal gas constant (8.314 \( \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \)), and \( T \) is the temperature in Kelvin. In general, the oxidation rate of metals increases with temperature [64, 65]. Other significant effects are possibly exerted by the metal purity [65, 66], the pressure of the system [8, 67], and the type and defects [68] present in the oxide scale. The detailed rate constant equation for the growth of FeO, Fe\(_3\)O\(_4\) and Fe\(_2\)O\(_3\) in air oxidation between 700 and 1000 °C [69, 70] will be discussed in Section 6.2.1 when it appears likely to cause problems.

2.2 Development of oxide scale at high temperature

2.2.1 Iron oxides

Since the iron cations can exist in the two valence states described above, iron oxides can have different crystal structures with different Fe/O ratios. These phases include wustite (Fe\(_{1-x}\)O), magnetite (Fe\(_3\)O\(_4\)) and hematite (\(\alpha\)-Fe\(_2\)O\(_3\)), as listed in Table 2.1 [71, 72].
Table 2.1 Crystallographic data for iron oxides [71, 72].

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Fe/O ratio</th>
<th>Crystallographic system</th>
<th>Space group</th>
<th>Structural type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetite</td>
<td>Fe$_3$O$_4$</td>
<td>0.75</td>
<td>Cubic</td>
<td>Fd$m$-227</td>
<td>Inverse spinel</td>
</tr>
<tr>
<td>Wustite</td>
<td>Fe$_{1-x}$O*</td>
<td>0.93</td>
<td>Cubic</td>
<td>Fm$m$-225</td>
<td>Defect NaCl</td>
</tr>
<tr>
<td>Hematite</td>
<td>α-Fe$_2$O$_3$</td>
<td>0.67</td>
<td>Rhombohedral</td>
<td>R3C-167</td>
<td>Corundum</td>
</tr>
</tbody>
</table>

*Wustite has a rather broad composition where (1-x) ranging from 0.83 to 0.95. (1-x)=0.93 is recommended as an average value.

Wustite has a defective halite structure (NaCl), with anion sites occupied by O$^{2-}$ and most cation sites occupied by divalent Fe$^{2+}$ ions. An alternative description of this structure is that of a cubic close-packed (CCP) array of anions stacked along the [111] direction where planes of anions alternate with planes of cations. Most of the iron is octahedral with a small proportion of Fe$^{3+}$ on the usually vacant tetrahedral sites. These octahedra share edges (Fig. 2.5a [71]) and Fe$^{2+}$ and O$^{2-}$ layers alternate along the [111] direction (Fig. 2.5b [71]). A cation-deficient phase written as Fe$_{1-x}$O (with 1-x ranging from 0.83 to 0.95) exists at 0.1 MPa pressure and temperatures higher than 570 °C [73]. Wustite is a p-type (p=positive carrier) semi-conducting oxide with a high concentration of lattice defects [23, 24]. These high cation vacancies result in a high mobility of cations and electron via metal vacancies and electron holes [74, 75].

Magnetite (Fe$_3$O$_4$) has an inverse spinel structure containing both divalent and trivalent iron ions [76]. The distribution of its cation is written as (Fe$^{3+}$) [Fe$^{3+}$Fe$^{2+}$] O$_4$, where the parentheses denote the tetrahedral sites and the square brackets denote the octahedral sites [77, 78]. In this case the ferric ion Fe$^{3+}$ relinquishes half of the octahedral sites to
the ferrous species Fe$^{2+}$, i.e. with 8 Fe$^{3+}$ ions located in tetrahedral sites plus (8Fe$^{3+}$ and 8Fe$^{2+}$) ions distributed into octahedral sites per unit cell. The structure consists of octahedral and mixed tetrahedral/octahedral layers stacked along the [111] direction (Fig. 2.6a [71]). Fig. 2.6b [71] shows the sequence of Fe- and O-layers and the section of this structure with three octahedral and two tetrahedral are depicted in Fig. 2.6c [71]. Magnetite with an excess of oxygen also exists, but this excess is much smaller than that with wustite, and the corresponding concentration of defects is also less [72, 79].

The crystal system of hematite ($\alpha$-Fe$_2$O$_3$) is a rhombohedral structure (Fig. 2.7 [71]) with a low concentration of structural defects. This structure can be described as hexagonal close-packed (hcp) arrays of oxygen ions stacked along the [001] direction, i.e. planes of anions are parallel to the (001) plane (Fig. 2.7a [71]). Two thirds of the sites are filled with Fe$^{3+}$ ions which are regularly arranged with two filled sites, followed by one vacant site in the (001) plane, thereby forming sixfold rings (Fig. 2.7b [71]). This arrangement of cations produces pairs of Fe(O)$_6$ octahedra. Each octahedron shares edges with three neighbouring octahedral in the same plane and one face with an octahedron in an adjacent plane (Fig. 2.7c [71]). The O-O distances along the shared face of an octahedron are shorter (0.2669 nm) than the distance along the unshared edge (0.3035 nm), hence the octahedron is distorted trigonally (Fig. 2.7d [71]). The arrangement of oxygen and iron around a shared face is depicted in Fig. 2.7e [71]. This shared Fe-O$_3$-Fe triplet structure influences the magnetic properties of the oxide because hematite is an n-type (n=negative carrier) semiconducting oxide in which the diffusion of anions is dominant [32, 80].
Fig. 2.5 Crystal structure of wustite (Fe\textsubscript{1-x}O), (a) arrangement of octahedral, (b) ball-and-stick model [71].

Fig. 2.6 Crystal structure of magnetite (Fe\textsubscript{3}O\textsubscript{4}), (a) polyhedral model with alternating octahedral and tetrahedral-octahedra layers, (b) ball-and-stick model, (c) ball-and-stick model of the arrangement of octahedra and tetrahedra [71].
Fig. 2.7 Crystal structure of hematite ($\alpha$-Fe$_2$O$_3$), (a) hexagonal close packing of oxygen anions with cations distributed in the octahedral interstices, (b) view down the c-axis showing the distribution of iron ions over a given oxygen layer, and the hexagonal arrangement of octahedra, (c) arrangement of octahedral, note their face sharing, (d) ball-and-stick model, (e) O$_3$-Fe-O$_3$-Fe-O$_3$ triplets [71].

2.2.2 High temperature oxidation of pure iron and steel alloys

The above mentioned form of iron oxides which can be obtained depends on the nature of the substrate and the thermal parameters. Due to the presence of alloying elements and impurities in Fe-C steel alloys, the oxidation rates, phase development and morphologies of oxide scale are dramatically different from pure iron under various processing parameters. This section will take up the oxidation of steel alloys from these four areas. Since some extensive reviews of the oxidation of metals have been given in
Ref. [4, 34, 81–84] and there are several articles and books [1, 3, 26, 43, 85–88] in which the subject is treated in detail, more attention will be given here to the relationships between theories, their limits of application, and recent experimental data.

Oxidation rates are generally measured accumulations of oxide (thickness or weight change of oxide scale) with time [2]. The high temperature oxidation of low carbon steel at the initial stage follows a linear law up to 20 s, and then changes to a parabolic growth rate, as shown in Fig. 2.8 [89]. The mixed para-linear kinetics is widely accepted to deal with the short time growth of oxide scale during hot rolling [60, 61, 89, 90]. With the oxidation of steels below 700 °C, the oxidation kinetics is similar to pure iron at various atmospheres and follows approximately parabolic kinetics [12, 91–93]. Furthermore, the distinct sub-layer thicknesses of oxide scale were observed by an elegant series of experiments [2, 32, 46, 56, 58]. The typical relatively thickness ratios of wustite, magnetite, and hematite range between 100:5:1 and 100:10:1 in a temperature range of 700 to 1200 °C. The oxidation of iron at temperatures between 400 °C and 550 °C results in thickness ratios between the magnetite and hematite in the range of 10:1 to 20:1. The phase development during the high temperature oxidation of steel alloys concentrated mostly on the evolution of wustite during isothermal holding because wustite will decompose into magnetite and ferrite below 570 °C [9, 64]. Typically oxide scales formed at temperatures less than 1000 °C contain predominantly wustite and magnetite in varying proportions, with a small amount of hematite (Fig. 2.9 [94, 95]). Furthermore, some studies [60, 89, 95] have revealed that the percentage of wustite decreased concurrently while that of magnetite and hematite increased substantially when the holding time was extended from 30 to 600 s over a temperature range of 850–1000 °C. However, no single integrated study on phase evolution of oxide
scale formed on microalloyed steels over a broad range of temperatures and various moisture conditions, has yet appeared.

Fig. 2.8 Thickness variation of oxide scales formed in air at a velocity of 4.2 cm/s [89].

Fig. 2.9 Proportions of iron oxides formed as a function of temperature [94, 95].
The surface morphologies of oxide scale are usually used to examine the blisters or spallation failure [96, 97] due to the variation of internal stress within multilayered oxides [98, 99]. Microscopic observations of the ‘rough’ oxide scale areas revealed an undulating or serrated pattern on the surface of oxide scale (Fig. 2.10 [51, 100]). Here a rough granular structure in Fig. 2.10a, b, suppressed the granular wustite in Fig. 2.10c, d, and the dense accumulation of fine particles in Fig. 2.10e.

**Fig. 2.10** SEM images of different oxide-scale areas. (a) ‘rough’-scale area on the sample oxidised at 1000 °C for 12 s; (b) ‘rough’-scale area on the sample oxidised at 1180 °C for 24 s; (c) Transition area between ‘rough’-and smooth-scale areas on the sample oxidised at 1100 °C for 24 s; (d) Transition area between ‘rough’-and smooth-scale areas on the sample oxidised at 1000 °C for 12 s; (e) Smooth scale area on the sample oxidised at 1180 °C for 24 s [51, 100].
Furthermore, cross sectional morphologies associated with steel oxidation were primarily used to further characterise the relationship within multilayered oxide phases. The iron oxides initially formed on pure iron in dry air at 500 °C consisted of a thin layer of hematite and a double layer of magnetite [91, 93]. These recent investigations on pure iron revealed that hematite, magnetite, and wustite made up 5%, 30–35%, and 60–65% of the oxide scale, respectively, after oxidation in dry air at 600 °C for a holding time of 24 h (Fig. 2.11 [91, 93]).

![Fig. 2.11 FIB cross section (600 °C, dry O2, 24h). The layers of hematite, magnetite, and wustite made up 5, 30–35, and 60–65% of the oxide scale, respectively. The sample was tilted 52° [91, 93].](image)

As discussed later, the oxidising rate of steel alloys depends on three variables, the temperature, chemistry of the steel, and the atmosphere of the gas [3]. The first is critical to the final properties of oxide scale because a number of cases [1, 86, 88] revealed that an increase in temperature facilitates the oxidation of metals quite significantly, and in analogy of the alloying strength in steel substrate, the alloying additions modified the oxidation quite dramatically. Normally, the amount of silicon
[101, 102], and chromium [103] aims to form a protective oxide scale, whereas, small additions of nickel [104, 105], copper, niobium, molybdenum, and vanadium led to a greatly increased adherence of oxide scale [106]. Manganese is normally used as a solvent [107], while the transport of carbon is via defects such as pores rather than lattice or grain boundary diffusion [108]. More extensive details of the effect of alloying elements are given in Ref. [109]. The atmosphere of gas as it interacted with oxides, especially water vapour, has made our understanding of the overall situation elusive [83, 84, 92, 110], while the different behaviour of steel alloys in air-moisture mixtures have further complicated the set of observations. A systematic investigation of the interactive effects of water vapour on the oxidation of steel alloys is therefore desired, but it must be recognised that these influences are not mutually exclusive. In the laboratory, some subtle influence could result from the oxidation time, the surface state of the samples [111], the flow rate of the reaction gas [112], and even the size of the sample in different preparation methods [59].

2.2.3 Oxide scale growth at continuous cooling

The growth and microstructure of oxide scale during the continuous cooling of low-carbon steels from different temperatures and at different CRs [4, 12, 113–116] have been investigated, and it was found that the oxide scale increased in thickness at a lower CR. The microstructural development of the oxide scale was observed with magnetite precipitates in the wustite layer at CRs of 10 to 60 °C/min [4]. A magnetite and iron eutectoid layer formed near the magnetite layer, while a wustite layer containing magnetite precipitates was detected at the inner region when the CR was reduced to 5 °C/min [100]. Various explanations for this phase evolution have been proposed,
based on an investigation on the isothermal decomposition of the thermally grown wustite [4, 9–12, 117]. This isothermal decomposition generally follows a C-curve trend and differed at different temperature ranges, as shown in Fig. 2.12 [9].

Fig. 2.12 A schematic CCT diagram for wustite formed at 900 °C in air and subsequent wustite decomposition therein cooled [9].

As shown in Fig. 2.12, the wustite was unstable and decomposed into magnetite and iron at a temperature range of 460–510 °C. Above that temperature, the transformation was commenced by iron precipitates, whereas, below 480 °C, magnetite precipitates were first. At temperatures down to about 350 °C, transformation was initiated by Fe$_3$O$_4$ precipitation followed by lamellar Fe+Fe$_3$O$_4$ growth. However, at a temperature between 220 and 270 °C, the wustite transformed directly into a fine, granular mixture of Fe+Fe$_3$O$_4$, whereas no transformation occurred at 200 °C and lower [12, 109]. This result differed slightly from those achieved from the C-curve determined in a recent
study under isothermal conditions, as shown in Fig. 2.13 [10, 12, 118]. It is worth mentioning here that the fundamental research described above made some attempt at providing practical applications for the hot rolling process. Fig. 2.14 shows a modified hot rolling process used to obtain the oxide scale desired on microalloyed steel, according to the CCT-diagram for wustite decomposition [119].

**Fig. 2.13** The isothermal formation of magnetite at the wustite-steel interface [10, 12, 118].

**Fig. 2.14** Schematic illustration for a hot rolling process modified to form the desired oxide scale on microalloyed steel [119].
2.3 The behaviour of oxide scales after hot rolling

2.3.1 The precipitation of magnetite

Since wustite decomposition during the growth of oxide scale at continuous cooling is important, this complete section is devoted to the precipitation of magnetite throughout the phase transformation of wustite. With proeutectoid products above 570 °C, the dominant precipitation is the magnetite phase, which can be verified by the Fe-O phase diagram (Fig. 2.3 [6]). The composition of wustite in equilibrium with iron (in the range of 51.19–51.38 at.% or 23.10–23.23 wt.%) is close to its eutectoid composition (51.38 at.%), with the formation of a small supersaturated level of iron (<0.19 at.% or 0.13 wt.%), whereas, the composition of wustite in equilibrium with magnetite varies significantly with temperature, ranging from 54.57 at.% at 1424 °C, 52.80 at.% at 900 °C to 51.38 at.% at 570 °C (or 25.60 wt.%, 24.40 wt.%, and 23.24 wt.%, respectively).

Earlier evidence [5, 58] suggests that it is impossible to suppress the high temperature precipitation of magnetite from the wustite layer formed on the iron substrate during continuous cooling, especially above 980 °C. The proeutectoid phase only precipitates at the region adjacent to the layer of magnetite where oxygen was supersaturated upon cooling after oxidation [120], as shown in Fig. 2.15 [12]. Below 570 °C, numerous previous studies focused on the phase transformation of wustite during isothermal holding [9–11, 20]. Detailed of this transfer process can be found from Fig. 2.12 [9], which was introduced earlier. Several research findings into the precipitation of magnetite under continuous cooling revealed that a wide range of oxide scale structures developed (Fig. 2.16 [20]) for a combination of starting cooling temperature and CR [4, 48, 109, 121]. These specific structures will be classified in the next section.
Fig. 2.15 The typical structure of oxide scale, showing a thin surface layer of hematite, a relatively thick intermediate layer of magnetite, a thick inner layer of wustite containing magnetite precipitates, and a magnetite seam at the scale-steel interface [12].

Fig. 2.16 Typical cross sectional SEM images of the oxide scale showing the precipitation of magnetite from thermally grown wustite formed at 750 °C in air, and then holding below 500 °C [20].
A noticeable microstructure described here for the precipitation of magnetite at either high or low temperature is another product of the magnetite layer (called the magnetite seam [12, 118, 122]) formed at the wustite/steel interface. Several attempts were made to identify the magnetite seam [12, 118, 123, 124] which was associated with the adherence properties of oxide scale. In a recent study [123] the orientation of the seam was reported \{110\}Fe//\{100\}Fe₃O₄, <110>Fe/<100>Fe₃O₄ in the case of transforming by continuous cooling from 400 °C, as shown schematically in Fig. 2.17a [123], where the lattice strain was calculated as 4%. By contrast, the Fe/FeO orientation relationship was \{100\}Fe//\{110\}FeO, <110>Fe/<110>FeO (Fig. 2.17b [123]) with a lattice strain of 25%. It is suggested that magnetite has better coherency with the steel substrate than wustite in terms of the conformity of lattice sites of iron oxide with that of the substrate, but these relationships are also limited by the thickness of the oxide scale (>8 µm) [15]. For a very thin oxide scale, a Fe/FeO orientation relationship was \{100\}Fe//\{100\}FeO, <100>Fe/<110>FeO with lattice strain of 6% [124].

![Fig. 2.17 Orientation relationship of (a) magnetite/steel interface, (b) wustite/steel interface [123].](image)
Moreover, there was a strong orientation relationship between the grains of magnetite and wustite in the oxide scale grown on the 0.11C-0.37Si-1.35Mn steel at 1000 °C, as shown in Fig. 2.18 [125], which is similar to the magnetite seam and intra-granular precipitates [17, 126, 127]. A possible explanation is that grains in the magnetite layer control the orientation of wustite because of the isothermal oxidation generated by the wustite from the reduction of magnetite at the magnetite-wustite interface [16, 19]. Several recent studies [12, 122] have proposed various mechanisms for the formation of the magnetite seam. The starting cooling temperature and CR were attributed to the formation of the magnetite seam. Some results showed that a high CR could stop this layer from growing any further [4, 5, 12, 58], nevertheless the exact value of the CR was not involved, but these explanations aim to obtain no magnetite seam, i.e. the weaker adherence of oxide scale, which can be easy for conventional descaling [4, 12, 128]. With the compact and dense magnetite seam attached to the steel substrate, which is needed to apply to the current non-acidic descaling technique, this is still a huge territory to explore.

![Fig. 2.18 EBSD-derived maps showing (a) phase/confidence index, (b) inverse pole figure (IPF)/image quality (IQ) map for a oxide scale formed on the steel (0.11C-0.37Si-1.35Mn) at 1000 °C [125].](image)
In addition, the phase transformation discussed above should be distinguished from the oxide scale generated below 570 °C. TEM studies (Fig. 2.19 [92]) have shown that the magnetite and hematite phase due to the wustite is unstable at this point, as described earlier. A duplex magnetite layer was also observed.

![Fig. 2.19](image)

**Fig. 2.19** Local electron diffraction with the TEM on an oxide scale (400 °C, 145 h, air 2 vol% H₂O): two layers of columnar grains form a duplex layer of magnetite, the equiaxed grains were identified as hematite [92]

### 2.3.2 Classification of tertiary oxide scale

The precipitation of magnetite described above leads to a wide range of microstructures that were developed for the tertiary oxide scale (after hot rolling) formed on steel alloys. These structures were initially classified into eight types, as listed in Table 2.2 [109]. Recent studies further summarised them into three types, as shown in Fig. 2.20 [4, 12].
Table 2.2 Classification table for tertiary oxide scale with illustrations for their occurrence at coiling temperature (CT) and integrity [109]

<table>
<thead>
<tr>
<th>Scale type</th>
<th>Image (steel side at bottom)</th>
<th>Description</th>
<th>Occurrence</th>
<th>Scale integrity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type 1</td>
<td><img src="image1" alt="Type 1 Image" /></td>
<td>Decomposed wustite</td>
<td>CT 350–550 °C, coil centre &amp; edge</td>
<td>Good</td>
</tr>
<tr>
<td>Type 2</td>
<td><img src="image2" alt="Type 2 Image" /></td>
<td>Mainly decomposed wustite and low fraction of retained wustite</td>
<td>CT, 550–700 °C unquenched/CT, 500–620 °C quenched; coil centre</td>
<td>Fair to good</td>
</tr>
<tr>
<td>Type 3</td>
<td><img src="image3" alt="Type 3 Image" /></td>
<td>Mixed phases, hematite, magnetite, decomposed wustite, retain wusite</td>
<td>CT &gt; 550 °C; (near) edge regions</td>
<td>Poor coherence</td>
</tr>
<tr>
<td>Type 4</td>
<td><img src="image4" alt="Type 4 Image" /></td>
<td>Mainly compact magnetite</td>
<td>CT, 550–700 °C, tightly wrapped edge regions</td>
<td>Fair to poor adherence</td>
</tr>
<tr>
<td>Type 5</td>
<td><img src="image5" alt="Type 5 Image" /></td>
<td>Compact magnetite, hematite</td>
<td>CT &gt; 550 °C, coil edges</td>
<td>Poor adherence</td>
</tr>
<tr>
<td>Type 6</td>
<td><img src="image6" alt="Type 6 Image" /></td>
<td>Mainly wustite</td>
<td>CT &gt; 700 °C, quenched, coil centre</td>
<td>Poor coherence</td>
</tr>
<tr>
<td>Type 7</td>
<td><img src="image7" alt="Type 7 Image" /></td>
<td>Inner layer containing wustite, outer layer of compact magnetite</td>
<td>CT &lt; 300 °C, coil centre and edges</td>
<td>Poor coherence</td>
</tr>
<tr>
<td>Type 8</td>
<td><img src="image8" alt="Type 8 Image" /></td>
<td>Magnetite, decomposed wustite, little retained wustite, no hematite</td>
<td>CT 300–375°C full width, or CT &gt; 550 °C edge, or CT 550–650 °C centre</td>
<td>Fair coherence</td>
</tr>
</tbody>
</table>
Type I in Fig. 2.20 is the oxide scale with primarily retained wustite and proeutectoid magnetite precipitates at the region near the magnetite layer. The type II oxide scale contains magnetite precipitates near the magnetite layer and also near the substrate. The type III oxide scale contains a mixture of magnetite precipitates near the layer of magnetite, magnetite precipitates adjacent to the substrate, iron-magnetite eutectoid, and retained wustite. This classification has many powerful applications, some of which are illustrated in further chapters, with a specific interest on the magnetite seam.

Fig. 2.20 Schematic diagram illustrating the conditions needed for different types of oxide scale to form, depending on the CT and CR [4, 12].

2.3.3 Oxide scales developed on hot-coiled strip

Since the coiling temperature (CT) mentioned above has a major impact on the final oxide scale, this section is dedicated to the microstructural development of the oxide scale at the edge/centre region across the width of hot-coiled strip coiled at a wide range of temperature. The initial structure of oxide scale after finishing hot-rolling and cooling
consists of a typical three-layered structure for the outer layer of hematite, the intermediate layer of magnetite, and the inner layer of wustite. This microstructure then developed into various final microstructures (Fig. 2.21 [129]) at the edge and central region in combination with the starting cooling temperature, cooling rate (CR) and oxygen availability. The CT of the hot-rolled strip was generally within the range of 500–740 °C. The thickness of this oxide scale increased with the increasing CT and decreasing CR [4, 12, 50, 51]. At the edges, for a CT above 600 °C, the compositions of oxide scale were a two-layered structure for the outer layer of hematite and the inner layer of magnetite (Fig. 2.21c [129]). For a lower CT (e.g. 500–520 °C), they became three-layered for the outer layer of hematite, the intermediate layer of magnetite, while the inner layer was a mixture of magnetite and iron (Fig. 2.21b [129]).

