Microstructural characterisation if high temperature oxidation of boiler materials for coal fuelled power plants

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Abstract

Due to the projected increase in global electricity demand, it is estimated that nearly 1400GW of new coal fired power plants will be built providing about 38% of global electricity demand in 2030. This growth will have a negative impact on the environment through the emission of CO₂, a greenhouse gas detrimental to the climate, unless stringent emission targets for the coal fired power plants are put in place. This has resulted in placing more emphasis on the need for adopting the best available technologies for ‘new built’ plants or through retrofit of existing plants or the construction of high efficiency power plants with CO₂ capture and storage technologies. The high efficiency power plants are mainly achieved by operating the boilers at higher temperatures of up to 700°C compared to the conventional power plants operating at ~ 565°C. This expected temperature increase will have an effect on the material degradation mechanisms of both the existing and proposed new alloy materials for the critical components of the boilers, that is, headers, superheaters, reheaters and wall membranes. This thesis explores the material degradation mechanisms associated with the high temperature oxidation and/or corrosion of the alloy materials found in these components.

To study the effect of temperature increase on the high temperature oxidation of ferritic steels (T22, T23, P91 and P92) and austenitic stainless steels (E1250 and 347HFG). The steels were exposed in water vapour containing environments and in dry air. The temperatures employed ranged from 510°C to 750°C for varying times ranging from 500 hours to 5,000 hours. The results of the oxidation experiments were investigated using a range of analytical techniques including; Scanning Electron Microscopy (SEM), Energy and Wavelength Dispersive X-ray Spectroscopy (EDS/WDS), X-ray Diffraction (XRD), Electron Backscatter Diffraction (EBSD), Transmission Electron Microscopy (TEM), and the use of a Dual beam Focused Ion Beam Microscopy (FIB-SEM) for both SEM investigation and TEM microscopy analysis. These techniques provided a means for the in-depth characterisation of the microstructure and chemical compositions of oxide scales formed for all the oxidation conditions studied.

On the ferritic steels, multilayered oxide scales developed, which consisted of outer Fe rich oxide layers and inner Fe-Cr rich oxide layers. However, this was dependent on the Cr concentration levels in the bulk of the alloy and other alloying elements such as Si, W and Mo. These constituent elements had an effect on the alloy microstructural development with increasing temperature and ultimately on the oxide growth kinetics, morphology and the chemistry of the resultant oxide scales. The oxide scale was identified to consist of a thin Fe₂O₃ layer adjacent to a thick Fe₃O₄ layer, and an inner mixture of spinel-type oxides consisting of Fe, Fe-Cr and Fe-Cr-Mn rich phases adjacent to the substrate. The proposed
oxide growth mechanisms for the ferritic steels were postulated to be due to the cationic species diffusion from the substrate along grain boundaries, which were considered as the main contributory diffusion paths and hence a higher flux of cations through them within the exposure temperature range, and across the scale to form oxides, whilst the presence of voids or cracks due to growth and thermal stresses in the scale together with oxide grain boundaries, allowed anion diffusion into the scale causing the growth of the internal oxide layers as well as the subsequent re-oxidation of the previously formed scales to higher state oxides.

Similarly, for austenitic stainless steels, multilayered oxide scales occurred on the surface consisting of outer Fe rich layers and an inner mix of Cr-O rich, Cr-Mn-O rich, Fe-O rich and Fe-Ni rich phases. The oxide growth mechanisms for austenitic stainless steels were also postulated to be due to the cationic species diffusion from the substrate along grain boundaries to form surface oxides, but equally the oxidant species inwardly diffused through pores, cracks and oxide grain boundaries causing the internal oxidation on these steels. Other constituent elements played a role in the oxidation behaviour such as; Ni, which occurred discretely in the surface oxides and extensively within the inner oxide layers, where jointly with Fe formed a porous Ni-Fe rich matrix, Nb; which formed porous oxides as well as shown to cause the onset of breakaway oxidation, Mn; which had a positive effect jointly with either Cr and Fe and Si; , which formed a thin Si-O rich phase at the oxide/substrate interface providing additional protection. Furthermore, the project looked at the effect of surface modification on both ferritic and austenitic stainless steels on the oxidation characteristics with the results of this study showing improved oxidation resistance for all the surface modification carried out and the exposure conditions investigated.
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1 INTRODUCTION

1.1 BACKGROUND
Over the period 2003 - 2030, it is estimated that nearly 1400GW of new coal fired plants will be built worldwide. These are expected to provide about 38% of global electricity demand by 2030 close to today’s share of global electricity supply. Existing coal fired plants are generally associated with large quantities of CO₂ emissions to the environment. This means that the expected growth by 2030 will be of concern to low carbon economies unless remedial measures are undertaken to cap the greenhouse gas emissions. To achieve this, existing power plants will have to adopt best available technologies, either through ‘new-build’ or ‘retrofit’ or design of new high efficiency power plants with CO₂ capture and storage technologies. Improving cycle efficiencies, a function of steam temperature and pressure, in existing systems and new builds, would mean that less coal would be burned, and therefore, lower greenhouse gas emissions per megawatt of electricity generated. Increasing cycle efficiencies necessitates that these power plants operate under far more aggressive environments, which demand materials capable of withstanding high temperature degradation mechanisms in the critical components of the system [1, 2]. These include tubes, piping and headers found in superheaters, reheaters and boiler walls. The principal degradation mechanisms observed in these components include creep damage, microstructural degradation, high temperature fatigue, high temperature oxidation and corrosion. These mechanisms have been shown to change with increasing steam temperatures, which for more efficient systems today are around 600°C compared to 535-565°C about 30 years ago. This is expected to increase to 700°C by 2030 thus putting an emphasis on new life assessment methodologies for these components which is the focus of this research.