At the central regions the microstructure of oxide scale was in presence of retained wustite (Fig. 2.21c [129]), particularly at higher CTs (e.g. 720–740 °C). This was due to
the lack of oxygen at the centre of the hot-coiled strip which led to the consumption of two high oxides (hematite and magnetite). Fig. 2.22 [60, 109] shows the variation of the phase composition as a function of the CT at the centre of the hot-coiled strip. Here the decomposed wustite has a very broad maximum CT of 550 °C, with an average fraction of up to 85%. This result implies that the final oxide scale in this temperature range consisted mostly precipitations of magnetite (i.e. a product of decomposed wustite), and as discussed earlier, it has strong adherence properties.

![Fig. 2.22 Variation of phase composition within the oxide scale as a function of the CT.](image)

The oxide scale is located near the centre of the coil across the width of hot-rolled strip [60, 109].

Furthermore, there were metallic iron particles at the central regions of a hot-coiled strip [129]. Several mechanisms have been proposed for this phenomenon; according to one, the metallic iron particles resulted from the oxides reduction reaction in conjunction with both failure evolution and the decarburisation effect [108, 130]. They may also
have formed as part of the eutectoid reaction products, with the preferential precipitation of iron particles along the wustite grain boundaries [131, 132]. This can be readily extended to another significant field, i.e. grain boundary diffusion [133]. On this basis the further studies of this precipitation along the grain boundary might contribute to an understanding of the complex interaction effect previously reported.

2.3.4 Mechanical properties of oxide scale

The effects that the above mentioned oxide scale produce during rolling depend on the properties of the oxide scale itself and its adherence at the oxide scale/metal interface. From this perspective, this section not only approaches the internal stress state and plastic deformation of oxide scales at the current time, but also looks into future applications of the tribological properties of oxide scale in the rolling gap.

The mechanical stresses in the oxide scale play a significant role in its integrity [134, 135], features that are still not fully understood. Generally, internal stresses are induced by the growth of oxides, thermal expansion mismatch, and applied forces [136, 137], some of which originate from many different causes. In earlier studies, the PBR described in Section 2.1.2 was used to explain the growth stress [138], while the stress relaxation mechanism was also considered in some explorations [137]. Recently, the growth stress evolution in multilayered oxides on pure iron was systematically investigated [109]. The relationship between the type of oxide scale and elastic strain, the thickness and integrity of the oxide scale was presented in an oxide failure mode map [139]. Some models were proposed to evaluate the residual stress [136], and predict the integrity of the oxide scale during the hot rolling and cooling of steels [139],
based on a parabolic growth law and thermal mismatch that eliminated the growth stress and rolling forces. Some experiments were designed to examine blistering due to oxide growth stresses during isothermal oxidation [96]. A recent experiment reveals that the presence of $\alpha$-Fe precipitates in a magnetite matrix (i.e. decomposed wustite in Table 2.3 [109]) could lead to a rough interface which would enhance the adherence of oxide scale [60]. Further elegant tests simulated for rolling processes will be introduced later.

### Table 2.3 Oxide phases and mechanical properties at room temperature [109]

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
<th>Fe/O ratio</th>
<th>Vickers hardness</th>
<th>Tensile strength (MPa)</th>
<th>Effect on oxide scale integrity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wustite</td>
<td>$\text{Fe}_{1-x}\text{O}$</td>
<td>0.93</td>
<td>±300</td>
<td>0.4</td>
<td>Bad</td>
</tr>
<tr>
<td>Magnetite</td>
<td>$\text{Fe}_3\text{O}_4$</td>
<td>0.75</td>
<td>±550</td>
<td>40</td>
<td>Fair</td>
</tr>
<tr>
<td>Hematite</td>
<td>$\text{Fe}_2\text{O}_3$</td>
<td>0.67</td>
<td>±1000</td>
<td>10</td>
<td>Bad</td>
</tr>
<tr>
<td>Decomposed wustite</td>
<td>$\text{Fe}_3\text{O}_4+\alpha$-Fe</td>
<td>0.93</td>
<td>±550</td>
<td>&gt;40</td>
<td>Good</td>
</tr>
</tbody>
</table>

The plastic deformation and fracture of oxide scales have been analysed with respect to their elastic and plastic properties, and their adhesion and toughness [140, 141]. Various studies have conducted compression [46, 47, 142] or tension tests [1, 143, 144] on oxidised samples with oxide scales comprising mainly wustite, that were able to sustain high amounts of plastic deformation before breaking [1, 46, 96, 143, 144]. Other studies [140, 145] have carried out hot rolling tests with a wide variety of oxide-scale thickness. A TEM observation (Fig. 2.23 [144]) suggested that oxide scale containing wustite was deformed during hot rolling with a hot work piece, and then the surface of the hot work piece was covered with oxide scale (Fig. 2.24 [144]). Furthermore, the mechanical
properties of the oxide scale at temperatures ranging from 650 to 1050 °C can be characterised as brittle, mixed, or ductile, based on its integrity (Fig. 2.25 [146]). The conclusions drawn from these works seem to indicate that thin oxide scales behave plastically at high temperatures when the deformation is limited to low reductions.

![Fig. 2.23 TEM diffraction pattern analysis of oxide scale crystal formed on 0.4C-5.0Cr-0.1Si alloy after rolling test at 1200 °C [144].](image)

![Fig. 2.24 Schematic illustration of the deformation behaviour of internal oxide scale during hot rolling [144].](image)
Fig. 2.25 The plastic behaviour of oxide scale as a function of temperature and reduction [146]; data from [1, 145, 146] were plotted together for a comparison.

The tribological properties of oxide scale in the rolling gap was attributed to several aspects such as providing thermal insulation [145, 147], to affect the friction and lubrication [148, 149], to accelerate work roll wear, and even to modify the rolling forces [150–152]. The role of oxide scale in these processes is very complex and still not clear because it is influenced by the natural and physical properties of the oxide scale as described above. As the oxide scales that build up on the steel surface are very thin, it is difficult to use conventional techniques to measure their properties. Recently, nano-indentation and nano-scratch techniques have successfully been developed by some scientists to investigate the properties of this thin film in the semiconductor field, and even the thermal oxide scale that formed on the alloys [153].
2.4 Methodology for investigating the oxide scale

The studies of oxide scale on steel alloys reviewed above have undergone amazing growth over the last few decades. This is due to: (1) the development of new high-resolution techniques for observing their atomic structures and behaviour and (2) increased modelling capability resulting from better theory and the rapid rise of powerful computer simulation methods. This section now takes up these related approaches of experimental and numerical simulation on oxide scale.

2.4.1 Experimental methods

Any investigation into high temperature oxidation is usually interested in oxidation kinetics and the nature of the oxidation process, i.e., the oxidation mechanism. These can take many forms. For discontinuous methods, the specimen to be measured is exposed to high temperature oxidation in various hot furnaces or TGA [154] for a given time, and it is then removed for observation. The oxide scale may also be stripped from the surface of the specimen. Alternative in situ investigation thermally images the morphology, topography, and diffraction pattern of an oxidising substrate using ESEM [155, 156] (Fig. 2.26a, b [155]) and HTXRD [157, 158] (Fig. 2.26c [158]) equipped with the hot stage or AFM with the heated micro-cantilever (Fig. 2.26d [159]). However, the limitation of these hot stages is generally 900 °C, above which a thermal tag inevitably occurs [157]. Hence, these in situ analytical techniques are normally applied for polymer and other organic sciences. In any case, these modern approaches provide an opportunity for future investigations on thermally grown oxide scale.
Chapter 2 Literature review

Fig. 2.26 Various hot-stage microscopes potentially applied in high temperature oxidation, (a) arrangement, and (b) in situ observation on the heating stage in ESEM [155], (c) at the hot stage (Anton Paar HTK10) in HTXRD [158], (d) the heated micro-cantilever in AFM [159].

Further characterisation techniques have been applied to the dissection of oxidation mechanisms with considerable success. The widespread adaption of FIB milling to produce TEM foil samples is likely to prove important [91, 93, 160]. EBSD now provides a rapid method for identifying the orientation of grains intersected by a polished surface [18] and therefore it can be applied to traditional metallographic cross sections where it can identify the preferred growth directions of oxidation products. The application of these techniques might improve our understanding of the interaction between alloying elements and the metal-oxide interface.
Furthermore, prior to metallographic preparation, a number of different protection methods for the oxidised surface were used to shield oxygen from the atmosphere to avoid any further oxidation [161]. For small surfaces in a laboratory, coating of Au, Pt, or Ni [22] can meet the above requirements. A low melting point wood alloy has also been proposed for EBSD observation [95]. In order to preserve the industrial oxide scale formed in high temperature metal processing, a specific oxide glass was used to cover the surface of the work-piece immediately after hot working [162]. However, no effective method for transformed oxide scale at room temperature has yet been reported.

### 2.4.2 Numerical simulation

Computer modelling is generally used to interpret the experimental results and further predictions. Most previous modelling focused on the heat transfer in the rolling gap [163, 164]. An integrated work [1, 165] using finite element method (FEM) has been done to predict the failure of oxide scale at the entry into the roll gap. The combined discrete/finite element model that was developed can predict the mechanical mixing in the thin sub-surface layer on a mesoscale level due to the specific tribological conditions in the roll gap (Fig. 2.27 [166]). Other attempts have also been made to simulate the stress-induced diffusion on Fe-Cr alloy. Fig. 2.28a [167] illustrates the geometry of a polycrystalline alloy with an initial Cr$_2$O$_3$ at the top surface. The 2D model (Fig. 2.28b) studied is part of a sample cut between the dashed line, as shown in Fig. 2.28a. These models were developed for the finite element analysis of oxidation induced metal depletion at the oxide-metal interface [168].
Fig. 2.27 Displacement of the discrete element particles/blocks in the Y (vertical) (a, b) and in the X (longitudinal) (c) directions predicted in the sub-surface layer while hot rolling aluminium [166].

Fig. 2.28 (a).3D and (b) 2D modelling structure of polycrystalline Fe-Cr alloy with a layer of oxide scale [167].

To the best of our knowledge, molar dynamics simulation [169, 170] means that the phase transition within oxide scale remains largely unknown because the compounds associated with iron oxides are complicated. Since pure metal either fcc or bcc array is still in its infancy, designing material atom by atom for compound still has a long way to go, particularly in the development of effective potential functions. In summary, a
true appreciation of the capabilities and shortcomings of the various methods, an understanding of the assumptions used in the models, and a feeling for what kind of problems are realistic candidates for simulation can only be obtained from experience.

2.5 Summary and implications

To know in order to control and even to improve, is an attempt to combine previous research of the part and the whole, while still being aware there is still a huge territory to explore. These include: (1) the growth kinetics for the sub-layer of the oxide scale, i.e. the rate constant equation for the growth of FeO, Fe$_3$O$_4$ and Fe$_2$O$_3$ (in Section 2.1.3), (2) the oxidation mechanism of steel alloys, especially the effects of water vapour and alloying elements (in Section 2.2.2), (3) isothermal oxidation combined with continuous cooling, particularly in the starting cooling temperature and CR (in Section 2.2.3), (4) the precipitation of magnetite mainly in low temperature eutectoid reaction (in Section 2.3.1), (5) the development of oxide scale on hot-rolled steel during laminar cooling and coiling process aims at phase evolution and processing parameters caused (in Section 2.3.3), and (6) the tribological properties for various types of oxide scale during cold metal processing (in Section 2.3.4). This present study is designed to fill these gaps and propose a novel microstructure of oxide scale which can be used in cold metal rolling to eliminate conventional acid pickling. All these issues, and more, are covered in subsequent chapters.
Chapter 3

Experimental instruments and analytical methodology

The purpose of this chapter is to introduce the experimental techniques and analytical methodology underpinning this research. First of all, the experimental instruments used in the experiments, the oxidation tests, hot steel strip rolling and tribological tests, will be presented, and then some diffractometers and microscopes are applied to identify and characterise the oxide scale. Following this, a brief summary highlights the major selection made in order to conduct the present work.

3.1 Experimental instruments

3.1.1 High temperature microscope (HTM)

In situ oxidation tests were performed on a laser scanning confocal microscope (LSCM-VL2000DX) equipped with an ellipsoidal infrared image furnace (SVF17SP) with a charge-coupled device (CCD) camera as a detector. In typical laser scanning confocal microscopy, a confocal pinhole in the laser optical imaging system is used which limits the depth of field. With oxidation experiments, the CCD camera provided a far better resolution and was also able to compensate for differences in light emission and a
greater depth of field [171, 172]. Fig. 3.1 shows the cross sectional view of the high temperature microscope furnace and experimental configuration of the test. The heating system consisted of a 1.5 kW halogen lamp positioned in the lower focal point of a small gold-plated ellipsoidal chamber that reflected the light to the other focus point where the sample was positioned. Thermocouples incorporated around the sample holder were used to determine and control the temperature by a digital PID controller (ES100P). A SuperClean™ gas filter was placed in the gas purification train to control the purity of the inert gas atmosphere in the top half of the furnace chamber. A real time oxidation video from a CCD light detector was captured to a computer at a rate of 25 frames per second for later editing. During the oxidation test a compressed industrial air was used as the dry oxidising gas. The gas pressure in the HTM chamber was kept at 1 atm during the tests. A polished sample was placed in the 4 mm diameter aluminium crucible, which was inserted into the HTM chamber.

Fig. 3.1 Cross sectional view of the high temperature microscope (HTM) set-up for in situ oxidation test.
3.1.2 Environmental Gleeble 3500 physical simulation system

Short-time oxidation tests in humid air were conducted using a Gleeble 3500 thermomechanical simulator combined with a controlled humid air generator. Fig. 3.2 shows a photograph of the Gleeble 3500, which is a fully integrated digital closed loop control thermal and mechanical testing system. The direct resistance heating system can heat specimens at a rate up to 10,000 °C/s, or can hold steady-state equilibrium temperatures. This system can also perform a high CR in excess of 10,000 °C/s at the surface of a specimen while high thermal conductivity grips hold the specimen. Thermocouples welded to the centre of the specimen provide signals for accurate feedback control of the temperatures of the specimen. The test chamber was connected to a high vacuum system. Two water tanks operate under high pressure air up 0.6 MPa, or under specific gases to provide cooling or make up the preferred environment to be introduced into the chamber.

Fig. 3.2 Photograph of Gleeble 3500 physical simulation system and the method for generating humid air with desired water vapour content.
An apparatus suitable for the controllable humid atmosphere was developed and attached to Gleeble 3500. The controlled moisture atmosphere was obtained by bubbling synthetic air through water heated up to the corresponding dew point in a water bath to generate humid air which continued to flow into the chamber at a rate of $2.5 \times 10^{-4} \text{ m}^3/\text{s}$. The content of water vapour in the humid air can be calibrated by adjusting the water temperature in the water bath. Because of the content of water vapour varied between 7.0 and 19.5 vol.% in humid air with respect to the hot rolling of plain carbon steel, the water temperatures were set at 30, 40, 50, and 60 °C, which corresponded to a water vapour content of 2.8, 7, 12 and 19.5 vol.%, respectively [110, 173]. It was noted that before the oxidation experiments the gas tube connecting the water bath and the Gleeble 3500 chamber should be pre-heated to prevent the water from condensing inside the gas tube.

### 3.1.3 Hille 100 experimental mill attached accelerated cooling (HR-AC) system

The experimental instruments described above enabled the oxidation mechanism and phase transformation in oxide scale formed during simulated hot rolling to be determined. The next step was how to obtain the oxide scale specified during practical hot rolling, so pilot plant tests were carried out on an experimental rolling mill, followed by a newly developed accelerated water cooling system, as shown in Fig. 3.3. Hot rolling experiments were performed on a 2-high Hille 100 experimental mill with 225 mm diameter rolls and a 254 mm diameter barrel roll. The rolls are made of high speed steel (HSS) with a hardness of HRC55 and $R_a$ of 0.4 µm on surface finishing. The rolling mill can be operated at rolling speeds of 0.12–0.72 m/s, and a load up to 1500 kN and a torque up to 13000 kN·m can be applied. Two load cells were equipped
to determine any compensation needed for the mill modulus and bearing clearances, and there were two torque gauges on the shaft to measure individual roll torque. Two position transducers were used to control the roll gap, and two DMC-450 radiation thickness gauges at the entry and exit, and a hydraulic AGC, were also available.

Fig. 3.3 Photograph of the 2-high Hille 100 experimental rolling mill combined with an accelerate water cooling (HR-AC) system, including temperature detectors located at the entry and exit of the cooling system, and the conjunction table roller between them.

After hot rolling the steel strips were cooled immediately through the accelerated water cooling system attached to the rolling mill. This accelerated cooling system consists of top and bottom double banks of water spray nozzles which mean the flow rates are much greater than conventional cooling methods such as spray or water column cooling.
The total flow of water was 17,000 L/min/m of cooling length corresponding to 9,200 L/min-m² assuming a 1.8 m width, which is more than double the maximum flow rate for conventional run-out table (ROT) cooling [174]. Two Raytek GPs non-contact infrared pyrometers were located above the roll gap entry and exit of the cooling equipment to simultaneously monitor and control the temperature of the sample and the CRs, as shown in Fig. 3.3. Prior to the rolling test, reheating was carried out using a high temperature electric resistance furnace with 350(W)×330(H)×870(D) size chamber at 30,000 watts and a current of 40 A. Nitrogen was introduced into the chamber of the reheating furnace to control the thickness of the oxide scale.

3.1.4 Universal Mechanical Tester (UMT2)-Tribometer

Tribology tests, strongly associated to the previous ones, revealed the mechanical properties of the as-fabricated oxide scale applied to the subsequent cold rolling without acid pickling. To determine the tribological properties, a CETR Universal Mechanical Tester (UMT2)-Tribometer in pin-on-disc mode was used to conduct unlubricated sliding wear tests at ambient temperature. The UMT2 is a pin-on-disc configuration, where the top pin was connected to the vertical and lateral linear motion systems, while the bottom part was fixed to a lower rotary drive. This involved an upper specimen (pin) that slid against a rotating disc as a lower specimen under a prescribed set of conditions [175, 176]. Wear measurement could be performed to an accuracy of 50 nm. A spindle can rotate the lower specimen from 0.001 to 5,000 rpm. The load cell can control the load in a range from 2–200 N. Accurate strain gauge sensors provide simultaneous measurements of load and torque in two to six axes. The forces can be measured with a resolution of 0.00003% of full size. A normal load sensor provided continuous feedback.
to the vertical motion controller, dynamically adjusting the sample position to ensure a constant contact pressure at the pin/disc interface. Data acquisition functions recorded the real time dynamic normal load, frictional force, coefficient of friction, and any reduction in the height of the pin during the test.

3.2 Analytical methodology

3.2.1 Optical microscope (OM)

A Keyence VHX-1000E Digital microscope and a Leica optical microscope (OM) were used to evaluate the thickness of the oxide scale, porosities, cracks, and the interface roughness of the oxide scale and steel substrate. The VHX-1000 provided a depth of field at least 20 times larger than optical microscopes, which means it can accurately observe the surface topography of a target with large peaks and valleys; imaging which conventional optical microscopes cannot achieve. Furthermore, it offers a wider range of measurement with 13 modes in total for on-screen, real time accurate measurement.

3.2.2 Scanning electron microscope (SEM)

A JEOL JSM 6490 low vacuum-scanning electron microscope (LV-SEM) equipped with energy dispersive x-ray analysis (EDS) was used to observe the microstructure of the samples and the morphologies of the oxide scales. The operating voltage was 20 kV and the working distance was set at 10 mm.
3.2.3 Atomic force microscope (AFM)

A Multi-Mode Scanning Probe Microscopy (SPM) from Digital Instruments operating in contact AFM mode (Nanoscope IIIA AFM) was used to obtain topographic images of the surfaces of the samples. The AFM measures the surface topography by tracking the AFM cantilever deflection using a laser beam reflected from the cantilever as the cantilever tip scans the surface. As the cantilever bounces vertically, the reflected laser beam reveals information about the vertical height of the sample surface. This AFM has a lateral resolution of 1–5 nm and a vertical resolution of 0.08 nm. The V-shaped nanoprobe cantilevers were made from silicon nitride (Si$_3$N$_4$) with a normal spring constant of 0.06 N/m and a nominal tip radius of 20–60 nm. The length of each cantilever was 100 and 200 µm respectively. The tips are shaped like a pyramid with 35° angles on all four sides. A tip with 0.12 m/s spring constant was used in the present study. The resulting images consisted of 512×512 pixels, and the scanning frequency was 1 Hz. The Digital Nanoscope software version 5.12b [177] was used to analyse the surface roughness profiles of the samples.

3.2.4 Focus ion beam microscope (FIB)

An XT Nova Nanolab 2000 workstation which integrates a dual beam high resolution focused ion beam and a high scanning electron microscope (FIB/SEM) were used to characterise the surface morphology of the specimen after oxidation, and prepare cross sectional specimens for further observation. A fine, energetic beam of gallium ions employed as the focused ion beam miller can scan over the surface of a specimen. As high beam currents the gallium beam rapidly sputters the surface of the specimen away,
which allows sub-surface cross sections to be prepared [178]. If the beam current is reduced, high resolution images can be formed by the emission of secondary electrons or ions from the surface of the specimen. During this FIB cross sectioning an accelerating voltage of 30 kV and high ion currents were used, and lower currents of 1 nA and 0.5 nA were used for nano-milling.

### 3.2.5 Triple ion beam cutter (TIC) system

A Leica EM TIC020 triple ion beam cutter system (Fig. 3.4) is used for precise processing of oxidised samples for subsequent cross sectional examination with electron microscopes. The ion cutting process was performed using argon ions that were ionised and accelerated by high voltage so they collide with the sample and displace surface atoms. This system generates ions in an energy range from 1 to 8 keV. The sample is shielded by a mask so that a 90° cut (cross section) is created into the sample. For cross sectional analysis of oxide scale, the edges of the oxidised sample were ground using SiC paper of 2000 grit and ion-milled at 6 kV for 5 h using the ion miller.

![Photograph of Leica EM TIC020 triple ion beam cutter system.](image)
3.2.6 Electron backscatter diffraction (EBSD)

Simultaneous EBSD-EDS analysis was performed on the Oxford Instruments Channel 5 EBSD system mounted on a JEOL JSM 7001F Schottky field emission gun-scanning electron microscope (FEG-SEM). The microstructure, phase identification, the crystallographic texture, and internal stresses were determined on oxidised specimens, and element distributions are accessed by EDS. Electron backscatter diffraction patterns (EBSPs) are observed when a fixed, focused electron beam is positioned on a specimen at 70° tilt, which maximises the yield of backscattered electrons in the direction of the scintillation screen [179, 180]. This system also provides a transmission kikuchi diffraction (TKD) mode where the short working distance (WD between 2 and 3.5 mm) in backscatter electron (BSE) detector as a complement. Channel 5 software suite fully integrated with image collection, versatile EBSD analysis and phase identification, was used to acquire the online texture information and analyse the offline scanning maps. The experimental parameters in this measurement were an accelerating voltage of 15 kV and incident beam currents of 1–50 nA, with a step size of 0.125 μm.