Figure 1, shows how changes in steam conditions (temperature and pressure) affect the overall thermal efficiency. Existing coal fired power plants, also referred to as conventional single reheat thermal cycle systems have subcritical\(^1\) steam pressure levels of about 160-180 bar and a steam temperature range of 535-565°C. The changes in steam conditions involve an increase in main and re-heat steam temperatures as well as pressure variations. Figure 1 demonstrates that increasing steam pressure at any given temperature above

\(^1\) Subcritical refers to boiler conditions having steam pressures of up to 19MPa or less than the critical pressure of 22.1MPa below which water and steam coexist as two phases. At 374°C and 22MPa of pressure, water and steam become indistinguishable and this is referred to as the Critical point. Increasing the temperature and pressure above the critical point pushes the steam into the supercritical (SC) range, which many of the large coal power plants operate today.
300bar has no substantial increase in efficiency of the boiler. Steam pressure increases have also been shown to complicate the design aspects of the boiler system.

![Figure 1 showing the effect of steam conditions on the cycle efficiency for a single reheat coal-fired unit [1]](image1)

Figure 1 showing the effect of steam conditions on the cycle efficiency for a single reheat coal-fired unit [1]

On the other hand increasing steam temperatures to 600/620ºC and for advanced ultra-supercritical2 (AUSC) plants to 700ºC, shows a marked increase in efficiency in excess of

---

2 Advanced ultra-supercritical refers to boilers operating above the critical condition with the inlet steam temperature to the turbine at 700-760°C.
8% [1, 3] as illustrated in Figure 1. Related to thermal efficiency improvements is the additional benefit of decreased CO₂ emissions, Booras et al.[4] studied efficiency of power plants where they showed that a subcritical 37% efficient 500MW Pittsburg plant burning coal produced 850 tonnes of CO₂ per kWh, whereas an ultra supercritical plant with 43% and 48% efficiency would produce 750 and 650 tonnes per KWh, an 11% and 24% emission reduction respectively.

The beneficial cycle efficiency improvements illustrated in Figure 2 are mutually related to material degradation mechanisms and one of the limiting factors in material usage is the susceptibility to high temperature steam oxidation. Literature reports [4-6] that failures do occur in boiler components and are as a result of tube overheating due to the oxide scales formed on these tubes. These oxide deposits cover the inner walls of boiler tubes and interfere with the heat transfer from the outer fire-side surface to the cooling action of water in the inner steam-side surface. The resultant effect is an increase in tube temperature due to oxide scale formation (estimated to be in the order of 2°C for every 25 µm of oxide scale), which significantly reduces the tube service lifetime [7].

![Figure 3 showing the effect of oxide build up on a superheater tube as a function of temperature and service life][7]

Shibly and Roberston [7] illustrated the effect of tube temperature build-up due to oxide scale formation on the service lifetime of a P91 superheater tube. Figure 3 shows their calculations based on a tube designed to operate at a pressure of 60MPa and a temperature
of 600°C with oxide build-up occurring over one year. Because of the oxide scale build up (black line), the tube temperature increased, which resulted in the annual life consumption of about 4% (at mid curve position, in red) with time. There was an immediate increase in tube metal temperature, but the effect on tube life was not noticeable after the first year but was after the second year, and assuming no oxide spallation occurred, the temperature rise became a critical issue (blue line).

Additionally, the oxide scale growth, which occurs at the expense of the parent metal, causes a reduction in the tube thickness. This reduction in the critical load bearing cross-section of the tube results in the increase of tube stresses and hence the cause of tube failures. The Hawaiian Electric Company (HECO) demonstrated the thinning effect on secondary superheater tubes failures in 1993, where failure regions exhibited a very thick (>0.76mm) steam-side grown oxide scale. HECO’s analysis of the ruptured area hardness levels and microstructural characteristics, estimated that the temperature near the ruptures was in excess of 649°C [7]. The oxide scales formed also tend to spall or exfoliate when the plant is cooled down, this causes coolant flow blockages especially at the bottom of pipe bends resulting in further overheating effects. Spallation effects can also create problems downstream at the steam turbines by causing turbine blade erosion. Overheating of the piping results in increased diffusivity of alloying element, which has been reported to initiate alloy depletion in the bulk material matrix. This leads to microstructural changes and associated long-term mechanical property degradation of the materials [8, 9]. Other factors shown to affect oxidation behaviour include temperature, type of environment and the chemical composition of the parent alloy, which affect the mechanism of oxide formation, its microstructural characteristics and the degree of protection conferred by the oxide deposits.

The problems identified above demonstrate the need to select the best commercially available materials for boiler tubing whilst taking into account the variation in steam conditions in various components of the boiler. The preferred material choices for boiler piping include; ferritic steels due to their lower coefficients of thermal expansion and higher thermal conductivity but these alloys suffer greatly from high oxidation rates and complete scale spallation. Austenitic and nickel based alloys on the other hand have lower oxidation rates but due to their high coefficients of thermal expansion tend to cause spallation of the outer oxide scale layers. However, the austenitic and nickel based alloys leave an intact inner rate controlling oxide scale after spallation. The selection of specific grades of these alloys depend on where they are applied in the boiler, that is, whether in reheaters, superheaters, headers or wall membranes, and is dependent mainly on the metal operational temperatures and the creep properties [3, 9, 10].
For example, the wall membranes are generally made of ferritic materials such as the T24 steel, but are limited to material operational temperatures of up to 550°C hence the alternative adoption of T/P92 steels. For aggressive operational conditions nickel base alloys are generally employed. For superheater and reheater tube alloys, if they are used in the low temperature range, ferritic materials used in membrane walls can be applied. However, in the final stages of superheaters where material temperature exceeds the maximum allowable temperature for ferritic steels, austenitic stainless steels such as 304H, 347HFG or HR3C are used. For temperatures exceeding 700°C, austenitic steels also fail requiring the use of nickel based alloys such as Incoloy 740, Nimonic 263, and Incoloy 718 or the newly developed austenitic steels such as HR6W. The commonly used materials in the headers pipes are the martensitic steels P/T91 or P/T92, but these are also capped to their maximum allowable temperature. High temperature regions of header pipes demand materials with higher strengths, and in this case, nickel based alloys and newer high temperature austenitic steels have been suggested [7, 9].