3.2.7 X-ray diffractometer (XRD)

An x-ray diffraction (XRD) using a GBC MMA diffractometer with mono-chromated Cu-\( K_{\alpha} \) radiation was used to detect the phase composition of the samples before and after oxidation. To determine the appropriate reflectors, a powder diffraction file (PDF) for iron oxides was obtained from the International Centre of Diffraction Data (ICDD) database. The operating voltage and current of the x-ray beam were set at 35 kV and 28.6 mA, respectively.
3.3 Summary

This chapter was devoted to the main instruments and important analytical techniques applied in this research, as listed in Table 3.1. Details of the experimental parameters and testing procedures will be given in the following chapters. Some experimental works, such as profilometers for measuring the surface roughness and dilatation tests for mechanical properties of the steel substrate, were also sparing in their use of examined cases in the corresponding sections.

Table 3.1 Summary of the experimental instruments and analytical methodology

<table>
<thead>
<tr>
<th>Item</th>
<th>Selection mode</th>
<th>Objective</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTM</td>
<td>Initial oxidation (&lt;30s)</td>
<td>Microstructure</td>
<td></td>
</tr>
<tr>
<td>Gleeble</td>
<td>Short time oxidation (960s)</td>
<td>Effect of water vapour</td>
<td>Oxidation test</td>
</tr>
<tr>
<td>HR-AC</td>
<td>Simulated hot rolling</td>
<td>Effect of TR &amp; CR</td>
<td>HR-AC test</td>
</tr>
<tr>
<td>UMT</td>
<td>Pin-on-disc schematics</td>
<td>Tribological properties</td>
<td>Tribological test</td>
</tr>
<tr>
<td>OM</td>
<td></td>
<td>Pore/thickness</td>
<td>Microscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>LV-SEM</td>
<td>Morphologies</td>
<td></td>
</tr>
<tr>
<td>AFM</td>
<td>Contact mode</td>
<td>Surface roughness</td>
<td></td>
</tr>
<tr>
<td>FIB</td>
<td>Milling mode</td>
<td>Sample sectioning</td>
<td></td>
</tr>
<tr>
<td>Ion Miller</td>
<td>Milling mode</td>
<td>Sample preparation</td>
<td></td>
</tr>
<tr>
<td>EBSD</td>
<td></td>
<td>Crystallographic texture</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td>General</td>
<td>Phase characterisation</td>
<td>Diffractometry</td>
</tr>
</tbody>
</table>
The prevailing concept of this chapter to characterise the initial oxidation behaviour of fine-grained Nb-V-Ti microalloyed steel in a wide range of temperatures under dry air, thereby to establish the constitutive relationship between the grain size of the steel substrate and that of the corresponding oxide scale. A series of isothermal initial oxidation tests were conducted in a high temperature microscope (HTM) with a charge-coupled device (CCD) camera as a detector. A variety of microscopy techniques were employed to study the morphology of the oxide scales formed and the nature of the oxide phases. An attempt has also been made to find what type of the steel substrate can generate this oxide scale, and further to delve the mechanism of their formation.

4.1 Experimental methods

4.1.1 Material and sample preparation

The material used was a commercial low-carbon microalloyed steel for an automotive beam. The chemical compositions of the studied samples are tabulated in Table 4.1. In order to fit into the heating stage sample holder, metal coupons containing the crucible with the external diameter of 5 mm and the inner diameter of 4 mm was used for the
high temperature oxidation for in situ exposures. The steel samples were sectioned into 2.7 mm × 2.7 mm × 2 mm thick pieces using a Struers Accutum-50 cutting machine. One of the broad faces on the samples was ground using SiC papers of 2400 mesh to a surface finish of 0.6 µm. Prior to the experiments, the samples were cleaned in ethanol using ultrasonic agitation and then stored in a desiccator. In addition, the dilatometry tests were carried out to determine dynamic continuous cooling transformation of the microalloyed steel, and the obtained austenitisation starting and finishing temperatures can be applied into the initial oxidation tests during heat treatment cycles. The dilatometry samples were 10 mm long hollow cylinders with a 5 mm diameter and 0.75 mm wall thickness, and were machined from the 5 mm microalloyed plate.

Table 4.1 Chemical composition of the microalloyed steel (wt%).

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>P</th>
<th>Al</th>
<th>V</th>
<th>Nb</th>
<th>Ti</th>
<th>S</th>
<th>N</th>
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</thead>
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<tr>
<td></td>
<td>0.1</td>
<td>0.15</td>
<td>1.61</td>
<td>0.21</td>
<td>0.014</td>
<td>0.034</td>
<td>0.041</td>
<td>0.041</td>
<td>0.016</td>
<td>0.002</td>
<td>0.003</td>
</tr>
</tbody>
</table>

4.1.2 Oxidation procedure

The initial oxidation tests were conducted in HTM using a CCD camera as a detector at temperatures of 550, 600, 750, and 850 °C. The following procedure was used for each oxidation experiment: (1) the sample was heated to 1050 °C at a rate of 1.7 °C/s under a high purity argon atmosphere, and held for about 5 min to homogenise the austenite grains; (2) the sample was then cooled to the desired temperatures at a rate of 1.7 °C/s and held for 0.5–2 min; (3) the protective gas was switched to industry-purity air at the desired flow rate for a duration of 30 s at a constant temperature; (4) the oxidation gas was switched off and (5) high purity argon was switched back to prevent further
oxidation, and then the sample was cooled to room temperature at a rate of 1.7 °C/s. This heat-treatment schedule is illustrated schematically in Fig. 4.1. It should be noted that the oxidation time was based on the industrial hot rolling process. The total time for the formation of tertiary oxide scale was 26 s in Table 4.2. Therefore, an exposure time of 30 s was used in the present oxidation experiments.

![Fig. 4.1 Schematic illustration of the heat treatment procedure in initial oxidation tests.](image)

**Table 4.2** Inter-stand time from descaler 2 to exit of F6 on the finishing mill for typical rolling, including the contact times in the roll-bite.

<table>
<thead>
<tr>
<th></th>
<th>Desc-F1</th>
<th>F1-F2</th>
<th>F2-F3</th>
<th>F3-F4</th>
<th>F4-F5</th>
<th>F5-F6</th>
<th>F6-F7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time inter-stand (s)</td>
<td>8.2</td>
<td>5.7</td>
<td>4.1</td>
<td>2.9</td>
<td>2.3</td>
<td>1.7</td>
<td>1.2</td>
</tr>
<tr>
<td>Accumulated time(s)</td>
<td>8.2</td>
<td>13.9</td>
<td>18.0</td>
<td>20.9</td>
<td>23.2</td>
<td>24.9</td>
<td>26.1</td>
</tr>
</tbody>
</table>

During the oxidation tests, an industrial compressed air was used as the dry oxidising gas. A stainless steel tube with the diameter of 3 mm was positioned on top of the sample holder so that the oxidising gas was directly injected onto the surface of the polished sample. By blowing air directly onto the specimen surface, the influence of a
varying oxygen partial pressure on the kinetics of oxidation is minimised [171]. It is therefore more likely that the specimen surface would be exposed to an instantaneous and constant partial pressure of oxygen of 0.21 atm during oxidation. The compressed air was introduced at a constant flow rate of $3.1 \times 10^{-5} \text{ m}^3/\text{s}$, rendering a velocity of 12 m/s. The flow rate of the inert gas was varied between $6 \times 10^{-6}$ and $5 \times 10^{-5} \text{ m}^3/\text{s}$.

Additionally, the dilatometry tests were conducted in a Theta II high speed thermo-mechanical simulator. The specimens were heated to the temperature of 1200 °C at a heating rate of 20 °C/s, held for 180 s to dissolve microalloyed carbides, and then cooled to room temperature at different rates.

### 4.1.3 Analytical methodology

The surface topography after oxidation was immediately examined in a Nanoscope IIIA atomic force microscope (AFM) in order to prevent the surface of the sample from being contaminated after each oxidation experiment. Several images were recorded at different locations for all samples to verify the reproducibility of the observed features. Then Au deposition, the samples were coated in epoxy resin to protect the oxide scale. For cross-sectional analysis, the edges of the sample were ground on 2000 grit SiC paper, and ion-milled at 6 kV for 5 h using a Ticx 020 Leica cross-sectional ion miller. A JEOL-JSM 6490 SEM and An XT Nova Nanolab 2000 FIB microscope were used to investigate the surface morphology, microstructures and the thickness of the oxide scale. These measurements for the thickness of the oxide scale can be used to define oxidation kinetics based on image analysis. A GBC MMA diffractometer with monochromated Cu-$K\alpha$ radiation was used to detect the phase composition of the samples after oxidation. Others associated with EBSD will be addressed in Chapter 6.
4.2 Results

4.2.1 Characterisation of the microalloyed steel

Prior to the oxidation experiments, the properties of the microalloyed steel substrate were analysed. Fig. 4.2a and b present typical OM and SEM images of the surface morphology of the etched steel using 2% nital solution for 20 s. The microstructure of steel substrate consists of 94% fine-grained polygonal ferrite and 6% perlite at a cooling rate of 20 °C/s and a cooling temperature of 660 °C. The grain size of the polygonal ferrite was determined as 3 µm by using circular intercept method according to ASTM: E112-10. The fine and dispersive pearlite are in the matrix of ferrite. High magnification SEM image (Fig. 4.2b) indicates that most of fine-grained ferrite in the microalloyed steel, where the bright line in Fig. 4.2b refers the grain boundaries in the steel substrate. The XRD spectrum of polished steel (Fig. 4.2c) indicates there is only ferrite present in the steel substrate because it was difficult to detect all the minor elements present by XRD [181]. Fig. 4.2d shows a typical dilatation vs. temperature curve of the steel specimens at the heating rate of 20 °C/s. The specimen contracts during heating although the increase of temperature as a result of the microstructure rearrangement during phase transformation. From this curve, the starting and finishing of phase transformation can be easily detected in Fig. 4.2d, where \( A_{c1} \) and \( A_{c3} \) are 725 and 865 °C, respectively. Previous experiments [182] indicate that the transformation zone of ferrite and pearlite is about 550–750 °C and the transformation zone of bainite is about 410–580 °C. The dilatation tests provide that the studied steel has broad process window to produce the ferrite-pearlite steel or ferrite-bainite steel.
Chapter 4 Isothermal oxidation of the microalloyed steel

Fig. 4.2 (a) OM microstructure of the microalloyed steel substrate showing polygonal ferrite and pearlite, (b) SEM image for surface morphology of the polygonal ferrite, (c) XRD pattern and (d) dilatation versus temperature curve of the steel specimens at the heating rate of 20 °C /s. $A_{c1}$ and $A_{c3}$ are the starting and finishing temperatures of austenitisation during heating.

4.2.2 In situ oxidation observation

Fig. 4.3 provides a series of in situ frames from the first 30 s of the oxidation experiments in industrial dry air at 550 °C, showing the initial formation and growth of oxide scale on the surface of the sample. The colour on the surface of the sample changed as the oxidation time proceeded. This may be due to variations in the thickness of the oxide scale, but other factors such as different oxide orientation and surface
conditions can also affect the colour change. Fig. 4.3a shows the microstructure of the sample that was heated to 1050 °C under argon seal and held for 5 min. Since the starting temperature in the austenite single phase zone, the microstructure is the pancaked austenite due to heavy deformed in the austenite unrecrystallization zone. The microstructure of the sample before air was introduced in Fig. 4.3c includes the clear grain boundaries of initial austenite. It is evident from Fig. 4.3d that oxidation initially took place at the grain boundaries after the oxidising gas exposure. The oxide scale spread rapidly over the steel substrate and the colour in the grains changed, as shown in Fig. 4.3d. As the oxidation time proceeded by 1 s (Fig. 4.3e), the oxide scale continued to grow, but it took about 30 s for a complete oxide scale to form, which is similar to the formation of tertiary oxide scale. The oxide scale after cooling in protective gas for 39 s (Fig. 4.3f), where the obvious boundaries can be observed as the oxide scale shrunk.

The cause to present the oxidation at 550 °C is based on a previous study [93, 183]. Generally, it was hard to detect the oxide growth at this temperature in dry air where magnetite is stable. Similar oxidation behaviours were observed at temperatures of 600, 750 and 850 °C. The oxide scale that formed during cooling in a protective atmosphere also shows the surface of the sample contracting, whereas at 750 °C there was only slight contraction due to rapid oxidation. With an increase of the oxidation temperature, the growth rates of the oxide scale increased significantly, so no more than 1 s was required for the oxide scale to cover the whole sample surface. It is noted that the surface grain size of the steel substrate has no dramatic change below 1050 °C [184, 185]. This allows the grain growth mostly occurs during recovery and recrystallization [186, 187]. Therefore, the selection of the different starting cooling temperatures aims to obtain spatial non-uniformity in the matrix grain size.
Fig. 4.3 Snapshots from video recorded an in situ for the formation and growth of oxide scale on the surface of the specimen for 30 s oxidation in dry air, (a) austenitising of steel substrate at 1050 °C, (b) at 850 °C, (c) transformed phase of steel substrate, (d) introduction of oxidising gas at 550 °C, (e) in oxidation process, and (f) the oxide scale under the protective gas cooling. The time indicated in the figure is the programme proceeding time rather than oxidation time.
4.2.3 Surface morphology and cross section characterisation

Fig. 4.4 presents the surface morphology of the formed oxide scale after oxidation tests at temperatures of 550, 600, 750 and 850 °C. The dashed lines marked indicate that the grains of the steel substrate and formed oxide share the same ridges. At 550 °C (Fig. 4.4a), less surface roughened other than along the grain boundaries, which indicates a minor oxidation occurred. These protrusions were sparsely observed along certain boundaries on the uniform surface of the oxidised samples at 600 °C (Fig. 4.4b). Although the surface morphology oxidised at 750 °C (Fig. 4.4c) becomes more homogenous, there are much higher oxides protruding from the grain boundaries, and some pores and micro-cracks also dispersed on the entire region. This could be attributed to the rapid oxidation at 750 °C and the accumulation of thermal stress caused by the subsequent cooling after oxidation process. Fig. 4.4d shows the surface oxides developed at 850 °C has regions of localised spallation and blistering failure. High magnification SEM images in Fig. 4.4e and f show that the spalling of oxide scale occurred at the centre of grains of the microalloyed steel substrate after oxidation at 850 °C. It is clearly seen that the grain boundaries of the steel substrate under the debris of oxide scale (Fig. 4.4f). This shows that the regions with different growth rates are related to the oxidation originating from the central of metal grains or at grain boundaries [171]. The relationship between different growth rates and the locations of the underlying grains could be seen in all the exposed environments. In the temperature range of 550 and 750 °C, the transformation of ferrite and pearlite in the microalloyed steel could occur as indicated by the results from dilatometry tests described above. Since it has been widely reported [1, 18, 60, 146] that the phase composition of oxide scale is more important than the thickness for the integrity of an oxide layer, the results
described here provide another possibility for dissecting the adherence properties of oxide scale associated with the grains size of the microalloyed steel substrate as a result from oxidation temperatures.

Fig. 4.4 SEM images of the oxidised samples 30 s exposure to dry air at (a) 550 °C, (b) 600 °C, (c) 750 °C, (d) 850 °C, (e) spallation of oxide scale occurred at the centre of grains of the microalloyed steel substrate after oxidation at 850 °C, (f) enlarge image of (e), where the dashed lines mark the ridge boundaries of the steel substrates.
In cross section, the tight oxide scale has different morphologies formed on the fine-grained (Fig. 4.5a) and coarse-grained steel substrates (Fig. 4.5b). For the fine-grained steel substrate, the oxide scale appeared uniformed in morphology, which is well adherent to the homogeneous grains of the steel substrate (Fig. 4.5a). While the oxide scale developed on the coarse-grained steel has regions of localised spallation failure, which is prominent when covering the non-uniformed grains of the steel substrate (Fig. 4.5b). Therefore, the homogeneous grains of the steel substrate can possibly enhance the potential contribution of grain-boundary diffusion to the integrity of the oxide scale [124, 51]. These results suggest that the adhesive failure at the steel/oxide interface could be caused by the compressive stress within the intergranular oxide scale sparsely formed on the coarse-grain steel substrate during the cooling process. Specifically, a representative EBSD grain size map for the steel substrate after oxidation at 850 °C (Fig. 4.5c) shows the grain size of the polygonal ferrite is about 10–20 µm, where grain size with large grains in red, small in blue. Here the distribution of grain size in the outer layer is much non-uniform than that of in the inner layer across the cross section. The spatial non-homogeneity of the grain size could cause adhesion properties of oxide scale to deteriorate. Further, the distribution of grain boundaries of the steel substrate in Fig. 4.5d indicates the presence of high-angle grain boundaries, which could have significant effects on the oxidation rate of the steel substrate. This will be discussed in Section 4.3.1.
Fig. 4.5 Cross sections of tight oxide scale formed on (a) fine-grained and (b) coarse-grained steel substrate. (c) Representative EBSD grain size map for the steel substrate after oxidation at 850 °C, (d) Histogram of grain boundaries of the steel substrate.

In addition, the cross-sectional characterisation of oxidised samples aims to further determine the mechanism of steel/oxide separation occurring at the interface itself (adhesive failure) or near it (cohesive failure) [135]. SEM images of FIB cross sections in Fig. 4.6 show the morphologies of oxide scale developed on the steel substrate at 550 and 600 °C in dry air. Many failures at 550 °C (Fig. 4.6b) are really cohesive in the oxide near the interface and involve oxide growth stresses, oxide and metal plasticity...
and thermal cycling effects due to differential thermal contraction. By contrast, adhesive failures appeared at 600 °C (Fig. 4.6d) relate to interfacial energy, and can affect the steady-state interface morphology, varying from impurity segregation and even the physical contact at asperities. Therefore, these results indicate the oxide scale formed at 550 °C depends significantly on the growth stress, mechanical properties of oxide scale and heat treatment, whereas, the oxide scale at 600 °C depends on alloying element accumulated and surface topography of the steel substrate. It suggests that the major effect properties of the oxide scale and the corresponding steel substrate has on the integrity of oxide scale.

**Fig. 4.6** SEM images of FIB cross sections showing the morphology of oxide scales developed on the steel substrate at (a, b) 550 °C and (c, d) 600 °C.
These features of the oxide failure described above mean that the separation stress within the oxide scale is less than the separation stress at the oxide/steel interface at temperature up to the 550 °C, and exceeded above 600 °C (Fig. 4.7). This result extends the adhesive properties of oxide scale at temperatures range of 850–870 °C during the FEM modelling assumption [1]. These stresses cause behind could be due to the volume changes associated with phase transformation in the steel substrate while heating or cooling the samples, which can lead to separation stresses in the oxide scale.

![Temperature vs Separation Stress Graph]

**Fig. 4.7** Schematic representation of the effect of temperature on the stresses separating the oxide scale and steel substrate.

### 4.2.4 Surface topography

In order to quantify the surface roughness of the oxidised samples, the surface topography was measured. **Fig. 4.8** shows the AFM images of the surface topography of the samples before (Fig. 4.8a) and after 30 s oxidation at temperatures of 550 and 600 °C in air. At 550 °C, the surface of sample shows mild oxidisation with a relative smooth surface topography, as shown in **Fig. 4.8b**. Further oxidation at 600 °C results in
the oxides protruding from the surface (Fig. 4.8c). It can be seen that the roughness of the surface increased significantly at higher temperatures, which suggests that the oxidation temperature exerts considerable influence on the oxidised surface topography of the microalloyed steel. It also indicates that a very low surface roughness value could be obtained with a lower oxidation temperature and a shorter exposure time in the air.

Fig. 4.8 AFM images of the surface topography of samples (a) prior to the oxidation test, and after 30 s oxidation at different temperatures in air, (b) 550 °C, (c) 600 °C, and (d) 750 °C.
4.2.5 X-ray structural analysis

After in situ analysis of high temperature oxidation, the oxide scale generated at the temperatures of 550, 600 and 750 °C were detected using x-ray diffraction technique at room temperature, as shown in Fig. 4.9. The composition of oxide scale is consistent with the expected oxidation behaviour at the intermediate temperature. The predominant oxide is magnetite with smaller amounts of sparse hematite and ferrite during the early oxidation stage. The variation of oxidation temperature has significantly influence on the phase composition of oxide scale, particularly, in the case of multiple oxide phases formed at the temperature of 750 °C. Nevertheless, it can be noted that there is few retain wustite phase as a product of initial oxidation, which indicates that wustite decomposition could be completed at this intermediate temperature. This is possibly due to that the high density of the grain boundaries of the steel substrate causes the diffusion of cation/anion ions to take place the phase transition Fe_{1-x}O \rightarrow Fe_3O_4.

![X-ray diffraction patterns of oxide scale formed at 550, 600 and 750 °C.](image)

**Fig. 4.9** X-ray diffraction patterns of oxide scale formed at 550, 600 and 750 °C.
4.3 Discussion

4.3.1 Initiation of oxidation mechanism

The oxidation rate can be expressed by the slope of the curve plotting the measured thickness of the oxide scale versus oxidation time based on SEM cross sectional image analysis. In this case, the variation in oxidation rates among the specimens is the greatest during the early stage, with the highest rates generally corresponding to the specimen with the largest grain size. Fig. 4.10 is an Arrhenius plot of the parabolic oxidation rate constants drawn from the oxidation of the low carbon steel [51] and the microalloyed steel in this experiment. The equation for the solid line is,

$$k_p = 260 \exp\left(-\frac{179200}{RT}\right)$$

(4.1)

where a least squares calculation of $k_p$ values for the fine-grained microalloyed steel. The data points of the steel substrate at 850 °C were excluded because of the structural irregularities in the oxide scale (Fig. 4.4) caused by the oxide/metal separation under the cooling process. The data given by the solid line are therefore considered to truly represent the growth of uniform, adherent, and multi-phased FeO-Fe$_3$O$_4$-Fe$_2$O$_3$ oxide scale on the fine grained steel substrate. It is noted that the absence of wustite below 570 °C could affect the variation of the overall oxidation rate. The previous calculations [69, 188] show that the reason for the decrease in the oxidation rate of Fe-Cu alloys with respect to pure iron is related to the practical disappearance of wustite from the oxide scales.
Fig. 4.10 Arrhenius plot of final parabolic rate constant. Activation energy for growth of uniform, adherent polycrystalline oxide scale (solid line) is 179.2 kJ/mol; data from the literature [51] is added for comparison.

The dot line in Fig. 4.10 is the least squares solution for \( k_p \),

\[
k_p = 340 \exp\left(\frac{-50800}{RT}\right)
\]  

(4. 2)

where scattered value drawn from Ref [51] for the low carbon steel. The data of the dot line have appreciably different activation energies, possibly because of poorer adhesion properties in oxide scale, although this could not be confirmed from their publication. The higher \( k_p \) values and the slightly lower activation energy in solid line reflect the finer grain size of the initial formed oxide and the fact that cations diffuse preferentially along grain boundaries.
Compared the parabolic rate constants of previous studies [20, 51, 68, 89] with the present work, the solid line signified the current study lies along the upper limit of the spread of $k_p$ values for the dot line. The activation energy of 179.2 kJ/mol corresponds closely to that of iron reported 194.9 kJ/mol (46.6 kcal/mol) between 640 and 805 °C [68]. Further, the lower value of activation energy exactly approximates to that 174.5 kJ/mol for Fe in the Fe grain boundaries diffusion between 530 and 650 °C [189].

According to Fisher’s model, enhanced element migration occurred in the grain boundary domains assuming a thickness of 50 nm [190]. This value corresponds to the thickness of the experimentally observed grain boundary oxides. It is known that the activation energy for grain-boundary diffusion decrease with increasing grain-boundary energy [191]. This kind of high-angle grain boundaries in Fig. 4.5d with higher energy might be especially helpful for grain boundary diffusion. Therefore, the smaller grain size and the higher grain-boundary energy can play an important role in increasing the effective diffusion coefficient of iron-ions and oxygen in steel substrate at intermediate temperature as a result of grain-boundary diffusion. In this investigation, the higher rate constants and the lower activation energy are considered to be the fine-grained steel substrate which accelerates preferential diffusion along grain boundaries during the early stage oxidation.

### 4.3.2 Effect grain refinement of the steel substrate on tight oxide scale

#### 4.3.2.1 Magnetite formation

Enhanced grain-boundary diffusion in the initial oxidation suggests that decreasing the grain size of the steel substrate could alter the diffusion process, and thereby to change
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the overall composition of oxide scale, which could be responsible for high desired magnetite content (more than 75%) in the proposed tight oxide scale. The fine-grained steel substrate has a large number of grain boundaries serve as ‘short-circuit’ channels for ions diffusion in the early stage oxidation \[3, 192–195\]. The inward diffusion of oxygen along the grain boundaries can be involved as a result of rapid grain-boundary diffusion through the oxide scale and the enhanced solid solubility of oxygen in the steel substrate. By this mechanism, the oxide scale is believed to grown on both sides: the reaction of iron-ions and oxygen at the oxide/air interface and the reaction of oxygen with the steel substrate near the oxide/steel interface. So there exists much more oxygen-rich layer (magnetite phase) in the fine-grained substrate than that in the coarse grained steel.

Moreover, metal and oxygen react to form a thin layer of oxide scale whose composition more-or-less mirrors the compositions of the steel substrate as the short-time oxidation during hot rolling. The alloying elements contained, such as manganese, chromium and silicon, could contribute to the early stage oxidation similar to those discussed in detail in Refs. \[107, 138, 196, 197\]. It is believed that selective oxidation of manganese and chromium occurred at grain boundaries on the surface \[197\], or dispersed all the cross-section oxide scale \[107, 197\], even further to lower the wustite point \[138\]. Normally, silicon was observed accumulating at the oxide scale/steel interface \[40, 198\]. In any case, the transport of these ions is generally via lattice or grain boundary diffusion \[3\]. Therefore, the increase of diffusion paths as the decrease of the grain size could enhance the accumulation of these alloying elements at the grain boundaries.
To further interpret these, the role of grain-boundary diffusion can be illustrated using a mathematical model with a corresponding effective-diffusivity coefficient of the species ($D_{\text{eff}}$),

$$D_{\text{eff}}=(1-f)D_L + fD_{GB}$$  \hspace{1cm} (4.3)

where $D_L$ and $D_{GB}$ are the diffusion coefficients in the lattice and along the grain boundaries, respectively, and $f$ is the area proportion of grain boundary. Assuming that grains have the shape of spheres or cubes, the volume fraction of interfaces $f$ may be estimated as $2\delta/d$ (where $\delta$ is grain-boundary width and $d$ is the average grain diameter). The grain-boundary width $\delta$ is of the order of an interatomic distance and $\delta \sim 0.5 \text{ nm}$ is a widely accepted value [190, 194, 195]. Since $D_{GB}>>D_L$ in most cases, Eq. 4.3 can be simplified as,

$$D_{\text{eff}} = D_L + \frac{2\delta}{d} D_{GB}$$  \hspace{1cm} (4.4)

If the grain size $d$ is very small, the $D_{\text{eff}}$ is dominated by the second term on the right side of the equation. The increase of the $D_{\text{eff}}$ thus depends on the relative magnitude of $D_L$ and $D_{GB}$, and the temperature dependence of $D_L$ and $D_{GB}$. Normally, grain-boundary diffusion has smaller activation energy than lattice diffusion, so that the ratio $D_{GB}/D_L$ decreases as the temperature increase [190]. Therefore, $D_{\text{eff}}$ increases dramatically with a decrease of $d$ at intermediate temperatures. If assuming $D_{\text{eff}}^*$ as the effective diffusivity of ions in the coarse-grained ($d = 10 \mu$m), Fig. 4.11 illustrates the ratio of $D_{\text{eff}}/D_{\text{eff}}^*$ is enhanced by grain refinement. For instance, if $d$ is reduced from the reference $10 \mu$m to
3 \, \mu m in this work, \( D_{\text{eff}} \) is about 1 order of magnitude larger than that of \( D_{\text{eff}}^* \) in the case of \( D_{\text{GB}}/D_L = 10^2 \), and over 2 orders of magnitude larger when \( D_{\text{GB}}/D_L \) equals \( 10^3 \) and \( 10^6 \).

Fig. 4.11 Relationship between the effective diffusivity ratio \( D_{\text{eff}}/D_{\text{eff}}^* \) and the grain size of the steel substrate \( d \), where the reference one \( D_{\text{eff}}^* \) with the grain size of 10 \, \mu m. This demonstrates that \( D_{\text{eff}} \) is enhanced by grain refinement.

### 4.3.2.2 Adhesion properties

Surface spallation failure did not occur on the fine-gained steel oxidised at 550 and 600 °C (Fig. 4.4a, b), whereas, the oxide scale which formed on the coarse-grained steel at 850 °C was often buckled between grains of the steel substrate (Fig. 4.4e) during cooling to room temperature. Two factors can account for the difference: first, the grain size of oxides is limited by the smaller grain size of the steel substrate, and is therefore sufficiently small to allow plastic deformation; secondly, the more numerous steel gain boundaries provide enough vacancy sinks to suppress spallation formation. Even though no clear trend or relationship has apparently been established between the grain size of
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the metal and that of the corresponding oxide scale, the oxide scale growth on fine-grain materials also tends to have smaller oxide grains [199]. In our experiments, some of these processes were underway during the initial oxidation period.

It should be pointed out here that the failure of the oxide scale is connected with the grain size non-uniformity of the corresponding steel substrate. The spallation of oxide scale corresponding to the coarse-grained surface at 850 °C (Fig. 4.4e) was found in some regions, whereas other regions were covered by the tight oxide scale formed on fine grained substrate (Fig. 4.4d). Another type of microstructural non-uniformity occurred in the cross section of the steel substrate (Fig. 4.5b), where indicated the formation of coarse-grained zones arranged in the outer layer of the steel substrate. Whatever the type, microstructure non-uniformity of the steel substrate is detrimental to adhesion properties of oxide scale, and should be avoided. A spatial non-homogeneity of the grain development could be a result of either non-uniformity in the matrix grain size or non-uniformity in the particle distribution or both of them [200]. The heat treatment is normally characterised by strain non-homogeneity across the cross section with the strain being greater in the outer layer. In any case, the data presented here could be related to the above types of microstructural non-uniformity.

Oxide/steel interface failures at 550 °C were really cohesive in the oxide near the interface, whereas, adhesive failures appeared at 600 °C at the oxide/steel interface (Fig. 4.6). This result further implies the steel substrate has significant influence on the integrity of the oxide scale and the mechanism of steel/oxide separation. Based on these findings, grain refinement effect of the steel substrate on adhesive properties was proposed to reveal spalllation and formation mechanism of the tight oxide scale, as
schematically shown in Fig. 4.12. The higher concentration gradient of the ions diffusion in the coarse-grained steel appears at the grain boundaries, which result in the non-uniform oxidation over the entire surface of the steel substrate (Fig. 4.12a). The oxide scale generated on the coarse-grains steel substrate thereby leads to the non-homogenous compressive stress. The residual stress can be relived during the subsequent cooling process and further some spallation failure observed on the steel substrate at room temperature (Fig. 4.12b). In comparison with coarse-grained steel, the intergranular oxide scale formed on the fine-grained steel can act as a wedge when cooling to the room temperature (Fig. 4.12d). As such, homogenous compressive stress can be dispersed in uniform oxide scale formed.

Fig. 4.12 Schematic diagram of spalling mechanism of oxide scale, (a) the oxide scale formed on coarse-grained steel substrate, (b) spallation failure by compressive stress when cooling, (c) the oxide scale formed on fine-grained steel substrate, (d) the formation of the tight oxide scale when cooling down to room temperature.
In addition to grain size of the steel substrate, different phase microstructures could be another trigger to cause adhesion properties of the oxide scale to deteriorate. From dynamic continuous cooling transformation diagram [185], the microstructure of steel substrate consists of ferrite and pearlite at a cooling rate of 1.7 °C/s and a starting cooling temperature of 550 and 600°C in this study. The duration, i.e. the holding time 2 min and the following 30 s oxidation, is much longer than the incubation time 100 s, to allow phase transformation of the steel substrate. While, the steel substrate starting cooling from 750 and 850 °C is in the austenite single phase zone. Therefore, the variation in diffusion rates of cation/anion ions through austenite and ferrite matrix [3, 171, 201] could have a certain effect on the initial oxidation process, and on the adhesion properties of the formed oxide scale.

In addition, the type of crystallographic surface also significantly affects the final topographies of oxide scale. The grain orientation of metal substrate has previously been proposed to affect the oxide growth at 350 °C [91]. It was found that the growth of oxides on a single crystal (001) surface was much faster than that on a single crystal (112) surface. It is therefore plausible to predict a similar effect could be exerted on the initial oxidation of microalloyed steel in this study, leading to the variation of adhesion properties.

4.4 Summary

Initial oxidation behaviour of the microalloyed steel was investigated through austenitising at 1050 °C then cooling to 550, 600, 750 and 850 °C by 1.7 °C/s, and following 30 s oxidation in dry air. A formation mechanism of the tight oxide scale was
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proposed to elucidate effects of grain refinement in the steel substrate on high desired magnetite content and the integrity of the oxide scale. The following conclusions can be drawn in this present work.

1. The surface spallation failure of oxide scale occurred at the centre of grains of the microalloyed steel substrate on the oxidation initiation. The oxide scale grown on the coarse-grain steel substrate can cause adhesive properties to deteriorate when cooling to the room temperature. This grain refinement effect is more sensitive to the oxide scale formed at 550 °C than that formed at 600 °C.

2. High and uniform magnetite content obtained in the proposed tight oxide scale could attribute to enhanced grain-boundary diffusion as a result of increasing high density of the grain boundaries of the fine-grained steel substrate. The higher values of oxidation rate constant and the slightly lower activation energy provide compelling evidence that the initial oxide scale grows on both cation/anion ions migration along oxide grain boundaries.

3. The advantageous approach by grain refinement at initial oxidation was proposed to increase the magnetite content to form the pickle-free tight oxide scale, which is promising potential for the application of the automotive microalloyed steel.
Influence of processing parameters on the precipitation of magnetite from grown wustite

The formation of oxide scale is affected by processing parameters in Fig. 5.1, such as the thickness reduction (TR), cooling rate (CR), finishing temperature (FT), coiling temperature (CT), and the cooling conditions under which the coils are stored. This is a principal concern of this chapter. Hot rolling combined with accelerated cooling (HR-AC) tests and subsequent grain reconstruction via EBSD technique was conducted to characterise the influence of different TRs and CRs on the oxidation of microalloyed low carbon steel over a wide range of temperatures. The EBSD applications to the study of phase transformation in tertiary oxide scale delivers accurate and quantitative data about the morphology and crystallography of oxide scale, e.g. crystallographic phases, crystallographic texture and misorientation distribution. An attempt has also been made to establish the formation mechanism of magnetite seam at the oxide/steel interface and the transformation behaviour of magnetite to hematite based on the stress relief, surface energy minimisation, and propagation of cracks along grain boundaries in magnetite. In addition, a chemical reaction mechanism for the decomposition of thermally grown wustite was developed to delineate the constitutive relationship between the phase evolution with oxidation and temperature. Pilot-plant on the influence of FT/CT is included in the list of publications 9, 10 and 14 without exhaustive here.
Fig. 5.1 Experimental plan for exploring the influence factors on the formation of the tight oxide scale.

5.1 Experimental and analytical methodology

5.1.1 Material and experimental procedure

The material used was a microalloyed steel with its chemical compositions listed in Table 4.1. The steel samples were cut into 400×100×3 mm³ sections with a tapered edge (see publication list Nos. 7 and 8). Prior to the experiments, the specimens were
ground using SiC paper of 2400 grit to a surface finish of 0.5 µm and cleaned in a solution of acetone. The following procedure was carried out during the HR-AC tests. Each specimen was reheated to 900 °C in the furnace in a nitrogen atmosphere and soaked for 15 min to ensure a uniform temperature. Upon removal from the furnace, each specimen was placed on the entry roll platform of the rolling mill and allowed to air cool to a predetermined temperature, after which each individual strip was given a single rolling reduction at a rolling speed of 0.3 m/s. The rolled specimen was cooled by an AC system down to the CT (600–350 °C) at different CRs. This experimental procedure is illustrated schematically in Fig. 5.2. The experimental conditions used in hot rolling and AC tests are also listed in Table 5.1. The surface morphology and microstructure after HR-AC tests were examined in a JEOL JSM 6490 SEM/EDS and A Keyence VHX-1000E Digital microscope (OM). The surface roughness of oxide scale after deformation was measured by a TR220 profilometer.

Fig. 5.2 Schematic diagram of laboratory processing schedule used to HR-AC tests.
Table 5.1 Experimental conditions used in HR-AC tests

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<th>Value</th>
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<tr>
<td>Furnace atmosphere</td>
<td>Nitrogen</td>
</tr>
<tr>
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</tr>
<tr>
<td>Air cooling before rolling, s</td>
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<tr>
<td>Table cooling time, s</td>
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</tbody>
</table>

5.1.2 Analytical methodology

Three samples selected for EBSD mapping are used to analyse the evolution of surface texture and transformation mechanism of magnetite to hematite after HR-AC test. Samples 221, 232 and 432 are highlighted in Table 5.2. After HR-AC tests samples were cut from the centre of the hot-rolled sheet along the RD-ND plane. For the samples after gold deposition, the edges for cross-sectional analysis were ground by SiC papers with 2400 mesh, and then ion-milled at 6 kV for 5 h using a TIC020 system. Thereafter, the sample surface of oxide growth is defined as the ND. The gauge length and width of the sample were parallel to the RD and TD of the hot-rolled strip, respectively.

Simultaneous EBSD-EDS analysis was performed on a JEOL JSM 7001F Schottky FEG-SEM with a Nordlys-II (S) EBSD detector, an 80 mm² X-Max EDS detector and the Oxford Instruments Aztec acquisition software suite. The sample was tilted 70°, and
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the corresponding EBSD map was acquired at an acceleration voltage of 15 kV, a probe current of around 2–5 nA, and a working distance of 15 mm. According to the average grain size and different thickness of the oxide scale after HR-AC tests, the fine step sizes were assigned 0.125, 0.095 0.125 µm to the TRs of 10%, 23% and 28%, respectively. Correspondingly, the areas of these EBSD maps were 120 × 90, 120 × 62 and 160 × 105 µm².

Post-processing of the acquired dataset was carried out using the Oxford Instruments Channel 5 software package. All the EBSD maps were first cleaned by removing wild orientation spikes and then filled in zero solutions via extrapolation up to six neighbours. In order to reduce orientation noise and concurrently retain orientation contrast information, an angular resolution for the grain reconstruction was maintained at a constant value of 2°. Consequently, $2° \leq \theta < 15°$ misorientations are defined as low-angle grain boundaries (LAGBs), whereas, the high-angle grain boundaries (HAGBs) are $\theta \geq 15°$. Secondly, phase analysis in EBSD can be conducted by feeding the structural data related to the crystal symmetry and lattice parameters of the suspected phases into the software. In this case, each phase found in the sample has a different space group (ferrite, Im$\bar{3}$m; wustite, Fm$\bar{3}$m; magnetite, Fd$\bar{3}$m; hematite, R$\bar{3}$c), and different lattice parameters, i.e. ferrite, wustite and magnetite in cubic symmetry with lattice parameters (a) of 0.287 nm, 0.431 nm, and 0.840 nm respectively, and hematite in a trigonal structure with $a=0.504$ nm and $b=1.377$ nm [95, 126, 202]. Finally for texture-based analysis, the EBSD phase maps were then divided into four subsets comprising ferrite, wustite, magnetite and hematite. Orientation distributions of the four subsets were calculated from the data on individual grain orientations collected. The grain orientation $g = (\phi_1, \Phi, \phi_2)$ is expressed by the three Euler angles in Bunge notation. [203] Ferrite and
magnetite have a cubic structure and their orientation distribution function (ODF) sections are depicted using the $\phi_2=0^\circ$ and $45^\circ$, for hexagonal hematite the ODF sections with $\phi_2=0^\circ$ and $30^\circ$ are used, in contrast. Note that ODF sections were calculated using the discrete binning method with a bin size of $5^\circ$ and Gaussian smoothing.

5.2 Results

5.2.1 Temperature variation

For the newly developed accelerated cooling (AC) system, Fig. 5.3 shows how the 8 controlled water spray nozzles were placed at the top and bottom of the run-out table. Two thermal detectors were positioned at entry and exit of the cooling system. In this case the initial temperature of the strips was around $760^\circ C$ and the final cooling temperature ranged from $600$ to $350^\circ C$. The wide range of CRs (10 to 100 °C/s) can be obtained by adjusting the valves on the spray nozzles.

**Fig. 5.3** Experimental arrangements of the 8 controlled water spray nozzles at the top and bottom the run-out table in AC system.
5.2.2 Effect of the cooling rate

For various CRs after HR-AC tests, the oxide scale has been characterised through the surface cracking, as indicated in Figs. 5.4 and 5.5. These failure features are more apparent at the edge of the strip from the CRs of 10 to 100 °C/s. With a CR of 50 °C/s, a few long and narrow cracks were produced across the width of the strip, there were more large cracks in the oxide scale, but when the CR increased to 100 °C/s, the secondary cracks near the edge were wider than in the central region and become curved in the rolling direction. The regularly spaced cracking curvature could correspond to inhomogeneous plastic deformation which resulted from the strip widening at the roll gap [204]. As for the TR of 5%, an increasing cracking spacing can be observed in Fig. 5.5 as the CR increased, but the extent of the cracking was relatively alleviated compared with those TRs of 20% and 40%.

Fig. 5.4 Surface cracking of oxide scale after a TR of 20%, the CRs of (a) 50 °C/s, (b) 100 °C/s, at the strip centre, (c) 10 °C/s, (d) 50 °C/s, and (e) 100 °C/s, at the strip edge.
Fig. 5.5 Micro cracks of oxide scale after the TR of 5% and the CRs of (a) 10 °C/s, (b) 20 °C/s, and (c) 50 °C/s.

The relationship between the CRs and adhesion of the oxide scale after HR-AC tests was established according to the cross sectional cracking shown in Fig. 5.6. The images at the right side were obtained using the binarisation processing based on the original OM images corresponding to the CRs. The failures occurred in the oxide scale generally have some micro-holes and cohesive oxide failure within the oxide scale, adhesive oxide failure at the interface of the oxide scale and steel substrate [135]. The oxidised sample cooled at 10 °C/s appears to be intact and the oxide layer adhered, although with some scattered pores. With the CR of 20 °C/s, the cross sectional morphology of oxide scale is either adherent or not along the thickness with some brittle cracks and attached debris. There is a great deal of small debris in the oxide scale cooled at 40 °C/s, and the
out-layer of oxide scale was in smaller pieces. When the CR increased to 100 °C/s, the oxide scale was badly damaged and showed poor adherence, although some small pieces of oxide remained attached next to regions that were almost free of scale. The results indicate that the adhesion properties of the oxide scale are quite well when the CRs were less than 20 °C/s.

**Fig. 5.6** SEM (left) and binary (right) images of cross-sectional oxide scale at the CRs of (a) 10 °C/s, (b) 20 °C/s, (c) 40 °C/s, and (d) 100 °C/s.

Furthermore, the higher magnification images (**Fig. 5.7**) show that possible failures occurred in the oxide scale: some micro-holes (**Fig. 5.7c**) and cohesive oxide failure (**Fig. 5.7 b, d**) within the oxide scale, adhesive oxide failure at the interface of the oxide scale and steel substrate (**Fig. 5.7e**). These observations suggest that the failures of the oxide scale to adhere could be attributed to the compression stresses that developed as the oxide layers grew and then cooled. This could be explained by the compression stresses that developed as the oxide layers grew and then cooled.
Fig. 5.7 Failures occurred in the oxide scale, (a) cohesive oxide failure in the inner layer enlarged in (b) and some micro-holes enlarging in (c), (d) cohesive oxide failure in the outer-layer, (e) adhesive oxide failure.

5.2.3 Effect of thickness reduction

Oxide scale has been characterised through different TRs in terms of macro cracking, surface morphology and cross sectional examinations. A series of semi-continuous transverse cracks were observed at the edge of the hot-rolled strip, as shown in Fig. 5.8. The cracking depth and width above were measured after different TRs and CRs in HR-AC tests in Fig. 5.9. In most cases, small cracks can be obtained at a CR of 20 °C/s and a TR of 12%. There are relatively small differences between the cracking depth and width of the oxide scale at the CRs below 20 °C/s. It inferred that the temperature variation on surface and underneath of the steel induces the uniformity of thermal stress, and thus lead to the surface cracking. At a higher TR, the crack spacing was found to be
5–10% narrower than the others. This is possibly because the plastic elongation of the surface of the strip occurs near the roll gap, whereas, the sub-surface material shears to generate plastic compression in the thickness direction.

**Fig. 5.8** Macro cracks in oxide scale, (a) full profile, (b) the depth of the cracks in the transverse direction, (c) the crack width measured along the rolling direction.

**Fig. 5.9** Edge cracking of oxide scale at different (a) CRs, and (b) TRs.

The variation of surface morphologies was driven by various TRs during HR-AC tests. **Fig. 5.10** shows the surface morphologies of the hot-rolled samples at different TRs. The oxidised microalloyed steels exhibit a much smoother surface as the TR increased from 5% to 40%. There are larger areas with blistering at the TR of 5%, whereas, the
narrow cracking in brighter colour appeared that of 40%. This could be attributed to plastic flow in the oxide scale occurred at the entry of the roll gap during hot rolling.