In summary, an understanding of how these materials behave under varying steam oxidising conditions is paramount to enable service lifetime prediction studies to be carried out. This will be instrumental in classifying parent alloys in terms of their effectiveness to resist steam-side oxidation whilst considering the operational conditions for superheater and reheaters, header piping and wall membranes in a coal fired power plant.

1.2 AIMS AND OBJECTIVES

The aim of this project is to study the growth and microstructural development of oxide scales formed on the critical high temperature components of fossil fuel power plants. This involves an in-depth study of oxide scale growth on various boiler materials under isothermal and non-isothermal conditions whilst comparing them with ex-service materials. The oxide scales formed and the bulk material characterization will be carried out using analytical techniques, including; optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), wavelength dispersive spectroscopy (WDS), electron backscatter diffraction (EBSD), transmission electron microscopy (TEM) and X-ray powder diffraction (XRD).

These techniques will provide important information regarding the substrate and oxide scale microstructures, the oxide scale compositions and individual component distributions, oxide scale features and characteristics, which are pertinent to explaining the oxidation behaviour of boiler tube alloy materials.
2 LITERATURE REVIEW

2.1 INTRODUCTION

Metals and their alloys are generally considered unstable in air at room temperature as they tend to form metallic compounds such as oxides or nitrides with lower reaction rates. At high temperatures, these metallic compounds dissociate to form their initial reaction compounds indicating that most metals in solid or liquid state are unstable in air at any temperature. Thus, oxidation phenomena are important reactions that involve metal alloys exposed to air or steam oxidising environments. The reactions involve adsorption of oxygen molecules from the oxidising environment followed by the nucleation of oxides crystals on the surface, which grow and coalesce to form a thin oxide layer. This layer grows to form a thicker scale as a function of time, temperature and the type of oxidising environment. For the growth processes to occur, electrons, cations or anions species have to diffuse across the scale under various mechanisms as schematically summarised in Figure 4 [11-13]. During oxide growth, other phenomena also occur such as nodule formation, porosity/void formation, internal oxidation, breakaway oxidation, and oxide scale spallation that significantly affects the scale characteristics [7, 8, 11, 14-18].

Figure 4 shows an illustration of the oxidation reactions between a metal and oxygen gas [11]
A key equilibrium condition for these oxidation reactions to occur is the dissociation pressure. This governs the oxidation reactions and the types of compounds formed on metal alloys. The rates at which these reactions occur depend on the oxidation kinetics and have been shown to increase rapidly with increasing temperature. For example, above 1600°C on most alloys, oxidation reactions are generally complete within a few minutes.
For alloys interacting with a gas such as oxygen, oxidation reactions occur at the metal/gas interface with the formation of oxide compounds. These compounds can be considered as either being reactive or inert in nature. If the compounds formed are inert, they form an intermediate scale lying between metal substrate and reactive gas. The scale layer can have numerous layers of varying oxide stoichiometry and may change as the reaction progresses. The scale formed can also be compact, dominated with pores or cracks or possess cavities such that subsequent reactions may occur through diffusion or passage of the reactive gas through these defects. Diffusion of reactive species can also occur through the grains, along the alloy grain boundaries or surfaces. Other than the oxidising gas, the reactive species (such as alloying elements) do preferentially react with the oxidising gas forming a scale layer with varying chemical composition across it or divided into individual scale layers of varying compositions.

If the compounds formed are reactive and where a metal alloy exhibits several oxidation states, a number of compounds with reactive gas are formed which are also arranged in layers with the one richest in reactive gas close to the oxide-gas interface. Figure 5 exhibits a scale formed on a steel substrate where three stable oxide phases formed, that is, wüstite, magnetite and hematite, which are of different stoichiometric compositions with oxygen.

![Figure 5 showing steel substrate with a thick wüstite layer closer to the substrate, followed by magnetite and an outer hematite layer [18]](image)

Figure 5, illustrates a multilayer oxide scale formed on a Fe-10Cr alloy, with one of its alloying elements, chromium, reacting with oxygen to form complex reaction products. The products formed may exist as heterogeneous mixtures (FeO + Cr2O3), as separate layers (Fe3O4 and Fe2O3), as a new double compound such as a spinel (Fe,Cr)3O4 or the excess compound may impose its structure on the whole of the reaction product with the minor constituents being built into the lattice structure of the main metal.
Therefore, to understand the mechanisms involved in high temperature oxidation, it is vital to carry out an in-depth study of the oxide layers for various metal alloy-gas combinations. This emphasises the need to discern the oxide scale compositions and crystal structures as well as the free energy of dissociation of the alloy-gas combinations. Additionally, understanding the defect structures present in these scales, which affect the exact oxide stoichiometry, will help explain the driving force for oxidation reactions.