![Fig. 5.10 Surface morphology of oxide scale at the TRs of, (a) 10%, (b) 20%, (c) 30% and (d) 40%.

With the cross sectional morphology, various cracking failure such as blistering and extrusion were examined on the basis of different thickness of oxide scale and TRs, as indicated in Fig. 5.11. The oxide scale with the thickness less than 15 µm can be expected a plastic elongation at the TR of 15%, whereas, that of much thicker than 100 µm has plastic flow at a lower TR. The extrusion of the fresh steel will be happened at much higher TRs. In any case, the fracture at the roll gap became more significant under a TR of more than 15 % to analyse the ductility of the oxide scale.
5.2.4 The variation of surface roughness

The deformation behaviour of the oxide scale formed the microalloyed steel depends on the plastic flow of materials during fast cooling after hot rolling. Fig. 5.12 reveals that the surface roughness (surface asperity) tends to be flattened as the TRs increases. The value of average surface roughness, $Ra$, reduced by about 57.9% as the TR increased from 10% ($Ra=2.416 \, \mu m$) to 20% ($Ra=0.985 \, \mu m$). This decrease in surface roughness as the TR increases confirms our previous calculated results [152], and this could be due to reduction of surface asperity. Nevertheless, there is only 14.5% increase in surface roughness at the CRs from 50 $^\circ$C/s ($Ra=0.957 \, \mu m$) to 100 $^\circ$C/s ($Ra=1.105 \, \mu m$). One possible reason is that the nucleation of the oxide scale at the higher CRs is greatly
inhibited as insufficient time for atomic inter-diffusion. Although there is a possible influence of friction between the rolls and sample, the sample surface will be fundamentally flat due to the rolling effect. Therefore, surface slip leads to surface scratches in the area where the contact stress is large and metal flow in different areas are very different [205, 206]. It is probable that a certain crystallographic orientation of near-surface grains plays a significant role in the development of the surface roughness.

![Surface profiles of the oxidised sample](image)

**Fig. 5.12** Surface profiles of the oxidised samples at (a) the TRs of 10%, (b) 20%, (c) the CRs of 50 °C/s, and (d) 100 °C/s.

### 5.2.5 Phase evolution of oxide scale

**Fig. 5.13** presents cross sectional BSE images of oxide scale formed at 550 °C, where the outer layer of magnetite, the layer of eutectoid and the oxide/steel interface are easily seen. Magnetite with its dark grey colour dominates the outer layer (**Fig. 5.13c**) and the oxide/steel interface (**Fig. 5.13d**), and scattered in the eutectoid layer (**Fig. 5.13b**). These investigations can be used to elucidate formation of the magnetite seam at the oxide/steel interface.


Fig. 5.13 (a, b) BSE images of the oxide scale formed at 550 °C, (c) the outer layer, (d) the interface of the oxide scale and the steel.

Fig. 5.14 shows the results of the horizontal and cross sectional direction EDS line scanning analysis from the external oxide scale in Fig. 5.13. In a horizontal direction the oxide scale (Fig. 5.14b) shows no specific fluctuation of elemental contents even though the line crossed several oxide grain boundaries. The cross sectional direction data (Fig. 5.14c) shows that the Mn diffused at the top surface of the oxide scale and Si accumulated at the oxide/steel interface (Fig. 5.14d). The reason could be that the Gibbs free energy reduction with iron spinel solid solution formation in hematite at high oxygen partial pressure [207] induced a bulk diffusion of Mn through grains of hematite to the top surface of the external oxide scale. Further investigation on the distribution of alloying elements, such as silicon and manganese, will be addressed in detail via advanced simultaneous EBSD/EDS analysis in Section 5.2.6.1.
5.2.6 Texture based analysis of tertiary oxide scale

5.2.6.1 Phase identification of the oxide layers

Fig. 5.15 shows EBSD phase maps of the samples reheated at 900 °C, cooled to 860 °C with the TRs and CRs of 10%, 10 °C/s; 13%, 23 °C/s; and 28%, 28 °C/s, respectively. The oxide scale consists of a two-layered microstructure with a thin outer layer of
hematite and an inner duplex magnetite layer, particularly, a seam of small globular grains next to the steel substrate. This noticeable layer of fine magnetite grains was found at the interface of the oxide scale and steel substrate, which become much flattening as the increase of the TR and CR (Fig. 5.15c). What is more, the retained wustite and eutectoid ferrite scattered sparsely all around the magnetite matrix. Hematite near the surface penetrates gradually into the cracks within the oxide scale shown in Fig. 5.15a and b, and its distribution reduces dramatically as the decrease of pores or cracks corresponding to that of the TR and CR of 28%, 28 °C/s.

**Fig. 5.15** EBSD phase maps for ferrite, wustite, magnetite and hematite of the samples with the TRs and CRs of (a) 10%, 10 °C/s, (b) 13%, 23 °C/s, and (c) 28%, 28 °C/s.
Furthermore, the distinct magnetite seam at the oxide scale/steel interface and the penetration of hematite can be further verified by simultaneous EDS chemical composition mapping via colour coding, as shown in Fig. 5.16. Here silicon is found to enrich at the oxide scale/steel interface (Fig. 5.16c), where fine-grained magnetite grows.

The formation of hematite along the crack of magnetite grains can be found in Fig. 5.16b, where the distribution of oxygen element has a relatively high intensity. In addition, manganese in Fig. 5.16d spreads sparsely over the entire oxide scale.

**Fig. 5.16** EDS maps of the sample at a TR of 10% and a CR of 10 °C/s (Fig. 5.15a), (a) iron map, (b) oxygen map, (c) silicon map, and (d) manganese map.
5.2.6.2 Orientation analysis

As seen in Fig. 5.17, the corresponding areas on inverse pole figure (IPF) maps show the evolution of the microstructure with progressively greater TRs and CRs. The grain boundary maps is also overlaid on corresponding IPF map, where LAGBs >2° as grey lines and HAGBS >15° as black lines. Grains with the colour coded displayed their orientations is related to a stereographical triangle, where Fig. 5.17d for the cubic symmetry material, such as wustite, magnetite and ferrite, while Fig. 5.17e for the hexagonal hematite. The intermediate magnetite layer on the IPF maps holds a columnar-shape microstructure between the outer granular grains and the magnetite seam, possibly attributed to the retained wustite during the lateral grain growth at high temperature [136, 202] The sample at the high TR and CR of 28%, 28 °C/s has also produced large amount of granular magnetite grains (2–3 μm in size in Fig. 5.17c). The most magnetite grains have the preferred orientation with <001> parallel to the ND, i.e. along the oxide growth direction, as the increase of the TRs and CRs. The grain growth of magnetite with <001>//ND texture may be determined by the minimisation of surface energy (SE), where the SE of the crystallographic planes magnetite are: SE(100)=1.5, SE(110)=1.8 and SE(111)=2.2 J m⁻² parallel to the oxide growth [202, 208]. Nevertheless, the lack of this sharp texture in magnetite of the sample at the lower TR and CR (Fig. 5.17a) suggests that the rolling process and subsequent cooling affect the texture and grain size of the formed oxide scale. Indeed, previous results also reveal that the (001) planes of magnetite depends critically on sample preparation and heat treatment [34]. In case of hematite with a strong preferential crystallographic orientation in the normal direction of the (0001) basal plane, the texture strength is thought to be driven by the low surface energy (1.52J m⁻²) of the (0001) plane of hematite [209].
Fig. 5.17 EBSD IPF orientation maps of the samples at the TRs and CRs of (a) 10%, 10 °C/s, (b) 13%, 23 °C/s, (c) 28%, 28 °C/s, a colour key for the (d) cubic symmetry of ferrite, wustite, and magnetite, and (e) hexagonal hematite.

5.2.6.3 Grain boundary characters

To investigate the formation and propagation of cracks along grain boundaries in magnetite and thereby resulting texture evolution, Fig. 5.18 provides the distributions of misorientation axes/angle (≥15°) of the sample after a TR of 10% and CR of 10 °C/s.
The distribution of misorientations axes for magnetite in angle ranges has been processed to give a high proportion of coincident site lattice (CSL) boundaries. The peaks in the 57–63° section (Fig. 5.18a) correspond to 60°/<111> (Σ3) misorientation marked in Fig. 5.18c. Misorientation peaks occur in hematite (Fig. 5.18b) for axes near <0001> in the angle range of 27–63°, and <1102> in the angle range of 63–83°. The distribution of misorientation angles (Fig. 5.18c) in cubic crystals has a maximum at 45° and a cutoff at 62.8°, whereas hexagonal hematite has a maximum at 60° and a cutoff at 95°. For hematite the relatively high densities correspond to 57.42°/<1210> (Σ13b) and 84.78°/<0110> (Σ19c) [210]. In addition to HGABs developed, magnetite contains very few LGABS at the TR of 13% and CR of 23 °C/s (Fig. 5.17b), whereas most of LGABs were found in the sample with the high TR (Fig. 5.17c). It is further inferred that the coupled effect of TR and CR could be imposed on wustite decomposition into magnetite below the eutectoid point of 570 °C [9, 20]. Indeed, the grain-refined magnetite could be affected by wustite decomposition of hot-rolled samples cooling from high temperature [6, 9]. In any case, these grain boundary characters in magnetite and hematite can provide deep insight for the penetration of hematite into magnetite scale during air cooling after hot rolling. This is possibly due to the low-temperature decomposed magnetite inherits from wustite phase at high temperature oxidation [10, 16]. Subsequently, the formation of emerging hematite from magnetite matrix could be explained by the transformation of fcc to hcp between magnetite and hematite. Both of transformation mechanism can also be affected by propagation of cracks along different types of grain boundaries in a parent phase. It is therefore suggested that a coupled effect of TR and CR could be essential to how texture and grain boundary take place in deformed oxide scale during HR-AC tests.
5.2.6.4 Texture development of the steel substrate, magnetite and hematite

In contrast to most fcc materials where after deformation generally peak type textures are found, the textures of bcc ferrite and cubic iron oxides are mostly fibrous in nature, i.e. that the orientation are concentrated along tubes running through the Euler space [180]. Fig. 5.19 shows schematically the ideal fibres in cubic materials and ODF distribution positions for hexagonal hematite for selected sections of fixed $\phi_2$ angles [99, 126, 180, 211–216]. The most relevant texture fibres for cubic materials are $\alpha$, $\gamma$ and $\epsilon$.
fibres lying on $\phi_2=45^\circ$ section at $\phi_1=0^\circ$, $\phi_1=55^\circ$, $\phi_1=90^\circ$, corresponding to crystallographic fibre axis around $<110>/\text{RD}$, $<111>/\text{ND}$, and $<011>/\text{TD}$, respectively, and $\eta$, $\theta$ and $\zeta$ fibres superimposed on $\phi_2=0^\circ$ section at $\phi_1=0^\circ$, $\phi_1=0^\circ$ and $\phi_1=45^\circ$, with the rotations of $<100>/\text{RD}$, $<100>/\text{ND}$ and $<110>/\text{ND}$, respectively. For hexagonal materials, the characteristics of the $\{0001\}<10\overline{1}0>$ and $\{0001\}<2\overline{1}\overline{1}0>$ texture components are given in terms of the Bunge system [180, 208, 213–217], also as shown in Table 5.3.

**Fig. 5.19** Schematic representation of the position of the (a) ideal fibres in cubic materials in the $\phi_2=0^\circ$ and $45^\circ$ ODF sections, and (b) important texture components in hexagonal materials in the $\phi_2=0^\circ$ and $30^\circ$ ODF sections.

The development of texture acquired ferrite, magnetite and hematite after HR-AC tests and their intensity distribution along associated fibres or texture components are shown.
in Figs. 5.20–23. It should be mentioned here ferrite was confined to the steel substrate rather than the eutectoid product in the oxide scale. Texture of the steel substrate (Figs. 5.20–22a) is weak exhibiting mainly shear components. It would be expected the $\zeta$ and $\epsilon$ fibres (Fig. 5.23a and b) in the surface region of a hot-rolled strip [19, 95, 126, 180], or dynamic phase transformation of deformed austenite during reheating and hot rolling [126, 218]. The texture of ferrite at the TR of 28% and CR of 28 °C/s (Fig. 5.22a) is much similar to the previous observation that the undeformed interstitial free (IF) steel substrate oxidised at 900 °C in free flowing air shows a strong ND rotated cube component [21]. Clearly, the strength of crystallographic texture in the steel substrate can be enhanced dramatically as the increase of oxidation temperatures, TRs and CRs [18, 19, 95, 202].

In analogy to the texture of ferrite at high temperature oxidation (similar to Fig. 5.22a), magnetite also holds a strong \{001\}<110> rotated cube component at a low TR and CR (Fig. 5.20b). With the increase of the TRs and CRs in Figs. 5.21 and 22, magnetite develops a strong $\theta$ fibre including \{100\}<001> cube and \{001\}<110> rotated cube components. These cube orientations slightly shift toward the <210> direction and finally lead to a relatively strong \{100\}<210> component with the intensity of $f(g)$=7.4 for magnetite, as shown in Fig. 5.23d. Since $\theta$ fibre was also found at the undeformed wustite left at 950 °C and 650 °C after reheating at 1050 °C [18, 19, 22, 126, 202, 219], it is inferred that the occurrence of \{100\}<001> cube and \{001\}<110> rotated cube components can be attributed to grain growth during high temperature oxidation, whereas, the \{100\}<210> texture dominates during subsequent deformation by external force. Nevertheless, in this case it cannot be seen any texture components along \{111\} close-packed planes in the most fcc materials.
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Fig. 5.20 $\phi_2=0^\circ$ and $45^\circ$ ODF sections for (a) ferrite, (b) magnetite, and (c) $\phi_2=0^\circ$ and $30^\circ$ ODF sections for hematite, of the samples at a TR of 10% and a CR of $10^\circ$C/s.
Fig. 5.21 $\phi_2=0^\circ$ and $45^\circ$ ODF sections for (a) ferrite, (b) magnetite, and (c) $\phi_2=0^\circ$ and $30^\circ$ ODF sections for hematite, of the samples at a TR of 13%, and a CR of 23 °C/s.
Fig. 5.22 $\phi_2=0^\circ$ and $45^\circ$ ODF sections for (a) ferrite, (b) magnetite, and (c) $\phi_2=0^\circ$ and $30^\circ$ ODF sections for hematite, of the samples at a TR of 28%, and a CR of 28°C/s.
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Fig. 5.23 Development of texture intensity $f(g)$ along the (a) $\zeta$, and (b) $\varepsilon$ fibres of ferrite, (c) $\theta$ and (d) $<110>$ fibres of magnetite, of the samples at the TRs of 10%, 13% and 28%, and the CRs of 10, 23, 28 °C/s.

As seen in Figs. 5.20–22c, the characteristic texture evolution of hematite in deformed oxide layers with increasing TRs and CRs are represented for the $\phi_z=0$ and $30^\circ$ ODF sections due to its trigonal crystal symmetry. The texture of hematite is composed of a
fibre running along {0001} basal planes which includes a dominant {0001}<10\overline{1}0> and relatively weak {0001}<2\overline{1}\overline{1}0> texture components. Specifically, a mixture orientations of {1\overline{2}\overline{1}0}<10\overline{1}0> and {0\overline{1}\overline{1}0}<2\overline{1}\overline{1}0> components with the maximum texture intensity of \( f(g) = 17.22 \) (Fig. 5.20c) is found in hematite at a TR of 10% and a CR of 10 °C/s. A principal activated {0001}<2\overline{1}\overline{1}0> fibre in Fig. 5.21c with the relatively high intensity of \( f(g) = 7.5 \) then occurred in hematite at a relatively high CR of 23 °C/s. Eventually, a {0001}<10\overline{1}0> texture component recorded a maximum intensity of \( f(g) = 14.4 \) in hematite at a high TR of 28% and CR of 28 °C/s (Fig. 5.22c). Hematite in a hexagonal structure generally has independent slip systems, namely {0001}<2 \overline{1} 0>, {1\overline{2}10}<10\overline{1}0>, {1\overline{2}10}<10\overline{1}1>, {1\overline{1}0}2<01\overline{1}1>, and {10\overline{1}0}<01\overline{1}1> [211, 217]. In this case, the rolling texture development of hematite has a strong {0001}<10 \overline{1}0> component, which is a direct consequence of the favored basal plane slip [180, 210].

5.3 Discussion

5.3.1 Discussion on eutectoid reaction mechanism

In order to better understand the possible reaction pathways that occur in the oxide layers, and which lead to a particular composition, a series of phase transformations were investigated based on experimental observations combined with the Fe-O phase diagram [6]. Generally, wustite decomposition was naturally classified into a high temperature proeutectoid above 570 °C and a partial eutectoid transformation below 570 °C, as marked regions A and B in Fig. 5.24. The above classification of phase transformation was effective for understanding the possible reaction paths that occur in
the oxide scale to obtain the desired composition of oxides by adjusting the processing parameters.

**Fig. 5.24** Schematic enlargement of Fe-O equilibrium phase diagram indicating the possible reaction pathways during coiling cooling after hot rolling.

Since the desired oxide scale has the same magnetite and retained wustite during cooling after hot rolling, it can be indicated by the average composition of point \(a\) through the region A in **Fig. 5.24**. The experimental results revealed that iron cations enable diffusion from the steel substrate into the oxide scale to occur after cooling at a sufficiently high temperature. This takes place after some reaction with the magnetite, until all magnetite has been consumed. The diffusion of iron cations into the wustite also results in the formation of an iron-rich type of wustite. These phenomena are demonstrated by the reaction path \(a \rightarrow b \rightarrow c\), and are represented by the following reactions.

\[
Fe_3O_4 + (1-4x)Fe \rightarrow 4Fe_{1-x}O \tag{5.1}
\]

\[
Fe_{1-x}O + (x-y)Fe \rightarrow 4Fe_{1-y}O \tag{5.2}
\]
**Fig. 5.24** shows there are essential differences with respect to the decomposition of oxygen-rich or iron-rich wustite. When an oxygen-rich type of wustite cools down depicted as the point $b$, it will intersect the boundary of the wustite phase field at point $d$ above a temperature of 570 °C. Some phase separation is thermodynamically favourable as the cooling process proceeds, one is magnetite (point $e'$) whereas wustite follows its phase boundary downwards and thus becomes more iron-rich (point $e$). The proeutectoid magnetite formation at region A above 570 °C from grown wustite followed reaction path $b \rightarrow d \rightarrow e/e'$. It also implies that wustite decomposition always involves the formation of iron-rich wustite and magnetite.

\[(1-4z)Fe_{1-z}O \rightarrow (1-4x)Fe_{1-x}O + (x-z)Fe_3O_4 \quad (z < x) \quad (5.3)\]

Therefore, the high temperature proeutectoid transformation above 570 °C is usually related to the case of slow cooling between point $d$ and 570 °C. In the case of fast cooling, especially with a CT below 570 °C, the partial eutectoid transformation into magnetite and ferrite is the thermodynamically preferred reaction \textbf{Eq. 5.4}, as shown in region B in \textbf{Fig. 5.24}.

\[4Fe_{1-x}O \rightarrow Fe_3O_4 + (1-4x)Fe \quad (5.4)\]

It is possible that a high temperature promotes the diffusion of iron from the steel substrate into the wustite, as well as the kinetics of iron-rich wustite being considerably slower than oxygen-rich wustite [118]. This can be explained by the different reaction paths illustrated in \textbf{Fig. 5.24}. Here an oxygen-rich type of wustite follows the reaction
path $b \rightarrow d \rightarrow f$ whereas an iron-rich of wustite follows the reaction path $c \rightarrow g$. Furthermore, the distance between point $d$ and the finishing line is much larger than the gap between point $g$ and the same finishing line. This provides strong evidence that thermodynamic driving force of oxygen-rich wustite is greater than iron-rich wustite. Moreover, the experimental results in region B confirm that Eq. 5.3 can also occur below 570 °C, simultaneously with the thermodynamically preferred Eq. 5.4, presumably because of Eq. 5.3 is without nucleation of the $\alpha$-Fe particles.

### 5.3.2 Microstructural evolution of oxide scale during hot rolling

On the basis of these experimental findings above, we will now consider the probable mechanisms for the microstructural evolution associated with phase transformations within the oxide scale during hot rolling. Accordingly, a schematic illustration of the microstructural evolution within the oxide layers at low and high TRs is proposed in Fig. 5.25, concurrently considering the tribological effect of hematite at the contact surface of steel and roll during hot rolling. Fig. 5.25a shows the initial wustite-magnetite microstructure at high temperature processing. On hot rolling (Fig. 5.25b) the cold rolls compressing to the surface of hot steels, this temperature gradient leads to the formation of hematite as the outer-layer oxide scale. The elongated wustite in the inner layer decomposes mainly into magnetite as the surface temperature of steel sample decreases, and finally the retained wustite sparsely scatters in the magnetite matrix, which corresponds to the experimental results shown in Fig. 5.15. For the oxide scale subjected to a low TR in Fig. 5.25c, the formation and propagation of cracks along the magnetite grain boundaries create paths for easy air penetration, and therewith allow further oxidation to hematite (Fig. 5.15a). This fracture regime also occurred in thin
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oxide layer of other alloys, called oxide cracking elsewhere [134, 208, 220]. It is believed that low-angle and low-ΣCSL boundaries in microstructure offer obstacles to the propagation of cracks, as they minimise the solute effects and reduce the interaction between the interfaces and glissile dislocation [186, 221]. In this case, the oxide scale is easy to crack in presence of Σ13b and Σ19c in hematite compared to Σ3 in magnetite (Fig. 5.18c). Nevertheless, a high proportion of LAGBs are found in all three phases of oxidised sample at a high TR of 28% in Fig. 5.17c, which resulting just little oxide scale cracking (Fig. 5.15c). As such, a large amount of fine granular magnetite grains with relatively dense arrangement can suppress the transformation of magnetite to hematite by oxidation of Fe$^{2+}$ to Fe$^{3+}$ (Fig. 5.25d). This is the similar case for prediction of hydrogen embrittlement and stress-aided grain boundary oxidation ahead of cracks [220, 222, 223].

**Fig. 5.25** Schematic illustration of microstructure evolutions of the oxide scale (a) before, (b) during, (c) a low TR, and (d) a high TR, after, hot rolling.
5.3.3 Formation mechanism of magnetite seam at the oxide/steel interface

The stress relieving mechanism [22, 217, 224] governing magnetite seam can be supported from two respects in this study. One is the enrichment of silicon at the oxide scale/steel interface (Fig. 5.16c), and another is the presence of θ fibre texture in magnetite layer. Generally, the accumulation of silicon element to the surface of the oxidised steel occurs before hot rolling based on a thermal equilibrium in FeO-SiO$_2$ phase diagram [102]. Thus, it is possible that the existence of irregularly shaped lamellar enriched silicon oxides layer can enhance the formation of magnetite at the interface of oxide/steel. Another, magnetite shares <100> fibre texture, also called θ fibre, with first-growing wustite[19, 126, 198]. It can be inferred that magnetite grains are first nucleated rather than the second oxidising due to the detachment of the oxide scale [34]. Since the fibrous grain shape stemming from over the magnetite seam near the oxide/steel interface (Fig. 5.17), this result may partly suggest that a lateral growth strain could exist during the high temperature oxidation. After HR-AC tests the stress relief could be occurred at the oxide/steel interface, where is almost strain-free. The transformed magnetite grains form through nucleation and grain growth by diffusion [9–11]. These results suggest that the preferred grain orientation of magnetite seam may well depend on the texture and concurrent of cations/anions at the oxide/steel interface. This is similar to those newly influential ideas [220] that stress-aided grain boundary diffusion at the interfacial local regions. It is also agreed with previous studies [22, 219] that the magnetite growth is governed by concurrent processes of inner oxide growth and its relaxation. As such, the stress-assisted oxidation is real and not just due to a detachment from the substrate. Thus, it is possible that during this time, the texture evolution can provide new insight into means of suppressing magnetite seam when it is
undesired and into means of producing specific layered structure when it is desired. In our experiments, some of these processes, such as tailoring the texture of initial magnetite, are underway during the grain growth of magnetite due to stress relief of the oxide scale and steel substrate.

5.3.4 Transformation mechanism of magnetite to hematite

Transformation of magnetite to hematite by oxidation of Fe$^{2+}$ to Fe$^{3+}$ can be another closely related process, which can be affected by the observed texture evolution in deformed oxide layers. Fe$^{2+}$ ions oxidised to Fe$^{3+}$ during high-temperature short-time processing, in case of hot rolling less than 30 s, [4] are largely dependent on crystallographic similarities of magnetite and hematite. (111) planes of magnetite and (0001) planes of hematite are both parallel and perpendicular to the three-fold axes. For magnetite, the oxygen ions layer in perfect cubic close-packed array has the separation distance of 2.42 Å along [110] direction. Hematite has a hexagonal close-packed array with a separation distance of 2.29 Å along [0001] direction. For a fcc crystal interfaced to a hcp crystal, the preferred orientation relationship is given by (111)$_{fcc}$//(0001)$_{hcp}$ and ($\bar{1}10$)$_{fcc}$//(10$\bar{1}$0)$_{hcp}$, where the close-packed planes and directions are matched across the interface [225–227]. According to the texture evolution of magnetite in deformed oxide layer in Figs. 5.21b, 5.22b and 5.23c, the formed magnetite after thermodynamically unstable wustite has <001> fibre texture. As such, a hematite layer will grow on the (001) planes of magnetite rather than the closed-packed planes (111). Because the interplanar angle between (111) and (001) planes is 54.76° in cubic structure, it is inferred that hematite grains must grow at an angle of 54.76° from the <001> crystal direction of magnetite. This is also agreed with previous findings [18, 202]. Thus, Fe$^{2+}$
ions resulting from diffusion at magnetite boundaries react with oxygen, and oxidise as thin platelets of hematite with $c$-axes perpendicular to the oxide growth and the $a$-axes in the plane of oxide growth ($\{0001\}<10\overline{1}0>$ texture component). These results confirm that if hematite grows on a (100) magnetite, its grains will be titled at an angle of 54.76° to the magnetite matrix, whereas for a (111) magnetite, the epitaxial growth of hematite (0001) will occur. Similar result has been recently reported for other single crystal oxide scales [225]. Hence, these findings can open a way for the decrease and further easy removal of hematite during hot rolling. On the one hand, a desired TR is assigned to reduce the occurrence of the cracking along the grain boundary of the magnetite grains in deformed oxide layer, thereby to minimise the further oxidation leading to the penetration of hematite wedging through cracks. On the other hand, to tailor the texture of initial magnetite to {111} components using particular lubrication, a uniform hematite layer can grow on the (111) planes of magnetite so as to avoid the hematite growth titling 54.76° from the (100) magnetite matrix. This is practically important to dramatically alleviate air pollution from ‘red scale’ (hematite) during high-temperature steel processing.

5.4 Summary

Effects of TRs and CRs in HR-AC tests on the deformation behaviour of oxide scale were investigated in detail in this chapter. Microstructure and texture evolution in the deformed oxide scale formed on the microalloyed steel and their influences on the formation of magnetite seam at the oxide/steel interface, and the fcc-hep transformation of magnetite to hematite were systematically analysed.
1. The increase in the CRs from 10 to 100 °C/s leads to significant cracks of the oxide scale. The uniform surface morphologies and good adhesion properties of oxide scale can be achieved at a CR of 20 °C/s and a TR below 12%. The surface roughness is lower while the integrity of oxide scale deteriorates as the TRs increases from 5 to 40%.

2. The oxide scale consisting of a thin hematite outer layer and an inner duplex magnetite layer, develops a high proportion of low-angle and low-\(\Sigma\)CSL boundaries, magnetite for 60°/<111> (\(\Sigma\)3), and hematite for 57.42°/<1\(\bar{2}\)10> (\(\Sigma\)13b) and 84.78°/<0\(\bar{1}\)10> (\(\Sigma\)19c). Grain refinement of magnetite (2–3 µm) at a TR of 28% can suppress the penetration of hematite into the oxide scale.

3. Magnetite develops a strong \(\theta\) fibre parallel to the oxide growth, which includes \{100\}<001> and \{001\}<110> texture components, resulting from the minimisation of surface energy for \{100\} planes of magnetite. In contrast, \{0001\}<\(\bar{1}\)010> component dominates in hematite as the favored basal plane slip. The Hematite growth on \(\theta\) fibre magnetite is 54.76° titled from the <001> crystal direction of magnetite.

4. A possible reaction pathway was also proposed to obtain the desired phase composition of the oxide scale. The stress relieving mechanism for the formation of fine-grained magnetite seam at the oxide/steel interface has been proposed based on the enrichment of silicon therein and the presence of \(\theta\) fibre texture in magnetite layer. Preferential crystallographic orientation of magnetite grains played an important role in fcc-hcp transformation of magnetite to hematite. In the case of \(\theta\) fibre in magnetite, the hematite growth is 54.76° titled from the <001> crystal direction of magnetite.
Table 5.2 Some experimental results for HR-AC tests.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Entry temperature °C</th>
<th>Exit temperature °C</th>
<th>Valve setting</th>
<th>Cooling rate (expected) °C/s</th>
<th>Cooling rate (measured) °C/s</th>
<th>Reduction (expected) %</th>
<th>Reduction (measured) %</th>
<th>Roughness Ra, μm</th>
<th>Cracking observed</th>
</tr>
</thead>
<tbody>
<tr>
<td>522</td>
<td>806</td>
<td>494</td>
<td>2, 20%</td>
<td>50</td>
<td>52</td>
<td>5</td>
<td>1.83</td>
<td>2.098</td>
<td>Lead/edge</td>
</tr>
<tr>
<td>531</td>
<td>808</td>
<td>746</td>
<td>3, 10%</td>
<td>10</td>
<td>10</td>
<td>5</td>
<td>3.42</td>
<td>1.621</td>
<td>Head/edge</td>
</tr>
<tr>
<td>532</td>
<td>798</td>
<td>643</td>
<td>3, 20%</td>
<td>100</td>
<td>25</td>
<td>5</td>
<td>5.25</td>
<td>2.518</td>
<td>Centre/edge</td>
</tr>
<tr>
<td>535</td>
<td>815</td>
<td>698</td>
<td>3, 5%</td>
<td>50</td>
<td>20</td>
<td>5</td>
<td>4</td>
<td>2.416</td>
<td>Centre/edge</td>
</tr>
<tr>
<td>221</td>
<td>785</td>
<td>728</td>
<td>2, 10%</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>10.08</td>
<td>0.985</td>
<td>Edge</td>
</tr>
<tr>
<td>232</td>
<td>796</td>
<td>661</td>
<td>3, 20%</td>
<td>50</td>
<td>23</td>
<td>20</td>
<td>12.58</td>
<td>0.957</td>
<td>Edge</td>
</tr>
<tr>
<td>233</td>
<td>796</td>
<td>447</td>
<td>3, 35%</td>
<td>100</td>
<td>58</td>
<td>20</td>
<td>13.17</td>
<td>1.015</td>
<td>Edge</td>
</tr>
<tr>
<td>423</td>
<td>784</td>
<td>245</td>
<td>2, 3, 30%</td>
<td>100</td>
<td>90</td>
<td>40</td>
<td>28.17</td>
<td>1.171</td>
<td>Edge</td>
</tr>
<tr>
<td>431</td>
<td>777</td>
<td>726</td>
<td>3, 10%</td>
<td>10</td>
<td>9</td>
<td>40</td>
<td>28.58</td>
<td>1.024</td>
<td>Edge</td>
</tr>
<tr>
<td>432</td>
<td>783</td>
<td>619</td>
<td>3, 20%</td>
<td>50</td>
<td>27</td>
<td>40</td>
<td>28.17</td>
<td>0.692</td>
<td>Edge</td>
</tr>
</tbody>
</table>

Note: 1. Sample ID, e.g. 5 3 1, 5 for the strip reduction 5%, 3 for the valve group number open in AC, 1 for the percentage of the valve open, 10%.
2. The value of surface roughness is the average for measured at the three location of the sample, i.e. the head, centre and lead, in rolling direction.
Table 5.3 Some important fibres that occur at $\phi_2$ equal to 0 and 45$^\circ$ or 30$^\circ$, their position in the reduced Euler space ($\phi_1$, $\Phi$, $\phi_2 \leq 90^\circ$), and their main texture components for crystallographic textures of cubic and hexagonal materials [99, 126, 180, 211–216].

<table>
<thead>
<tr>
<th>Material</th>
<th>Fibre name</th>
<th>Fibre axis$^a$</th>
<th>Euler angles (°)</th>
<th>Important texture components</th>
</tr>
</thead>
<tbody>
<tr>
<td>bcc phase</td>
<td>$\alpha_{\text{bcc}}$-fibre</td>
<td>&lt;011&gt;//RD</td>
<td>0, 0, 45 – 0, 90, 45</td>
<td>{001}&lt;110&gt;, {112}&lt;110&gt;, {111}&lt;110&gt;</td>
</tr>
<tr>
<td></td>
<td>$\gamma$-fibre</td>
<td>&lt;111&gt;//ND</td>
<td>60, 54.7, 45 – 90, 54.7, 45</td>
<td>{111}&lt;110&gt;, {111}&lt;112&gt;</td>
</tr>
<tr>
<td></td>
<td>$\eta$-fibre</td>
<td>&lt;001&gt;//RD</td>
<td>0, 0, 0 – 0, 45, 0</td>
<td>{001}&lt;100&gt;, {011}&lt;100&gt;</td>
</tr>
<tr>
<td></td>
<td>$\zeta$-fibre</td>
<td>&lt;011&gt;//ND</td>
<td>0, 45, 0 – 90, 45, 0</td>
<td>{011}&lt;100&gt;, {011}&lt;211&gt;, {011}&lt;111&gt;, {011}&lt;011&gt;</td>
</tr>
<tr>
<td></td>
<td>$\epsilon$-fibre</td>
<td>&lt;011&gt;//TD</td>
<td>90, 0, 45 – 90, 90, 45</td>
<td>{001}&lt;110&gt;, {112}&lt;111&gt;, {4411}&lt;11 11 8&gt;, {111}&lt;112&gt;, {11 11 8}&lt;4411&gt;, {011}&lt;100&gt;</td>
</tr>
<tr>
<td></td>
<td>$\theta$-fibre</td>
<td>&lt;001&gt;//ND</td>
<td>0, 0, 0 – 90, 0, 0</td>
<td>{001}&lt;100&gt;, {001}&lt;110&gt;</td>
</tr>
<tr>
<td>fcc phase</td>
<td>$\alpha_{\text{fcc}}$-fibre</td>
<td>&lt;011&gt;//ND</td>
<td>0, 45, 0 – 90, 45, 0</td>
<td>{011}&lt;100&gt;, {011}&lt;211&gt;, {011}&lt;111&gt;, {011}&lt;011&gt;</td>
</tr>
<tr>
<td>hcp phase</td>
<td>{0001}&lt;10\overline{1}0&gt;</td>
<td>&lt;10\overline{1}0&gt;//ND</td>
<td>0/60, 0, 0.60/0.60$^b$</td>
<td>{0001}&lt;10\overline{1}0&gt;</td>
</tr>
<tr>
<td></td>
<td>{0001}&lt;2\overline{2}10&gt;</td>
<td>&lt;2\overline{2}10&gt;//ND</td>
<td>0/30, 0, 0.90/0.60$^b$</td>
<td>{0001}&lt;2\overline{2}10&gt;</td>
</tr>
<tr>
<td></td>
<td>{\overline{1}2\overline{2}0}&lt;10\overline{1}0&gt;</td>
<td>&lt;10\overline{1}0&gt;//ND</td>
<td>0/60, 90, 0</td>
<td>{\overline{1}2\overline{2}0}&lt;10\overline{1}0&gt;</td>
</tr>
</tbody>
</table>

$^a$RD, rolling direction; ND, normal direction, and TD, transverse direction, $^b$The ideal axial ratio ($c/a$) for a hexagonal close-packed structure.
Chapter 6

Enabling mechanism and modelling

The purpose of this chapter is to investigate the enabling mechanism during the phase transformation of thermally grown oxide scale under cooling conditions after hot rolling. This is then extended to specific precipitation of magnetite during continuous cooling based on diffusion simulation and an enthalpy-based finite element method.

6.1 Enabling mechanism

6.1.1 Formation of magnetite at different temperatures

To compare the oxide phases coexisting according to the eutectoid reactions, the selected experimental observations extracted from the previous chapters were summarised, as shown in Fig. 6.1. Here the formation of magnetite precipitation was related to high temperature proeutectoid reactions and wustite decomposition covering a wide range of temperatures. Above 900 °C, the detected magnetite depends on the dissolvability of homogenous magnetite precipitates in the wustite matrix and increases at the elevated temperature [5]. Around 750 °C, the homogenous velocity of magnetite precipitates in the wustite matrix decreases dramatically and reveals the small granular magnetite [5, 60, 118]. When the temperature ranged between 570 °C (the eutectoid
point of the Fe-O system [6]) and 727 °C (the eutectoid point of the Fe-C system [4]),
the magnetite seam begins to grow at the oxide/steel interface [118, 122] due to the
concentration fluctuation of anion/cation ions in oxide scale [28, 131]. Wustite
decomposes into magnetite with coarse lamellar microstructure in the range of 350 and
570 °C. After a holding time of 400 min, the maximum amount of magnetite can be
obtained at 400 °C (460–510 °C depending on its composition [47, 60]). Magnetite with
\(\alpha\)-Fe particles gradually increases provided by vacancy immigrations in the oxide scale
at 270 to 350 °C [120, 131]. Below 200 °C, no other transformation occurs [9, 60]
because the periodic arrangement of the continuous vacancies in wustite matrix
increased the interchange time [72].

Fig. 6.1 Schematic illustration of magnetite precipitation from thermally grown wustite
formed on steels in different temperature ranges.

Phase evolution obtained in previous tests found that the initial wustite with rich iron
was liable to form iron-rich wustite other than eutectoid products (\(\text{Fe}_3\text{O}_4\) and \(\alpha\)-Fe) [20].
This suggests that wustite decomposing at low temperature depends on the concentration of oxygen or iron ions among the oxide layers, and not the proeutectoid reaction that depends on the variation of temperature. In any case, the formation of magnetite at high CRs was suppressed to exempt the magnetite seam between 570 and 750 °C [32], whereas, for a long holding time, its formation from decomposing wustite is accelerated between 350 and 570 °C.

6.1.2 Thermodynamic analysis

Compared with the formation of monoxide Fe$_3$O$_4$, the mixture precipitates of Fe$_3$O$_4$ and $\alpha$-Fe from the wustite matrix is more complicated due in part to the migration of $\alpha$-Fe ions in the lattice that resulted from a similar lattice percentage of oxygen in Fe$_3$O$_4$ and Fe$_{1-x}$O [16, 72, 73]. This can be explained qualitatively with the aid of Gibbs free energy curves. Since $G(x)$ the Gibbs free energy per atom is defined relative to a standard state consisting of isolated atoms, its value $\Delta G$ for the given reaction must be negative for a phase change to occur [64, 73]. According to the nucleation processes, Fig. 6.1 illustrates the approximated positions of free energy functions of the various possible condensed phases, $\alpha$-Fe, FeO and Fe$_3$O$_4$, in the Fe-O system for $T=525$ °C [29, 71]. $\Delta G$ has a maximum negative value for eutectoid reaction, FeO→$\alpha$-Fe+Fe$_3$O$_4$, at the temperature approximately the eutectoid reaction point in the Fe-O system [6]. The equilibrium Fe$_3$O$_4$ phase is more negative and narrower (Fig. 6.2), and is even assumed to be a line compound just below the eutectoid transformation of wustite. Since cation-deficient Fe$_{1-x}$O, (1-$x$=0.83–0.95 [71]), the phase FeO ($x$ neglect in Fig. 6.2) has an extremely wide range of stability. Furthermore, the oxygen concentration axis that considers the effects of pressure is similar to the Fe-O equilibrium phase diagram [6].
The minimum free energy for each phase was obtained from tabulated thermochemical data at temperatures of 325, 425, and 525 °C (Table 6.1).

![Diagram of Gibbs free energy diagram for the Fe-O system at the temperature of 525 °C consisting of α-Fe, FeO and Fe₃O₄ phases.]

**Fig. 6.2** Schematic representation of Gibbs free energy diagram for the Fe-O system at the temperature of 525 °C consisting of α-Fe, FeO and Fe₃O₄ phases.

**Table 6.1** Values of Gibbs free energy for Fe₁₋ₓO, Fe₃O₄ and α-Fe below 570 °C.

<table>
<thead>
<tr>
<th>Temperature, °C</th>
<th>( G_v(\text{Fe}_{1-x}\text{O}), \text{kJ/mol} )</th>
<th>( G_v(\text{Fe}_3\text{O}_4), \text{kJ/mol} )</th>
<th>( G_v(\alpha\text{-Fe}), \text{kJ/mol} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>325</td>
<td>-306.709</td>
<td>-1226.324</td>
<td>-19.559</td>
</tr>
<tr>
<td>425</td>
<td>-316.436</td>
<td>-1255.225</td>
<td>-24.513</td>
</tr>
<tr>
<td>525</td>
<td>-326.937</td>
<td>-1287.418</td>
<td>-29.964</td>
</tr>
</tbody>
</table>

In **Fig. 6.2**, \( \Delta G' \) signifies the precipitation reaction \( \text{Fe}_{1-x}\text{O} \rightarrow \text{FeO} + \text{Fe}_3\text{O}_4 \), where the metastable equilibrium exists in iron-rich wustite. \( \Delta G_{\text{max}} \) represents the free energy change connected with the eutectoid reaction \( \text{FeO} \rightarrow \text{Fe} + \text{Fe}_3\text{O}_4 \). \( \Delta G_v \) values for α-Fe and \( \text{Fe}_3\text{O}_4 \) nucleation from the parent wustite are associated with the difference between the
tangent from the wustite free energy curve taken at a given composition of wustite \( X_0 \) and the minimum in the \( \alpha \)-Fe and \( Fe_3O_4 \) free energy curves, where \( \Delta G_v(Fe_3O_4) \gg \Delta G_v(\alpha\text{-Fe}) \). It indicates that the magnetite phase starts first followed by a few \( \alpha \)-Fe particles during wustite decomposition. Furthermore, the deviations from stoichiometry can be achieved by the slopes of the common tangents compared to the slopes of the \( G \) curves at \( \delta=\theta \) (\( \delta=\Delta G/\Delta x \)) given in Table 6.2. For both \( Fe_{1-x}O \) and \( Fe_3O_4 \), \( (dG/dx)_0 \) is much less negative than the common tangents to \( G(Fe) \) and \( G(Fe_3O_4) \), respectively. This confirmed that the phases with metal excess are stable at this temperature. For \( Fe_3O_4 \) the slope of the tangent to \( G(\alpha\text{-Fe}) \) and \( G(FeO) \) is more negative than \( (dG/dx)_0 \) which shows that the Fe-rich \( Fe_3O_4 \) is more stable and therefore easier to be observed. In the case of phase states associated with the lowest free energy in Fig. 6.2 depending on the oxygen composition (x axis), it should be noted that this result is appropriate at the eutectoid composition without pre-eutectoid reactions involved.

<table>
<thead>
<tr>
<th>Slope</th>
<th>Fe_{1-x}O</th>
<th>Fe_3O_4</th>
<th>( \alpha )-Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>( (dG/dx)_0 )</td>
<td>-326.937</td>
<td>-1287.418</td>
<td>-29.964</td>
</tr>
<tr>
<td>( \Delta G(FeO,Fe_3O_4) )</td>
<td>( \Delta x = 0.072 )</td>
<td>-13340</td>
<td>-13340</td>
</tr>
<tr>
<td>( \Delta G(\alpha - Fe,Fe_3O_4) )</td>
<td>( \Delta x = 0.572 )</td>
<td>-2198.346</td>
<td>-2198.346</td>
</tr>
</tbody>
</table>

Since the variation in the volume free energy \( \Delta G_v \) for each potentially nucleating phase, the relevant interfacial energy \( \gamma \) is required to form the new surface. The steady-state
nucleation rate of the individual phases $N_v$ is defined as the number of stable nuclei produced in a standard state of untransformed solid [9],

\[ N_v = K \exp \left( -\frac{1}{kT} \left( \frac{Q}{(\Delta G_v + \varepsilon)^2} + \frac{A \gamma^3}{(\Delta G_v + \varepsilon)^2} \right) \right) \]  

(6.1)

where $K$ and $A$ are constants, $Q$ is the activation energy for diffusion in the untransformed solid, $\varepsilon$ is the elastic strain energy in a standard volume of new phase, $k$ is the Boltzmann constant and $T$ is temperature. Thus, the nucleation rates increase considerably with a decrease in the ratio $\gamma^3 / (\Delta G_v + \varepsilon)^2$. For isothermal transformation, the precipitation of magnetite is known to grow into a coherent interface with wustite [72, 207], and thus to ignore the value of the interfacial energy $\gamma$ at the magnetite/wustite interface. Given that $\Delta G_v(Fe_3O_4) \gg \Delta G_v(\alpha-Fe)$ mentioned above, it is therefore reasonable to deduce that the nucleation rate of magnetite is appreciably higher than $\alpha$-Fe below the eutectoid temperature. For continuous cooling the nucleation rate of magnetite can be further investigated using crystallographic techniques [16] because $(dG/dx)_0$ is coupled with the magnitude of the atomic or electronic disorder constant in oxide layers.

### 6.2 Diffusion simulation

Diffusion analysis aims to predict the oxidation rates of reaction products within oxide scales during laminar cooling after hot rolling. The oxidation rate generally complies with the linear, parabolic, para-linear or mixed parabolic law [60, 69], depending on time-temperature treatments, the cooling scheme, atmospheric conditions and the grades
of steel. A rate constant can be determined from the slope where the change in weight of the surface area on specimens before and after oxidation tests is plotted versus time [4, 12, 26]. An attempt to predict the kinetics constant of multilayered oxide phase using a heat transfer finite element model was conducted by considering the convection and radiation of oxide scale under the water jet impingement region, and the stable film boiling region during laminar cooling.