2.2 THERMODYNAMIC FUNDAMENTALS

As discussed in section 2.1, the oxide scales formed during high temperature oxidation are dependent on the dissociation pressure of the different oxide phases formed in equilibrium with the metal. This is determined from the standard free energy of formation of the oxide. The standard free energy calculations are carried out using the Ellingham/Richardson diagram, Figure 7, which identifies the most stable oxides at different oxidation temperatures. These diagrams do have limitations and generally do not take into account the oxidation reaction kinetics, and when more than one oxide is formed, the diagrams cannot verify which oxide will form in the given environment. Therefore, combining the kinetics of oxide formation and the thermodynamic calculations provides a better understanding of the oxidation behaviour. Additionally, since oxidation studies are generally carried out under isothermal conditions, employing isothermal sections of binary metal/gas phases or ternary metal/reactive-element/gas phase diagrams further aid in identifying thermodynamically stable oxides [14-16, 18, 20].
2.2.1 Ellingham Richardson diagram

The simplest of oxidation reactions between a metal (M) and oxygen gas (O) can be written as \( M + O_2 \leftrightarrow MO_2 \) with a standard free energy given as

\[
\Delta G^0 = -RT \ln \left( \frac{a_{MO_2}}{a_M a_{O_2}} \right)
\]

Equation 1

Where \( a_{MO_2} \), \( a_{O_2} \) and \( a_M \) are the activities of the oxide and metal respectively, \( R \) the gas constant, \( T \) the absolute temperature and \( P(O_2) \) as the oxygen partial pressure. If the activities of pure metals and oxides are assumed as unity and oxygen partial pressure used for the oxygen activity, then at equilibrium Equation 1 can be written as

\[
\Delta G^0 = -RT \ln(P(O_2)) \text{ or } P(O_2) = \exp \left( \frac{\Delta G^0}{RT} \right)
\]

Equation 2

The standard free energy \( (\Delta G^0) \) is normally expressed as a function of the absolute temperature, \( T \) in the form

\[
\Delta G^0 = -\Delta H^0 - T \Delta S^0 \Delta G^0 = \Delta H^0 - T \Delta S^0
\]

Equation 3

Therefore, plots of standard Gibbs free energy for the reactions against the temperature result in straight lines if the reaction enthalpy and entropy do not change with temperature. These lines are plotted for a range of different oxide phases, Figure 7, and aid in the determination of the oxide dissociation pressures at different temperatures. From the diagram, the equilibrium partial pressure of any metal/metal oxide can now be obtained by starting from the point marked O corresponding to an equilibrium pressure of 1 atmosphere, and intersecting the \( \Delta G^0 / T \) line at a point corresponding to the desired temperature and then extending it to the nomographic scale at the right or bottom edge. For example, for \( \text{Cr}_2\text{O}_3 \) (blue lines) at 800°C, the equilibrium partial pressure of oxygen is about \( 10^{-28} \) atmospheres, implying that the formation of \( \text{Cr}_2\text{O}_3 \) is thermodynamically favoured at 800°C in an environment with oxygen potential greater than \( 10^{-28} \) atmospheres. Similarly, for hematite \( \text{Fe}_2\text{O}_3 \) (green lines), the equilibrium partial pressure at which hematite thermodynamically favourably forms is about \( 10^{-14} \) atmospheres at 600°C. This means \( \text{Cr}_2\text{O}_3 \) will form closer to the substrate where there is low oxygen partial pressure while hematite will form on the outer scale region with higher partial pressure [11, 12, 14, 15].

Important points to note when using the Ellingham / Richardson diagram are that:

- The standard free energy of most metals has a linear relationship with temperature implying that oxidation reactions result in a decrease in entropy.
- A change in slope of the lines at different points correlate to a phase change which could be melting, boiling or a change in structure, such as from BCC to FCC in Fe, or due to a slight change in entropy.
- The most stable oxide has the largest negative value of \( \Delta G^0 \) and represented by the lowest line in the diagram.
- The ability to determine the oxygen potential of the environment in terms of \( pO_2 \), \( pH_2/pH_2O \) and \( pCO/pCO_2 \), or the oxygen partial pressure in equilibrium with the metal/oxide of interest using the additional nomographic scales.

Figure 7 showing Ellingham-Richardson diagram for various metal oxides, lines in green and blue illustrating conditions favourable for the formation of hematite and chromia at selected temperatures [11]
Therefore, an oxide is likely to form on exposure to a gas if the existing oxygen partial pressure in the gas is higher than the dissociation oxygen partial pressure of the oxide. This is normally the case for atmospheric or higher partial pressures and metal oxidised based on iron, nickel chromium, aluminium and many other metallic species. Basically, the effective oxygen partial pressure adjacent to the substrate becomes controlled by diffusion of the oxidising species across the oxide, or dissociation of the oxides present at the interface. For the oxide scale formed to confer protection to the underlying substrate, it must be solid, form a continuous, complete and dense, crack free layer along the surface and remain adherent to the surface. And the most thermodynamically stable oxides, with the lowest dissociation pressure will grow preferentially and the scale can become organised into layers with the most stable oxide next to the alloy surface. Thus, Figure 7 shows that the commonly found oxides that are stable in oxidising environments at elevated temperatures, and which can be grown on most alloys are \( \text{Cr}_2\text{O}_3 \), \( \text{Al}_2\text{O}_3 \) and \( \text{SiO}_2 \). Most alloys employed in high temperature applications contain sufficient Cr that they can form Cr rich oxides. However, the presence of other alloying elements and Cr dissolution in oxides of these elements, dissolution in Fe based magnetite results in the formation of the Fe-Cr rich spinels that confer protection to the underlying substrates compared to the Cr free Fe based oxides [10, 21, 22].

2.3 MECHANISMS OF OXIDATION

2.3.1 Transport mechanisms

Bradford [11], Birks et al. [14], Kofstad [15], Kubaschewski and Hopkins [16] and Khanna [20] among others have reviewed various mechanisms by which atoms, ions and electrons diffuse from and into to the substrate, through the oxide scale formed and to the oxide/gas interfaces. If the assumptions were that there was no diffusion through pores and along grain boundaries, only cations and anions would be transported across a compact oxide layer, and the migrations of electrically neutral atoms or molecules would be neglected.