### 6.2.1 Basic equation of the diffusion model

Since the fundamental laws of diffusion in an analogy with the theory of heat conductivity have been proposed [228], the heat transfer model of the steel strip with oxide scale during laminar cooling can be illustrated in Fig. 6.3. The model takes into account the heat flux through the thickness and width of the steel strip.

**Fig. 6.3** Schematic representation of heat transfer model for three-layered oxide scale formed on a hot strip during laminar cooling.
Under the assumption of a steady state, the oxide scale is set as a uniform thickness and with fine morphological features, while neglecting pores or cavities within their boundaries. The general equilibrium equation of heat transfer can be expressed by,

$$\frac{\partial}{\partial y} \left( \kappa \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \kappa \frac{\partial T}{\partial z} \right) + \dot{q} = \rho c \frac{\partial T}{\partial t}$$

(6.2)

where $\dot{q}$ is the heat transfer rate, $\kappa$, $\rho$ and $c$ are the thermal conductivity, the density and the heat capacity of the material respectively, $T$ is the oxidation temperature and $t$ is the diffusion annealing time, $y$ and $z$ are the thickness and width coordinates of the oxide scale respectively. This is the basic equation to be solved, subject to the oxide structure of the given oxidise phase and the boundary conditions imposed on the system. A variety of initial and boundary conditions are as follows. Heat losses in the water jet impingement zone during laminar cooling can be described by,

$$q_{\text{water}} = h_{w1}(T - T_{\text{w1}})$$

(6.3)

where $h_{w1}$ is the heat convection coefficient when the jet of water make contact with the surface of the steel strip \[229\], as illustrated schematically in Fig. 6.4. $T_{\text{w1}}$ is the temperature of the cooling water. Furthermore, the contribution from heat losses in the stable film boiling zone during laminar cooling, including air convection, can be expressed by

$$q_{\text{air}} = h_{w2}(T - T_{\text{w2}}) + \sigma \varepsilon(T^4 - T_{\text{w2}}^4)$$

(6.4)

where $h_{w2}$ is the film coefficient (Fig. 6.4) when the vapor film attached to the surface of the steel strip \[229\], $T_{\text{w2}}$ is the temperature of the vapor film, $\varepsilon$ is the emissivity of the material and $\sigma = 5.6699 \times 10^{-8} \text{ W/(m}^2\text{K}^4)$ is the Stefan–Boltzmann constant.
Fig. 6.4 Schematic illustration of the film coefficient and heat convection coefficient of boundary conditions.

For clarity, the approximation used to simplify the exact temperature vector of the govern equation can be obtained as the one which minimises the following functional,

$$I = \frac{1}{2} \int \left[ \lambda \left( \frac{\partial T}{\partial x} \right)^2 + \lambda \left( \frac{\partial T}{\partial y} \right)^2 - 2(\dot{q} - \rho c \frac{\partial T}{\partial t})T \right]dA + \frac{1}{2} \int_{S_1} h(T - T_\infty)^2 dS_3 \quad (6.5)$$

The resulting governing equation can be written as,

$$([K] + \frac{2}{\Delta t} [K_3])\bar{T} = (-[K] + \frac{2}{\Delta t} [K_3])\bar{T}_0 + \bar{P} \quad (6.6)$$

where $[K]$ is the stiffness matrix, $[K_3]$ is the additional under the unsteady state, $\Delta t$ is the interval of time step, $\bar{T}$ the nodal temperature vector and $\bar{P}$ is the equivalent nodal load matrix.

Kinetics models were established to couple with the growth of the multilayered oxide scales and distribution of different oxide phases, where the growth of oxide scales was assumed by following a parabolic law [1, 4, 163, 164]. The parabolic rate constants of the first kind for the growth of FeO, Fe$_3$O$_4$ and Fe$_2$O$_3$ in air oxidation between 700 and 1000 °C can be determined from Table 6.3 [1, 69]. The subsequent rate constant of a
multilayer oxide scale can be simulated from the first kind of these compounds. The rate coefficient here is assumed to be dependent on the oxidation temperature, being independent of concentration, position, and time. The diffusion matrix itself is a homogenous and isotropic semi-infinite medium. This condition ensures that the amount of mass transformation presented in the boundary can be neglected.

### Table 6.3 Different parabolic rate constants for the modelling

<table>
<thead>
<tr>
<th>Item</th>
<th>(k_1 / \text{g}^2 \text{cm}^{-4} \text{s}^{-1})</th>
<th>(k_2 / \text{g}^2 \text{cm}^{-4} \text{s}^{-1})</th>
<th>(k_3 / \text{g}^2 \text{cm}^{-4} \text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>(12.47 \exp(-1724 \times 10^3 / RT))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td>(1.98 \times 10^{-2} \exp(-169.5 \times 10^3 / RT))</td>
<td>(\left[ k_1^{(Fe_3O_4)} + k_1^{(Fe_2O_3)} \right]^2 + k_1^{(Fe_3O_4)} \right]^2)</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>(1.49 \times 10^{-3} \exp(-169.5 \times 10^3 / RT))</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Temperature is expressed in K, \(R = 8.31441 \pm 0.00026 J/\text{mol} \cdot K\)

### 6.2.2 Simulation conditions

Heat transfer within the multilayered oxide scale and steel strip was simulated by FEM using ABAQUS/Standard software. The metal substrate here was low carbon steel and the thickness of oxide scale was set at 50 µm. The compromised thickness of the oxide scale was acceptable for the integrity of the oxide, while neglecting some pores and spallation defects based on experimental results obtained in previous chapters. The whole structure of the oxide scale was divided into 9461 nodes or 4524 elements of DC2D6, where wustite was considered to be 45 µm, magnetite was 4.5 µm, and hematite was 0.45 µm, according to the reported proportions [4, 58]. The steel substrate
was meshed to 1174 nodes or 2209 elements (see publications Nos. 11 and 13), based on assumed symmetrical cooling on the top and bottom surfaces.

The thermal characteristics of the steel strip and oxide scale are listed in Table 6.4 [1, 163, 164]. The FT and CT were set at 860 and 560 °C. For the heat convection coefficient \( h_{w1} \), a based formulation can be worked out, as documented in [229],

\[
h_{w1} = P_r^{0.33} (0.037 \text{ Re}^{0.8} - 850) \frac{\lambda}{W} \quad (6.7)
\]

where \( P_r \) is the Planck constant, \( P_r = \mu_f c_p / \lambda_w \), \( \mu_f \) is the dynamic viscosity, \( c_p \) is the specific heat at a constant pressure, \( \lambda_w \) is the thermal conductivity, \( \text{Re} \) is the Reynolds number, \( \text{Re} = \frac{w \rho \nu}{\mu_f} \), \( w \) is the width of the impingement zone, \( \nu \) is the velocity of the jet. Similarly, the film coefficient of heat convection \( h_{w2} \) can be calculated by [229]

\[
h_{w2} = \lambda_s \left( \frac{g \Delta \rho}{8 \pi \lambda_s \alpha_c} \right)^{\frac{1}{3}} \alpha_c = \frac{\lambda_s \theta_s}{2i_f \rho_s} \quad (6.8)
\]

where \( \Delta \rho \) is the difference of the density, \( \theta \) is the difference of the temperature, \( i \) is the specific enthalpy, the subscript \( s \) and \( fb \) are the saturated vapour and steady film boiling, respectively. In this numerical simulation, the specific relationship between the film coefficient and temperature applied is illustrated schematically in Fig. 6.5a. Furthermore, the expression of the film coefficient can be loaded with discrete profile by the FILM code in ABAQUS software. Moreover, the emissivity of the surface strip \( \varepsilon \) can be determined directly by the following relationship [228], which often prevails at such high temperatures.
From the experimental research and the resulting material properties given above, the use of these parameters related to the reaction of oxidation yields fundamental material laws. These laws can easily be implemented in a finite element code enabling realistic simulations including initial oxidation to be carried out. The accuracy of diffusion simulation was verified by means of oxidation tests on small steel specimens, with a varying heat treatment history [1, 4]. There was a good agreement with the experimental results.

Table 6.4 Thermal characteristics of steel and iron oxides phases in oxide scale.

<table>
<thead>
<tr>
<th>Item</th>
<th>Austenite</th>
<th>FeO</th>
<th>Fe(_3)O(_4)</th>
<th>Fe(_2)O(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\kappa) (W/m·K)</td>
<td>16.5+0.111(T^*)</td>
<td>3.2</td>
<td>1.5</td>
<td>2</td>
</tr>
<tr>
<td>(\rho) (kg/m(^3))</td>
<td>8050–0.5(T)</td>
<td>725</td>
<td>870</td>
<td>980</td>
</tr>
<tr>
<td>(C_p) (J/kg·K)</td>
<td>587.8+0.068(T)</td>
<td>7750</td>
<td>5000</td>
<td>4900</td>
</tr>
</tbody>
</table>

* Temperature is in °C.

6.2.3 Results and discussion

Fig. 6.5b shows the temperature distribution of the whole structure along the dimensionless thickness direction of the steel strip. The individual temperature of the oxide scale and steel substrate are marked at the appropriate region in the figure. A sharp gradient exists in the thickness range of the oxide scale as a result of its low thermal conductivity [1, 164]. The abrupt decrease in temperature possibly led to the generation of some thermal stress at the interface of the oxide layer and substrate which
further affected the integrity of the oxide scales. An additional important aspect revealed by Fig. 6.5b is that the above assumption is a good approximation, and the kinetics coefficients correctly represent diffusion near the oxide/steel interface.

![Fig. 6.5](image.png)

**Fig. 6.5** (a) Film coefficient in heat convection as a function of temperature together with the theoretical relationship fitted to the experimental data. (b) Temperature distribution along with the normalising thickness of steel strip and oxide scale.

The overall parabolic rate constant for the simultaneous growth of the three layers $k_3$, is shown in **Fig. 6.6a**. In the temperature range of 800 to 850 °C, the growth rate constant rapidly increased, but a relatively gentle increase also occurred in the range of 700 to 800 °C. The second rate constant for the growth of the two outer layers of Fe$_3$O$_4$ and Fe$_2$O$_3$ $k_2$, is illustrated in **Fig. 6.6b**. The oxygen pressure prevailing at the Fe-Fe$_3$O$_4$ interface was assumed to correspond to the FeO-Fe$_3$O$_4$ equilibrium, although the second rate constant $k_2$, and $k_3$ are in the order of magnitude, $10^{-10}$ and $10^{-8}$ respectively. The diffusion coefficient of ions contributes to a higher oxidation rate in the FeO layer than in the Fe$_3$O$_4$ and Fe$_2$O$_3$ layers. In practice, the oxygen pressure at the substrate-oxide scale interface may differ from that assumed in these models.
The results show that the main reason why the oxidation rate in the hot rolled steel strip decreased during laminar cooling after finishing rolling was the disappearance of the FeO phase in the oxide scales. This agrees with the establishment of the steepest thermal gradients within the oxide scale that can lead to the highest growth rate [163, 164]. Furthermore, the selected oxidation and internal oxidation of microalloyed low carbon steel can cause a rate constant that is somewhat different from this study [60, 164]. Therefore, the final thickness of the oxide scale can be calculated using the growth rate constant in the individual oxide layer, and then the analysis of the evolution for the individual oxide phase can be calculated.

6.3 Enthalpy-based modelling

Since the magnetite seam generated between the oxide scale and steel substrate plays a critical role in the integrity of the oxide scale formed on low carbon steel [1, 4, 13, 164],
it is necessary to explore the phase transformation of the oxide scale at 570 °C [13] and
to elucidate the formation mechanism of the magnetite seam. The enthalpy method and
the effective heat capacity method provided a wide range of phase transition
temperatures of phase change materials [228, 229], but the discontinuity problems with
the isothermal transformation in this solid-solid phase change are difficult to deal with.
In order to avoid the discontinuity problems of the isothermal transformation using the
conventional temperature-based approach, an integration algorithm in conjunction with
the temperature function of enthalpy relationship in reciprocal form was proposed. By
considering the temperature dependence of the thermal conductivity and radiation
boundary conditions, an attempt was made to conduct the model coupled with the
temperature and phase transformation in two-dimensional geometry. The results make it
possible to predict the distribution of different oxide phases within oxide scale during
cooling after hot rolling.

6.3.1 Enthalpy-based algorithm

The heat transfer model for a typical three-layered oxide scale was treated differently
from the transformation enthalpy view. Without loss of generality, since the treatment
of convective terms gives no more difficulties than for the stationary case of Section
6.2, it could be ignored in what follows. Then the equilibrium equation of heat transfer
was written in an open set $\Omega \subset R^3$,

\[
\frac{\partial H(T)}{\partial t} - \text{div} \left[ k(T) \text{grad } T \right] = Q(t) \quad \text{in } \Omega
\]  

(6.10)

where $\text{div}(\cdot)$ and $\text{grad}(\cdot)$ are the divergence operator and the gradient operator
respectively, $T(x)$ is the temperature field depending on the space position $x \in \Omega$, $H(T)$ is
the volumetric enthalpy, \( k(T) \) is the thermal conductivity, and \( Q(x) \) is the source of internal heat generation. In isothermal phase change, the enthalpy function \( H \) has a jump discontinuity at the temperature of phase change \( T_m \) (Fig. 6.7a) and its dependence upon temperature may be written as,

\[
H(T) = \begin{cases} 
  c_w T , & T \leq T_m \\
  c_w T_m + L + c_m (T - T_m) , & T \geq T_m 
\end{cases}
\]

(6.11)

where \( c_w \) and \( c_m \) are specific heat before and after phase change respectively, \( L \) denotes the latent heat.

**Fig. 6.7** (a) Conventional enthalpy versus temperature relation (b) temperature versus enthalpy relationship in isothermal phase change.

The solution of the governing equation (6.10) is subject to the initial and boundary conditions imposed upon systems. A Neuman condition can be expressed by,

\[
k(T) \frac{\partial T}{\partial n}(x) = \overline{q}(x), \quad \text{on } \partial \Omega
\]

(6.12)

where \( n \) is the outward unit normal to the boundary surface, and \( \overline{q}(x) \) a given normal heat flux, and a linear Fourier condition is,
where \( T_{\text{ext}} \) is the temperature of the cooling water, and \( \gamma \) is the heat convection coefficient. Furthermore, a radiation boundary condition,

\[
k(T) \frac{\partial T}{\partial n}(x) = \alpha(T) = \sigma \varepsilon (T^4 - T_w^4) \quad \partial_\Omega
\]  

(6.14)

where \( \alpha(T) \) is a nonlinear function of temperature. For this latter, \( T_w \) is the temperature of the vapour film, \( \varepsilon \) is the emissivity of the material and \( \sigma = 5.6699 \times 10^{-8} \text{ W/(m}^2\cdot\text{K}^4) \) is the Stefan-Boltzmann constant. The solution for the nodal temperature vector described above can be obtained when the following function is required to reach the minimum,

\[
\int_\Omega \psi \frac{\partial H(T_\psi)}{\partial t} d\Omega + \int_\Omega \nabla \psi \cdot k(T_\psi) \nabla T d\Omega + \int_{\partial_\Omega} \psi \gamma T d\Gamma - \int_{\partial_\Omega} \psi \alpha(T_\psi) d\Gamma - r_\psi(\psi) = 0
\]  

(6.15)

where the notation is introduced,

\[
r_\psi(\psi) = \int_\Omega \psi Q d\Omega + \int_{\partial_\Omega} \psi \widehat{q} d\Gamma + \int_{\partial_\Omega} \psi \gamma T_{\text{ext}} d\Gamma
\]  

(6.16)

Instead of using the conventional enthalpy and temperature relation, the temperature function of enthalpy relationship given by \( T = \tau(H) \) is illustrated in Fig. 6.7b for isothermal phase change. Then the linearisation of the function \( \tau(H) \) is given by

\[
T^{(i+1)} = T^{(i)} + \Delta T^{(i)} = \tau(H^{(i)}) + \tau'(H^{(i)}) \Delta H^{(i)}
\]  

(6.17)

where \( \Delta H^{(i)} = H^{(i+1)} - H^{(i)} \), and where \( \tau' \) is the derivative of \( \tau \) with respect to its argument. Due to the nonconvexity of the function \( \tau(H) \), incrementation is relaxed as in Ref. [230] by replacing the quantity \( 1/\tau'(H^{(i)}) \) by a constant quantity \( \mu \) in the all domain and during the whole iterative process as:
\[ \Delta H^{(i)} = \frac{1}{\tau'(H^{(i)})} \left[ \Delta T^{(i)} + (T^{(i)} - \tau(H^{(i)})) \right] = \mu \left[ \Delta T^{(i)} + (T^{(i)} - \tau(H^{(i)})) \right] \] (6.18)

Thus, the relaxation parameter \( \mu \) must satisfy,

\[ \mu \leq \frac{1}{\max \tau'(H)} \] (6.19)

where \( \tau'(H) \) is determined from the temperature enthalpy relation of Fig. 6.7b. Therefore, considering that \( H^{(i)} \) and \( T^{(i)} \) are known quantities from the last iteration, this allows the enthalpy field to be incremented with the help of the actual increment of the temperature field.

### 6.3.2 Conditions of numerical simulation

The integration algorithm presented above was applied to the finite element model. A detail description of this numerical model can be found in Section 6.2.2. The problem to be solved is given by,

\[ \frac{\partial}{\partial y} \left( \kappa \frac{\partial T}{\partial y} \right) + \frac{\partial}{\partial z} \left( \kappa \frac{\partial T}{\partial z} \right) + \dot{q} = \rho c \frac{\partial T}{\partial t} \] (6.20)

where the thermal conductivity \( k \) is taken as a constant. In view of the algorithmic treatment, it gives the following reciprocal form (see Fig. 6.7),

\[ \tau(H) = \begin{cases} 
\frac{H}{c_w}, & H \leq H_w = c_w T_m \\
T_m, & H_w \leq H \leq H_w + L \\
T_m + (H - H_w - L)/c_m, & H \geq H_w + L 
\end{cases} \] (6.21)

For initial conditions, the FT and CT are set at 860 and 560 °C respectively. Moreover, the thermal properties of the oxide scale are listed in Table 6.3. The density and thermal conductivity of the composite were constant in this investigation.
6.3.3 Results and discussion

To verify the proposed model, temperature distribution within the oxide scale and steel substrate can be obtained during the isothermal transformation of wustite. In Fig. 6.8a, the numerical result shows temperature distribution at the first 5 s along the thickness of the oxide scale, and reveals that it was not distributed uniformly across the vertical surface. The temperature has a lower value at the oxide/steel interface compared to the internal, which can be attributed to the high latent heat capacity of the phase material as well as its low thermal conductivity. Correspondingly, based on the variation of temperature and enthalpy field of the oxide scale, it provides the possibility of deducing the transformation mechanism of oxide phase where the evolutionary process of a three-layered oxide structure will be a continuous and simultaneous precipitation of magnetite at the two interfaces of magnetite/wustite and wustite/substrate during the eutectoid transformation of thermally grown wustite.

As seen in Fig. 6.8b, the oxide scale and steel substrate completely cooled down to the temperature at the upper surface after 45 s. The position closer to the outside surface shows a faster decrease in temperature, whereas the temperature decreased slower at lower positions. The phase change process of the steel substrate can be clearly identified in the upper region, but it is not obvious for the oxide scale at the lower region. The temperature profiles show that presented the phase change of oxide scales was very slow compared to austenite. Accordingly, controlling the phase transformation process of oxide scale is a challenge to explore the formation mechanism of oxide scale.
A gentle phase change of oxide scale adjacent to the steel substrate proves that the formation of the magnetite seam in close-range steel substrate was led not only by wustite decomposition, but also and mostly by the diffusion of iron ions from the steel substrate. Therefore the concentration distribution of iron ions from the steel substrate or wustite decomposition can facilitate wustite transformed into rich-iron wustite, and then accelerate the generation of magnetite. Once the diffusion of iron ions reaches a certain level at the interface, the monolayered magnetite seam could form between the steel substrate and the wustite layer. Above all, the magnetite seam will finally determine the adhesive strength of the oxide scale and steel substrate.

6.4 Summary

The enabling analysis, the numerical diffusion model, and an enthalpy-based algorithmic technique were used to investigate the phase transformation of thermally grown oxide scale under cooling conditions after hot rolling. The following conclusions can be drawn.
1 Thermodynamic analysis of magnetite precipitation provides compelling evidence that the nucleation rate of magnetite is higher than α-iron due to the high Gibbs free energy of Fe₃O₄ and the low thermal stability of the oxygen-rich wustite below the eutectoid temperature. This contributes to the dominance of the magnetite phase in oxide scale.

2. In the diffusion simulation, the wustite phase resulted in a significant increase in the oxidation rate above 800 °C, and the steeper thermal gradients within the oxide scale can also increase the growth rate. However, the growth rate constant, for the simultaneous growth of the two outer layers of magnetite (Fe₃O₄) and hematite (Fe₂O₃), decreased significantly with respect to the three-layered oxide scale.

3. An enthalpy-based finite element method was proposed to avoid the discontinuity problems of the isothermal transformation using the conventional temperature-based approach. This promising method strongly supported the variation in concentration that resulted from wustite decomposition while enhancing the formation of magnetite seam adjacent to the steel substrate.
Chapter 7

**Tribological properties of magnetite precipitate from the oxide scale**

The aim of this chapter is to generate a specific oxide scale during hot rolling, and then to simulate the tribological properties of magnetite particles during cold rolling. The oxidation experiments were performed on a Gleeble 3500 thermal-mechanical simulator with a humid air generator. The tribological properties of magnetite precipitates have been investigated using a Tribometer in pin-on-disc configuration. A probable lubrication mechanism is proposed based on the contribution of magnetite precipitation.

7.1 Experimental

7.1.1 Materials

The material used in the oxidation experiment was commercial hot-rolled strips from microalloyed low carbon steel for automotive beams. The mechanical properties for the grade of steel are shown in Table 7.1. In a pin-on-disc configuration, the pin consists of a roll material and the disc consists of a steel strip with a specific thickness and composition of oxide scale after oxidation treatment. The chemical compositions of the samples are given in Table 4.1.
Table 7.1 Mechanical properties for the microalloyed low carbon steel.

<table>
<thead>
<tr>
<th>Yield strength, MPa</th>
<th>Tensile strength, MPa</th>
<th>Elongation, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>≥355</td>
<td>510–610</td>
<td>≥24</td>
</tr>
</tbody>
</table>

\[ L_0 = 5.65\sqrt{S_0} \]

\*\(L_0, S_0\) are the gauge length and cross sectional area of the working zone for the tensile sample, respectively.

7.1.2 Oxidation test

The steel strips were cut into 120 × 25 × 5 mm\(^3\) size specimens for the oxidation tests. The surface finishing of these specimens had an average roughness of \(R_a\) 0.6 µm. Prior to the tests the specimen surfaces were ground with SiC paper of 2400 grit to remove the thin oxide protective film, degreased in an ultrasonic cleaner, washed in water and ethanol, and then dried immediately.