Since oxide scales are considered as ionic compounds, the transport mechanisms through them are categorised into those belonging to stoichiometric crystals and non-stoichiometric crystals systems. Many inorganic compounds such as oxides, sulfides and other intermetallic phases in alloy systems do not have an exact stoichiometries composition but rather show a more or less excess or deficit of one or another constituent component. In general, the lattice building blocks (ions and atoms) leave their lattice sites either with increasing frequency as the temperature increases and go to an interstitial lattice site or due to the spatial energetic reasons, move to the surface and leave an unoccupied lattice site behind. This unoccupied site serves as a position that can be occupied by particles lying much deeper in the crystal. The unoccupied lattice site (referred to as a vacancy) moves
towards the interior, while the ions migrate to the surface until a condition of equilibrium is achieved when the ion and vacancy movements are of equal magnitude. At constant pressure or volume and constant crystal composition, the concentration of the lattice defects is determined solely by the oxidation temperature. The above conditions of ion and vacancy migrations have resulted in oxide compounds being classified in-terms of their defect structures discussed in the following sections [23, 24]:

2.3.1.1 Defect structures of oxides

The defect structures existing in ionic compounds are classified as either Schottky or Frenkel defects. Schottky defects are those defects in which the mobility of ions is made possible by the ionic vacancies. To maintain electroneutrality in these compounds, there must be an equivalent number or concentration of vacancies on both cationic and anionic sub-lattices as seen in alkali halides. Frenkel defects on the other hand, are those in which only the cations are mobile and the anionic sub-lattice remains perfect. Electroneutrality in this case is maintained by cations forming interstitial atoms leaving vacancies in cationic sub-lattice and is found in silver halides. The Schottky and Frenkel defects provide a mechanism for ionic diffusion essential for oxide scale growth.

Since metallic oxides are generally considered as non-stoichiometric compounds, also classified as semiconductors, growth cannot only occur by mere diffusion of Schottky and Frenkel defects. Electrons must also be able to migrate from the metal, through the oxide, to the adsorbed oxygen at the oxide/gas interface and this occurs through negative and positive charge carriers in the non-stoichiometric compounds. These compounds are usually electrically neutral and transport through them can be explained by assuming that either the cations (most likely) or anions have variable valence. Moreover, the defects in these compounds are confined to the oxygen or the metal lattices, though it is important to note that many oxide compounds may contain an appreciable concentration of both cation and oxygen defects. Additionally, the concentration of different defects in the oxide will also depend on the temperature and the oxygen partial pressure.

Furthermore, non-stoichiometric oxides are categorized as either being of p-type or n-type. For n-type oxides, \((M_{1+\delta}O)\) - with metal excess or \((MO_{1-\delta})\) - with oxygen deficient and according to Wagner Hauffe rules, the addition of foreign cations of a valence higher than cations of the parent oxide will decrease the concentration of oxygen vacancies in \((MO_{1-\delta})\) or concentration of interstitial ions in \((M_{1+\delta}O)\). The result is a decrease in the conductivity of the oxide causing lower oxidation rates. The addition of lower valence cations will have a negative effect by increasing oxidation rates. For p-type oxides, \((M_{1-\delta}O)\) - with metal deficit or \((MO_{1+\delta})\) - with oxygen excess), the addition of higher valence cations increases the
concentration of vacancies in \((M_{1-\delta}O)\) or concentration of the interstitials in \((MO_{1+\delta})\) while lower valence cations have the opposite effect. For example, addition of \(\text{Cr}^{3+}\) ions in \(\text{FeO}\) would increase the concentration of iron vacancies causing an increase in the conductivity of the scale and hence a higher oxidation rate. Small additions of \(\text{Cr}\) in iron always increase the oxidation rate of iron hence the need for higher \(\text{Cr}\) levels beyond the doping limit to confer oxidation resistance to iron [20, 24].

2.3.2 Short circuit diffusion paths

Diffusion also takes place through line and surface defects, which include grain boundaries, and dislocations. Diffusion through line and surface defects is generally faster as they have high diffusivities and considered as easy diffusion paths compared to the lattice diffusion [15, 25]. The diffusion coefficients for line and surface defects are \(10^4-10^6\) times larger than the lattice diffusion coefficient [26]. Thus the activation energies for diffusion along line and surface defects in solids are much less than those for volume diffusion. In polycrystalline materials, the contributions of different types of diffusion mechanisms are a function of temperature, partial pressure of the components, grain size, boundary orientation, porosity among others [11, 14, 20, 27].

Philiberts [28] review further showed the complexity in diffusion through oxide scales whose microstructure depended on both the substrate, the nature of the atmosphere, the shape of the samples, in addition to the elementary processes involved during oxidation such as lattice and short-circuit diffusion, interface reactions, stress generation and the related processes.

2.4 OXIDATION KINETICS

The transport mechanisms of cations and anions across the scale are obtained by investigating the oxidation rates with changes in oxygen pressure and temperature. And since the oxidation product is retained on the metal surface, the rates of oxidation can be measured and expressed as weight gain per unit area. A number of scale growth rates have been formulated to show how oxide film thickness changes with time. This can be linear, logarithmic, parabolic or cubic or combinations of any two or three rates but depended on oxidising conditions [14-16, 20]. For linear oxidation rates, this occurs when the oxidation of an alloy occurs at a constant rate represented by Equation 4.

\[
x = k_L t
\]

Where, \(k_L\) is the linear rate constant and has the units \(\text{cm s}^{-1}\) when oxide scale thickness is measured or \(\text{g cm}^{-2} \text{s}^{-1}\) when mass gain measurements are carried out. A linear rate law is mainly observed under conditions where a phase boundary reaction is the rate determining
step for the oxidation reaction. Thus, diffusion through the scale is unlikely to be rate limiting when the oxide scale is thin. In this condition, the substrate/oxide and oxide/gas interfaces are not assumed to be in thermodynamic equilibrium, although there are cases where the reaction at the substrate/oxide interface has been found to play a rate determining role.

Linear rate conditions as stated are common to thin oxide scales or during the initial stages of oxide scale formation and may continue for a long or short time, but this depends on the oxidation conditions. At early stages of oxidation, a thin oxide is formed and diffusion through this scale will be rapid and virtual equilibrium is established at the oxide/gas interface, which means that the metal activity at this interface will be significantly high. As the oxidation reaction continues at a linear rate, the oxide scale becomes thicker, such that the flux of ions through the scale is approximately the same to the surface reaction rate. These transport processes occur until the activity of the metal cations at the scale/gas interface approaches the value in equilibrium with the atmosphere. Since the activity of the metal cations cannot fall below this value, a further increase in oxide scale thickness must result in a reduction in the metal activity gradient across the scale and, hence a reduction in the ionic flux and the reaction rate. In this condition, the transport of ions across the scale becomes the rate controlling process and the rate fall with time according to a parabolic rate law.

Wagner quantified the diminishing growth rate as the decrease in the oxide scale thickness with time, which means that as the scale becomes thicker, the diffusion distance from the substrate through the oxide to the oxide/gas interface increases. This results in the reduction of the flux of reactive species and hence a decrease in oxide scale growth rate. He formulated the parabolic rate law as represented in Equation 5

\[ x^2 = 2k^i t \]  
Equation 5

Where, \( x^2 \) is the square of the oxide scale thickness and is proportional to time, \( t \), and \( k^i \) the parabolic rate constant (in cm\(^2\) s\(^{-1}\)). This can also be expressed in terms of the measurement of the mass gain of the specimen (\( m \)) or a less common method involving the measurement of the metal surface recession. For the former, this is given as per Equation 6, where \( k^{ii} \) is the parabolic constant (in g\(^2\) cm\(^{-4}\) s\(^{-1}\)).

\[ \left( \frac{\Delta m}{A} \right)^2 = k^{ii} t \]  
Equation 6

These rate equations are schematically represented in Figure 8. For the oxidation of a large number of metals at low temperatures, below 400°C, a logarithmic rate law is used to describe the kinetics of oxidation. This is given as per Equation 7.

\[ x = k_{log} \log(t) + C \]  
Equation 7
Where, \( k_{\text{log}} \), and \( C \) are constants at constant temperature. At temperatures below 400°C, the initial reaction is rapid then slows down to a low or negligible value. Birks and Meier [14] and Kofstad [15] have provided several explanations by which logarithmic rate laws apply but these are not applicable to the high temperature conditions observed in this study.

![Figure 8 Kinetic curves representing various high temperature oxidation processes [29]](image)

The commonly observed oxidation kinetics for most oxides at high temperature are the parabolic growth rates [11, 15, 16]. In general, for engineering design, the oxidation kinetics of metallic alloys are very important as they provide an estimate of the design life of the metal to be used at a specific temperature and environment.

### 2.5 OXIDE SCALE MORPHOLOGY

In high temperature oxidation of metals, the oxide scale layers formed can either be single, duplex, triplex or multi-layered. This occurs when a metal alloy has more than one valence state and oxidises to form different oxides but depending on the oxygen partial pressure. The most metal rich oxide will form next to the bulk metal and the most oxygen rich oxide next to the gas phase. This dependence on oxygen partial pressure is evident whereby, if it is so low below the dissociation pressures of the higher oxide or oxides, only the thermodynamically stable inner oxides will be formed. The total oxidation process is further dependent on the characteristics of the oxide in different layers of the scale. For example, a higher oxide may form a porous non protective layer growing on a compact scale of a lower oxide resulting in paralinear oxidation behaviour. In other cases, different oxide layers may be compact as observed in oxidation of iron (with valences +2 and +3) where above 570°C, oxide scale consists of \( \text{FeO/Fe}_3\text{O}_4/\text{Fe}_2\text{O}_3 \) [18, 30-32]
Steam oxidising conditions tend to form triplex oxide layers. Steels and in particular the 9Cr steels, form duplex structures under low oxygen content, which are observed as an inner Fe-Cr rich spinel and an outer magnetite layer all linked to Fe diffusion. At higher oxygen levels, the outer magnetite layer is converted to hematite giving a triplex layered structure. Harrison [33] showed that the ratios of the scale thicknesses in a multilayered scale for a metal forming two or three layered oxides tends to a limiting constant value. He further showed that on 9Cr steel oxidised in steam at 500°C and forming three oxide layers, the proportion of the outer hematite layer growing on magnetite with oxygen partial pressures greater than \(10^{-20}\) atm is dependent on metal oxidation rate and not the oxygen partial pressure.

2.5.1 Oxide orientation and texture

During oxide growth on metal substrates, several textures and orientations are observed. In the early stages of oxidation and at lower temperatures, some oxides appear to grow with an amorphous structure. A solid amorphous structure such as that found on SiO\(_2\) with a tetrahedral structure, contains more oxygen than metal in their formulas. The oxygen atoms are seen to occur on the corners of the tetrahedral structure with the metal ions at the center. This allows large anions or molecular oxygen to move through them more readily than smaller cations forming amorphous oxides. Furthermore, amorphous oxides tend to crystallise as they age and these include Al\(_2\)O\(_3\), Ta\(_2\)O\(_5\) and Nb\(_2\)O\(_5\). Other types of oxides with M\(_2\)O and MO formulas have structures in which cations can move more readily and are always crystalline in nature. These include NiO, Cu\(_2\)O and ZnO [11]