Oxidation tests were conducted in humid air over a short period of time using the Gleeble 3500 thermo-mechanical simulator. To control the moisture in the atmosphere, the industrial air was passed through a tank containing distilled water which was held at a constant temperature. Generally, water vapour between 7.0 and 19.5 vol% in humid air is relevant to hot rolling plain carbon steel [110, 173]. During laminar cooling after hot rolling, the steel strip through the last stands is subjected to most cycling water to cool it down to CT. In this case the content of water vapour in humid air was therefore set at 19.5 vol%.
The specimens were oxidised at 800 °C for 120 s in 19.5% H\textsubscript{2}O moist air, through a desired CR and then held at 550 °C for 30–300 min in an argon seal, as shown in Fig. 7.1. The following specific procedure was used for every oxidation experiment: (1) the specimen was heated to the austenitising temperature of 900 °C in an argon protected atmosphere at a heating rate of 10 °C/s; (2) it was then held for 20 s at 900 °C, before the argon was switched off and the oxidising atmosphere introduced, while the temperature was reduced to 800 °C; (3) the sample was then cooled down to 550 °C in a moist atmosphere where humid air was released and flowed into the Gleeble chamber at 1.7×10^{-4} m\textsuperscript{3}/s for 120 s; (4) after holding for 30–300 min at 550 °C, the sample was quenched to room temperature at 40 °C/s, and the argon flow was switched on to prevent any further oxidation during isothermal treatment.

![Fig. 7.1](image-url) | High temperature oxidation in the Gleeble 3500, (a) illustration of sample setup, (b) thermo-cycle for oxidation tests

In the oxidation experiment, different methods were used to protect the integrity of oxide scales. Uniform oxide scales were consistently obtained for each experiment. First, during the cooling process in the Gleeble 3500, a high CR of 40 °C/s was selected to bring the sample down to room temperature, after which it was immediately removed...
from the chamber and pre-mounted using epoxy resin. This procedure avoids blistering or other failures of oxide scale due to the steep temperature gradient. Second, a modified pre-mounting procedure was followed. The mixture of the epoxy resin and the hardener was left until it was almost ready to solidify, and then it was spread as a thick paste onto the surface of oxidised sample. As such, there is no liquid flowing around and it also avoids any non-uniform contraction between the liquid resin and the solid oxide scale while the resin solidified. These samples will then be used in the subsequent tribological test.

7.1.3 Tribological test

Tribological tests were carried out under a pin-on-disc configuration on a CETR UMT multi-specimen test system [175, 176], as shown in Fig. 7.2a. In this case the pin was a high chrome steel ball 6.35 mm in diameter. The pin consisting of tempered martensite and cementite has an initial hardness of 67 HRC (or 890 HV) and a roughness $R_a$ of 0.24±0.04 µm. The grade of the disc, a strip material, was microalloyed low carbon steel (Table 4.1) with an initial hardness of 162 HV and a roughness $R_a$ of 0.04±0.02 µm. Two different types of surface morphologies for strip materials were investigated in this experiment. One was a relatively fresh metallic surface, while the other was an oxidised surface where the surface was oxidised at 800 °C for 120 s in 19.5% H$_2$O moist air and then held at 550 °C for 60 min in an argon seal. The same procedure used to prepare the samples for oxidation test was used to obtain fresh steel surfaces. These samples were cut into $20 \times 24 \times 5$ mm$^3$ size pieces with a Struers Accutom-50 cutting machine. With the pre-mounting oxidised samples it was necessary to cut a sample from the middle part around the welded position of the thermal couple, where the oxidised
surface was absent from the steep thermal gradient during oxidation. After that each sample was cold mounted in a stainless steel stub with an inner diameter of 50 mm, as shown in Fig. 7.2b, and positioned as close to the centre of this ring as possible. The purpose of cold mounting was to meet the specific size required for the lower sample holder on the pin-on-disc apparatus used in this experiment. The steel surfaces of the solidified-resin-mounted samples were polished to 1 µm, and the other oxidised surfaces were held in reserve. Eventually, the opposite surface of the sample was flattened to a specific thickness with the parallelism of 6 µm between the top and bottom surfaces. It is noted in this study that the sample was 14 mm thick when the resin was 50 g and 6 g harder during cold mounting. Three samples with different oxidised precipitation surfaces and two samples with fresh metallic surfaces were prepared for the friction test.

![Fig. 7.2](image)

**Fig. 7.2** (a) Schematic of the pin-on-disc apparatus and (b) photograph of a test sample.

The operating conditions applied for each friction test were: (1) normal loads of 2.5, 8 and 18 N, (2) linear sliding speeds of 0.05, 0.15 and 0.35 m/s. In order to obtain enough pressure to make contact with a low normal load, the pin was presented a hemispherical surface to the contact area. For the loads ranging from 2.5 to 20 N, hertzian pressures varied from 130 to 280 MPa at the start of the friction test. All the tests were conducted at a room temperature of about 20 °C, so that different precipitations of oxide scale
formed in hot rolling were used to examine the effects on cold rolling at room temperature. During the experiments a Coulomb-type coefficient of friction was recorded in situ from a strain gauge sensor. This coefficient corresponds to the ratio of macroscopic forces which are the resistant force to the motion and the normal force applied on the pin [148, 150]. A stylus-type Hommel Tester T1000 profilometer with ISO11562 filter was used to measure the surface roughness of the samples. Relatively soft regions were selected for the test in order to observe the tribological properties of oxide scales in the contact zone without destroying them too fast. Three tests were conducted for each test condition in order to verify the reproducibility of the results.

After each friction test, the surfaces of all the samples were coated with gold for 10–15 s using a sputter coater. A JEOL JSM 6490 SEM in conjunction with EDS analysis was used to examine the precipitation morphology and microstructures of oxide scale formed on the surface of the sample and to investigate the worn surfaces. Moreover, the thickness of the oxide scale was also measured through the cross section of the oxidised samples. An XRD using a GBC MMA diffractometer with monochromated Cu $K_a$ radiation was used to analyse the phase composition of the oxide scale.

It was noted that the operating conditions for the friction tests were relatively different from the industrial rolling conditions. Nevertheless, the aim was not to simulate the hot rolling process but to reproduce part of the contact mechanics established between the strip with a certain composition of oxide scale and the work roll used in the finishing stands. The mechanical contact of a typical rolling bite was decomposed, only the sliding part of the motion was considered, not the rolling part of the motion. Furthermore, the tribological configuration of contact in this study, a sliding motion
with an initial hertzian pressure close to the contact pressure in the rolling bite, allowed
displaying the impact of the composition of oxide scale on friction and wear
mechanisms. In the present study, only the results with a normal force of 18 N and a
linear sliding speed of 0.35 m/s were emphasised. Nevertheless, the phenomena
observed in this case remained valid for the other test conditions.

7.2 Results and discussion

7.2.1 Precipitation of magnetite

Fig. 7.3 shows the cross section of oxide scales after oxidation at 800 °C for 120 s in
dry air and 19.5% water moist atmosphere, and then held at 550 °C for 60 min. Here the
eutectoid layer in the two-layer oxide structure has precipitated evenly in dry air but not
with moist air. The oxide scale formed in the dry air has a less compact structure and a
clear interface with the substrate (Fig. 7.3a). The oxide scale formed in 19.5% water
moisture (Fig. 7.3b) however, shows a thin and compact magnetite seam adherence to
the steel substrate. Fig. 7.4 compares the thickness of oxide scales across the width of
the oxidised specimens formed under two different atmospheric conditions at 800 °C
and held at 550 °C for 120 min. It reveals that the oxide scale is in the range of 8–11 μm
thick, which is relatively thinner at the centre of specimens than that nearest edge region,
in both dry and moist atmospheres. Moreover, the oxide scale formed in 19.5% H₂O
moisture air was generally thicker than in dry air. This indicates that the oxidation rate
is faster in moist air than dry air for this type of microalloyed low carbon steel.
Fig. 7.3 Oxide scale of microalloyed low carbon steel formed at 800 °C for 120 s then held at 550 °C for 60 min in (a) dry air (b) 19.5 vol.% water vapour contents. Eutectoid structure consists of α-Fe, Fe₃O₄ and retained FeO.

Fig. 7.4 Thickness of oxide scales formed at 800 °C and held at 550 °C for 120 min in dry air and 19.5% H₂O moisture.

Fig. 7.5 shows the XRD results of an oxidised surface at 800 °C in dry industrial air for different holding time at 550 °C. The main phases of oxide scale are Fe₃O₄ and Fe₂O₃. As the tests were carried out directly on the oxidised surface and the x-ray went through the oxide scale and reached the metallic phase, the Fe phase appears in the XRD results. Since the layer of oxide scale was becoming thicker over time, the peak intensity of the Fe phase should have reduced with the oxidation time, but instead the peak intensity of the Fe phase showed no sign of decrease with oxidation time because the eutectoid
reaction, $4\text{FeO} \rightarrow \alpha\text{-Fe} + \text{Fe}_3\text{O}_4$, occurred during the holding time at 550 °C. **Fig. 7.6** shows the XRD results of an oxidised surface at 800 °C in 19.5% H$_2$O moisture air for different holding times at 550 °C, where the oxide scale consisted mainly of Fe$_3$O$_4$ and Fe$_2$O$_3$. The constitution of Fe$_2$O$_3$ decreased with the holding time, which can be explained by the fact that the oxide scale formed under moist conditions has a non-uniform structure (**Fig. 7.3b**), and thus it is much easier for Fe$_2$O$_3$ to spall from the Fe$_3$O$_4$ surface when the samples were being prepared. It was noted that the thin outermost Fe$_2$O$_3$ phase was detected by XRD in **Figs. 7.5** and **7.6**, but it was absent from SEM photographs in **Fig. 7.3**. Generally, the crystal structure of Fe$_2$O$_3$ [202] and the different sample preparations for XRD and SEM led to the difference in the content of Fe$_2$O$_3$. Nevertheless, during industrial hot rolling where oxidation occurs over a short term, the effect of Fe$_2$O$_3$ can be neglected because the red dust (Fe$_2$O$_3$) was almost washed away by online cooling and then coiling after hot rolling.

**Fig. 7.5** XRD patterns of oxidised surface at 800 °C in dry air and held at 550 °C for 60 and 120 min.
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Fig. 7.6 XRD patterns of oxidised surface at 800 °C in 19.5% H₂O moisture and held at 550 °C for 60 and 120 min.

7.2.2 Tribological properties of magnetite precipitates

Fig. 7.7a shows the original morphology of the sample surface with globular precipitation of magnetite particles on the surface of the wustite during isothermal treatments at 550 °C holding for 60 min. Here small precipitates of magnetite as free particles were dispersed all over the wustite after the oxidation test. These free magnetite particles based on the literatures [231, 232] could act as a lubricant and perhaps act as a protection against wear when the oxides make contact between the work rolls and the strip. It was noted that in the EDS analysis (Fig. 7.7b) most of the intensity was Fe and O, with no other alloying elements being observed.

Fig. 7.8a illustrates the coarse lamellar precipitation of magnetite particles formed on the wustite surface during isothermal treatments at 550 °C holding for 120 min, where
magnetite precipitates was coarsely compacted into the surface. When the compact surface of oxide scales occurred in the contact area between the work roll and the steel strip until the glazed surfaces formed, the predominant mechanism of wear could become adhesion and the coefficient of friction could be increased [233]. As for the coarse lamellar structure according to the literature [234] the filling of irregularities and the higher volume occupied by the oxide with regard to the healthy metal contributes to the increase in surface roughness. It is interesting to note that a manganese element was also detected in this precipitation surface (Fig. 7.8b), which could confirm that alloying elements go into a solid solution of the oxide scale formed on this kind of steel surface, and thus improve crystal continuity [202]. The fact that silicon oxides and other alloying element oxides were not detected may be because there were only a small percentage of these products compared to the whole oxide phases.

Fig. 7.9a shows the fine lamellar precipitation of magnetite particles formed on the wustite surface during isothermal treatments at 550 °C holding for 300 min, where surface morphology was similar to the coarse lamellar structure (Fig. 7.8). This is because from a coarse lamellar to a fine lamellar structure, the eutectoid reaction, 4FeO→α-Fe + Fe₃O₄, only involved the growth of precipitation grains, whereas no other new products were generated [202]. This microstructure of magnetite precipitation could make it easy to form glazed surfaces when there is contact between the work roll and the steel strip. In this case we propose that the reason for the decrease in the coefficient of friction could be because the fine lamellar structure smooths the interface as the oxide scale becomes thicker [234].
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Fig. 7.7 SEM/EDS analysis of globular precipitation of magnetite particles on wustite surface during isothermal treatments at 550 °C holding for 60 min.

Fig. 7.8 SEM/EDS analysis of coarse lamellar precipitation of magnetite particles on wustite surface during isothermal treatments at 550 °C holding for 120 min.

Fig. 7.9 SEM/EDS analysis of fine lamellar precipitation of magnetite particles on wustite surface during isothermal treatments at 550 °C holding for 300 min.
The relationship between the sliding speed and coefficient of friction was shown in Fig. 7.10. The fine lamellar structure, a typical occurrence for the magnetite precipitation, was used in Fig. 7.10 under conditions of normal force 18 N and dry air flow between the surfaces. The points plotted are the means of at least three tests, provided with the standard deviation in Fig. 7.10. The coefficient of friction at high speed was relatively low and the oxides favour adhesive wear due to friction. However, there is a minimum coefficient of friction for this case. The occurrence of this value was due to the formation of a thicker film at low sliding speeds which affected the wear resistance. Therefore, it is implied there is also a minimum thickness of oxide scale needed to act as lubrication [234].

![Graph showing the relationship between sliding speed and coefficient of friction.](image)

**Fig. 7.10** Effect of sliding speeds on coefficient of friction under a normal force of 18 N and dry air flow between surfaces.

In the case of friction test with oxidised surfaces, the propagation of cracks in the bulk under shearing stresses may cause the oxide scales to detach at the contact surface [235]. The shear strength of oxide scale is defined as the maximal interfacial shear stress [236], where an interfacial fracture will be triggered on the oxide and steel
substrate interface. In this study the shear strength for the detachment of oxide scale was determined based on an image analysis technique [109]. Fig. 7.11 shows the correlation between the roughness at the interface steel/oxide scale and the shear strength of the oxide scale. As seen in Fig. 7.11, with $R_a$-values up to 0.38 µm there was only a slight influence on the shear strength of the oxide scale whereas with higher roughness values ($R_a > 0.38$ µm) the shear strength increased significantly. This indicates there is a minimum value for the shear strength of oxide scale where it adheres strongly to the steel substrate.

![Fig. 7.11 Correlation between roughness at interface steel/oxide scale and shear strength of oxide scale.](image)

**7.2.3 Formation mechanism of magnetite precipitates**

In order to fabricate the oxide scale with a desired amount of magnetite precipitates after hot rolling which will contribute to the natural lubricate additives during cold rolling, the real challenge is therefore to clarify the formation mechanism of the specific oxide scale. In the case of oxidised surfaces at 550 °C, the reaction belongs to the
decomposition of thermally grown wustite, which is a solution of ferric ions, rather than oxygen diffusion during high temperature oxidation [9]. The specific reaction pathways can be seen in Section 5.4. Reaction Eq. 5.3 proceeded rapidly and exceeded reaction Eq. 5.4 to a considerable extent at a temperature of maximum decomposition rate in a range of 250 to 350 °C [12] over several hours, which is a direct consequence of the favoured magnetite precipitates than ferrite.

Fig. 7.12 presents the Fe$_3$O$_4$ precipitating microstructure from oxide scales formed on the contact surfaces during friction tests, which will probably have the desired tribological properties for cold rolling. In this case it is supposed to be pre-oxidised FeO on the substrate, as shown in Fig. 7.12a. On one hand some Fe$_3$O$_4$ particles appeared on the surface of FeO layer (Fig. 7.12a) due to further oxidation, but on the other hand a proeutectoid Fe$_3$O$_4$ (Fig. 7.12b) also occurred and depleted some oxygen within the FeO. In Fig. 7.12c, the oxidised Fe$_3$O$_4$ nucleated into a thin film, whereas some eutectoid structures such as Fe$_3$O$_4$ and $\alpha$-Fe, exhibited at the site of proeutectoid products. Since the eutectoid reactions depleted the oxygen near the outer layer, Fe$_3$O$_4$ particles started to precipitate at the interface of FeO and the substrate. Eventually, a typical three-layered eutectoid structure of oxide scale was generated, with an outer layer of Fe$_3$O$_4$ film with a relatively decreased hardness, a eutectoid structure composed of $\alpha$-Fe, Fe$_3$O$_4$, retained FeO with preferable ductility, and then an inner layer of Fe$_3$O$_4$ with desired adhesive ability to the steel substrate.
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Fig. 7.12 Schematic illustration of magnetite precipitation from oxide scale during friction tests.

7.3 Summary

The following conclusions can be made according to the oxidation tests under dry and moist (19.5% H₂O) atmospheres for a microalloyed low carbon steel. The oxide scale consisted mainly of Fe₃O₄ and Fe₂O₃ owing to the instability of FeO at ambient temperature. The water content had a significant influence on the precipitation of Fe₃O₄ from thermally grown FeO. The moisture of the atmosphere not only increased the thickness of the oxide scale, it also influenced the microstructure and morphology of Fe₃O₄ precipitation within the oxide scale. The oxide scale exhibited a thin compact Fe₃O₄ seam adjacent to the steel substrate, which was absent in dry air.
During the tribological tests, the microstructure and mechanical properties of Fe\textsubscript{3}O\textsubscript{4}
precipitation and the friction conditions were investigated. Two types of Fe\textsubscript{3}O\textsubscript{4}
precipitates, globular or lamellar structure were developed for tribological experiments.
The experimental results shown there were two types of precipitation structure which
revealed quite different tribological properties. The free particles in the globular
structure could act as a lubricant and consequently help to resist wear, whereas the
compact particles in the lamellar microstructure may favour adhesive wear. The link
between lamellar structure and adhesive wear depends on the type of lamellar structure.
A fine lamellar structure has a smooth contact interface, so the coefficient of friction
decreases, whereas a coarse lamellar structure with irregularities leads to an increase in
roughness. The investigation into the effect of the sliding speed and shear strength on
friction showed there is a critical thickness of oxide scale for optimum lubrication,
which shows that the oxide scale adheres very strongly to the steel substrate.

Eventually, the evolution mechanism of magnetite precipitates within the oxide scale
has been clarified with respect to the defined primary, secondary, and tertiary Fe\textsubscript{3}O\textsubscript{4}
precipitates. A new three-layered microstructure of Fe\textsubscript{3}O\textsubscript{4} precipitation has been
presented: an outer Fe\textsubscript{3}O\textsubscript{4} film with decreased hardness, a eutectoid products layer with
certain ductility, and a Fe\textsubscript{3}O\textsubscript{4} seam which adheres strongly to the steel substrate.
Chapter 8

Conclusions and recommendations

8.1 Conclusions

In this present work a facile and controllable magnetite microstructure is proposed to apply to pickle-free steel with desired tribological properties during metal processing. The details and conclusions have been described in previous chapters, but the following general conclusions can be drawn from the present investigation.

8.1.1 Initial oxidation of microalloyed steel

- The in situ observations of oxidation by high temperature microscope indicate that grain boundary diffusion is the dominant transport mechanism to control the initial oxidation of microalloyed steel in the temperature range of 550 to 850 °C. As such the distribution of the grain boundary in the steel substrate determines the adhesion-related failure mechanisms associated with the oxide scale generated.

- The oxide scale grown on the coarse-grain steel substrate can cause adhesive properties to deteriorate when cooling to the room temperature. This grain refinement effect is more sensitive to the oxide scale formed at 550 °C than that formed at 600 °C.
The tight oxide scale was proposed to elucidate effects of grain refinement in the steel substrate on high desired magnetite content and the integrity of the oxide scale.

8.1.2 Effects of processing parameters on oxide scale

- The HR-AC system was successfully developed and made it possible to control the cooling rate by means of water flow rather than by controlling the sample thickness in conventional apparatus.

- The increase of cooling rates (10–100 °C/s) leads to significant cracks of the oxide scale. The uniform surface morphologies and good adhesion properties of oxide scale can be achieved at a cooling rate of 20 °C/s and a thickness reduction below 12 %.

8.1.3 Texture evolution of tertiary oxide scale

- Simultaneous EBSD-EDS techniques combined with TIC cross-sectional sample preparation were successfully applied to the study of fcc-hcp phase transformation in tertiary oxide scale. Accurate and quantitative data about the morphology and crystallography of oxide scale were obtained, particularly on the preferred growth and deformation directions of oxidation products.

- Magnetite develops a strong θ fibre parallel to the oxide growth, which includes {100}<001> and {001}<110> texture components, resulting from the minimisation of surface energy for {100} planes of magnetite. In contrast, {0001}<1010> component
dominates in hematite as the favored basal plane slip. The Hematite growth on θ fibre magnetite is 54.76° titled from the <001> crystal direction of magnetite.

8.1.4 Enabling mechanism and modelling

- Thermodynamic analysis provides compelling evidence that the nucleation rate of magnetite is higher than ferrite due to the high free enthalpy of magnetite and the low thermal stability of oxygen-rich wustite below the eutectoid temperature.

- An enthalpy-based algorithmic technique has been presented based on the results from experimental and diffusion simulations. This approach enables the precipitation of magnetite to be predicted accurately.

8.1.5 Tribological properties of oxide scale

- Oxidation tests on the Gleeble 3500 indicated that water vapour in air not only increases the thickness of the oxide scale, it also influences the microstructure of magnetite precipitation within the oxide scale.

- Tribological tests in pin-on-disc configuration shown that the free particles in the globular structure could act as a lubricant and thereby resist wear, whereas the compact particles in the lamellar microstructure may favour adhesive wear. The fine lamellar structure with smooth contact interface decreased the coefficient of friction, whereas the coarse lamellar structure with the irregularities increased the roughness.
8.2 Recommendations for future work

- A combination of the various in situ techniques presented here provides the frameworks for future investigation on the oxidation of the other steel compositions. Notable weaknesses which beg future attention are the transport properties of oxidised surfaces, and the temperature dependence of surface properties and the metal-oxide interface, all of which could enhance the adherence performance of the oxide scale.

- The accelerated cooling technique developed in this present work has proved to be very effective. This approach is strongly recommended to study the phase transformation of the other steel grades. Furthermore, the combination of ion milling and EBSD provides a rapid method for identifying the orientations of grains intersected by a polished surface. Extending this technique to alloys exposed to mixed gases is experimentally challenging, but might prove rewarding.

- The enthalpy-based numerical simulation has thrown up many future studies involving the modelling of phase transformation and grain growth kinetics in this context. More research is needed to model the interactions between oxidising species and with the oxides phase based on an atomic-level description of the movement individual species within the grain boundary.

- The oxidation tests on the Gleeble 3500 and tribological tests in pin-on-disc configuration provided a framework to assess the tribological characteristics of oxide scale generated. A large number of friction trials and stalled cold rolling tests are needed for further investigation on the wear mechanics of magnetite particles.
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