Crystalline oxides grow on metal substrates with their crystal structures aligned with the substrate. This alignment phenomenon is referred to as epitaxy or the best fit between two crystal structures. For example, (001) planes of Cu\(_2\)O grow parallel to the Cu (001) plane with the [110] directions of Cu\(_2\)O parallel to the [110] of copper. Similar observations for wüstite and iron, where the (100) plane in FeO lies parallel to the (100) plane in Fe, and the [110] direction in the (100) plane in FeO lies parallel to the [100] direction in the (100) plane in iron. Subsequently, magnetite Fe\(_3\)O\(_4\) resulting from partial decomposition of wüstite phase is oriented identically with wüstite. Work carried out by Higginson et al. [34] on texture development of iron oxide scales using EBSD illustrated strong relationships between textures of wüstite and magnetite, where FeO showed a strong (100)[001] component similarly observed in Fe\(_3\)O\(_4\) as well as the (110) in [001] component. Epitaxy causes stress development in the oxide layer as the scale grows; this is attributed to the slight misfit between the oxide and metal crystal structures. The stresses generated cause dislocation arrays in the oxide forming pathways for diffusion and hence mass transport through the scale. These results in a mosaic structure developing in the oxide scale consisting of small
crystallites with orientations slightly tilted or twisted with respect to each other. The stresses observed in these oxide layers increases as the films grow thicker until at some point the bulk scale tends to become polycrystalline and epitaxy is gradually lost [35].

As the oxide layer becomes thicker, its grain size increases. Crystals which are favourably oriented for growth will grow at the expense of their neighbouring grains until the oxide surface consists of a few large grains having similar orientation. Orientation and texture effects on oxide scales are also affected by temperature, preferred crystal face with a lower free energy of formation, oxide thickness and oxygen pressure among others. Juricic et al. [36] studied the evolution of microstructure and internal stresses on iron polycrystals and on (110) iron single crystals. They showed that oxide growth, epitaxy and fibril textures of hematite and magnetite varied for both substrates. The scale formed on the single crystal with a (110) surface, showed an inner zone with a [110] fibre texture which weakened with increasing thickness. On the polycrystalline substrate, no preferred orientation was observed, the scale however showed a [001] texture. During initial magnetite growth, the grains attempt at having a common crystallographic orientation [001] of minimal free energy. On long term oxidation conditions, both substrates showed a [001] orientation. They also concluded that the observed internal stresses in the scale were independent of substrate microstructure, but stress relief occurred in magnetite layer due to formation of a fine grained seam at the metal-oxide interface.

In summary, a polycrystalline metal surface that is not preferentially oriented, the first thin film to form has a random orientation but due to the variation in growth rate with orientation, the oxide grains would be of different thicknesses. And as oxidation proceeds, some of the oxide crystals grow more rapidly at the expense of others due to having favourable orientation. Furthermore, the oxide scales formed can be amorphous or crystalline in nature, with the former having a direct effect on the diffusion of molecular species through them for the inward oxide formation. For crystalline oxide scales, their growth has a strong correlation with the substrate orientations giving rise to epitaxy oxide phenomena, which also results in stress development with continued oxide growth, and the subsequent effect on the transport mechanisms through the scales.

2.6 OXIDATION OF PURE METALS AND ALLOYS

2.6.1 Introduction

Steels are widely used materials due to the desirable characteristics and properties which are applicable to many engineering applications. The majority of steels are carbon containing alloys (containing 0.03-0.12% carbon), with the carbon content dependent on the mechanical property requirements. During processing to the desired end product, such as
pipes, tubes and flat rolled sheets, they undergo oxidation forming thick oxide layers. These are generally referred to as primary, secondary or tertiary oxide scales depending on which stage of the processing they occur. These oxide scales are normally removed mechanically by a hydraulic de-scaler during processing [18]. Under high temperature conditions, the oxidation behaviour is different than that observed in ambient temperature for most metals. The presence of alloying and impurity elements observed in steels significantly affect the oxidation behaviour at elevated temperature compared to the parent iron oxidation. Thus, several factors must be taken into account during high temperature oxidation such as [14]:

- The varying affinity to oxygen for the alloying elements making up the alloy
- The formation of ternary or higher oxides
- Some level of solid solubility between the oxides
- Different mobilities of cation species in oxide phases
- Effects occurring due to the dissolution of oxygen into the alloy resulting in sub-surface precipitation of oxides with one or more alloying elements, also termed as internal oxidation phenomena.

Steel contains various alloying elements added mainly to improve the desired mechanical properties. Their presence in the bulk matrix affects the overall oxidation behavior of steels under high temperature oxidation conditions. These alloying elements include chromium, aluminium and silicon, which are less noble than iron and provide a degree of oxidation resistance to steels but above certain concentrations. Other elements such as copper, nickel and tin usually accumulate at the scale-substrate interface and have little effect on steel oxidation behaviour. This emphasises the role of alloying elements on the oxidation behaviour of steel alloys [18, 37].

2.6.2 Iron oxidation

Pure iron is hardly ever used in high temperature applications, and is considered as having a very exothermic reaction even at ambient conditions compared to iron in its various alloying grades. When iron is oxidized, it forms three thermodynamically stable oxides; wüstit (FeO), magnetite (Fe₃O₄) and hematite (Fe₂O₃), illustrated in equilibrium diagram, Figure 9. Several authors [32, 34, 38, 39] have studied oxide scales formed on low alloy steels at various oxidation conditions using EBSD, EDS and X-ray diffraction techniques all agreeing on the existence of these three oxide scale layers. The use of the equilibrium phase diagrams such as the iron-oxygen system, have proved resourceful in understanding oxide scale formation. The diagram, Figure 9, shows that wüstit (W) is not thermodynamically favoured to form below 570°C and that the scale formed would consist of magnetite (M) and hematite (H). Above 570°C, the scale consists of all the three oxides starting with FeO next
to the metal, followed by Fe$_3$O$_4$ next to FeO and Fe$_2$O$_3$ as the outermost layers (shown by red arrow). This observation has been attributed to FeO being rich in metal requiring less oxygen partial pressure and Fe$_2$O$_3$ as the oxygen rich oxide requiring a high partial pressure of oxygen to form. Figure 10, schematically shows the oxide layers on a low alloy steel; starting with the internal oxide precipitates of wüstite and alloying elements within the substrate, followed by a thick wüstite layer with its outer region having magnetite precipitates, then a magnetite layer and an outer hematite layer.

**Figure 9** Equilibrium phase diagram of Iron-Oxygen binary system showing the conditions for wüstite, magnetite and hematite formation [40]

**Figure 10** Schematic representation of Low alloy steel oxidation, showing internal oxidation and varying Fe-O stoichiometry across the scale [41]

*Wüstite* (of the structure halite) is considered a p-type conductor, with a wide range of stoichiometry, from Fe$_{0.95}$O to Fe$_{0.88}$O dependent on temperature and oxygen partial
pressure, p(O)₂. This shows that the concentration of lattice defects must be unusually high indicating that the diffusion rate through this layer is high and essentially cationic in nature.

*Magnetite*, Fe₃O₄, also exists with an excess of oxygen, but the excess is much smaller compared to FeO. It is characterised by an inverse spinel structure with all Fe⁺² and half of the Fe⁺³ ions occupying octahedral sites and the other half of the Fe⁺³ occupying the tetrahedral sites. Defects occur on both sites and as a result, iron ions may diffuse over both tetrahedral and octahedral sites. Oxide behaves as a p-type conductor with metal ions moving outwards. *Hematite*, Fe₂O₃ of the structure corundum, is an n-type conductor in which anions largely diffuse as shown by Bevan *et al.*[42], however, Bruckman *et al.*[43] also showed that cationic transport occurs. Hematite commonly exists as α-Fe₂O₃, which is rhombohedral and considered for high temperature oxidation or can be found as metastable β-Fe₂O₃ form. In α-Fe₂O₃, oxygen ions exist on a HCP arrangement with iron ions in the interstices and cubic in structure respectively. [15-17]. At temperatures below 900°C, the mobility of the cation vacancies in wüstite becomes considerably less so that the outward diffusion of Fe²⁺ ions becomes slower than the adsorption giving a parabolic rate relationship. If at 900-1000°C the oxygen partial pressure exceeds 1 x 10⁻³ - 3 x 10⁻² atmospheres, a transition from linear to parabolic growth rate occurs. Under these conditions, magnetite and hematite are formed on top of wüstite and the oxidation reaction becomes diffusion controlled [16]. Thus, from the above considerations, a simplified diagram can be formulated for the oxidation mechanism of iron above 570°C as shown in Figure 11.

![Figure 11 showing oxidation transport processes in the Iron - Oxygen system, with electrons, ions and vacancy migrations occurring across the scale of varying Fe-O stoichiometry [14-16, 20]](image)
The phase boundary reactions numbered 1-4 are given as follows:

1. \[ \text{Fe} = \text{Fe}^{2+} + 2e^- \]  
   \[ \text{Equation 1} \]

2. \[ 4\text{FeO} = \text{Fe}^{2+} + 2e^- + \text{Fe}_3\text{O}_4 \]  
   \[ \text{Equation 2} \]

3. (a) \[ 3\text{Fe}_3\text{O}_4 = \text{Fe}^{n+} + ne^- + 4\text{Fe}_2\text{O}_3 \]  
   \[ \text{Equation 3} \]
   (b) \[ \text{Fe}_2\text{O}_3 = 2\text{Fe}^{3+} + 3\text{O}^{2-} \]  
   \[ \text{Equation 4} \]

4. (a) \[ \text{Fe}_2\text{O}_3 = 2\text{Fe}^{3+} + 6e^- + \frac{1}{2}\text{O}_2 \]  
   \[ \text{Equation 5} \]
   (b) \[ \frac{1}{2}\text{O}_2 + 2e^- = \text{O}^{2-} \]  
   \[ \text{Equation 6} \]

At the iron-wüstite interface, iron ionises according to phase boundary reaction 1. The iron ions and electrons migrate outwards through the FeO layer over iron vacancies and electron holes respectively. At the wüstite/magnetite interface 2, magnetite is reduced by iron ions and electrons according to boundary reaction 2. Iron ions and electron surplus to this reaction proceed outward through the magnetite layer, over iron-ion vacancies on the tetrahedral and octahedral sites and over electron holes and excess electrons respectively. At the magnetite/hematite interface, magnetite is formed according to boundary reaction 3a, the value of \( n \) being 2 or 3 for Fe\(^{2+}\) and Fe\(^{3+}\) respectively. If iron-ions are mobile in the hematite, they migrate through this phase over iron vacancies together with electrons and new hematite will form at the Fe\(_2\)O\(_3\)/gas interface according to boundary reaction 4a. At this interface, oxygen also ionizes according to reaction 4b. If oxygen ions are mobile in the hematite layer, an n-type semiconductor, the iron-ions and electrons in excess of requirements for the reduction of hematite to magnetite will react with oxygen ions diffusing inwards over oxygen vacancies forming new Fe\(_2\)O\(_3\), boundary reaction 3b. The corresponding electrons then migrate outwards through the hematite to take part in the ionization of oxygen at the Fe\(_2\)O\(_3\)/gas interface. Since the scale formed above 570°C is predominantly FeO, its growth controls the overall kinetics. Additionally, the rapid reaction rates affect scale adhesion causing a porous inner layer of FeO on iron [14-17, 20, 44].

In summary, the initial oxide growth, at temperatures between 350 and 500°C, Fe\(_3\)O\(_4\) nucleates first, and then grows laterally over the surface of the iron. Subsequent growth follows parabolic kinetics, where the rate is dominated by the diffusion of Fe\(^{2+}\) and Fe\(^{3+}\) through the oxide grain boundaries. With time, and if the oxygen partial pressure is sufficiently high, Fe\(_2\)O\(_3\) nucleates on the surface of Fe\(_3\)O\(_4\). Once Fe\(_2\)O\(_3\) forms on the surface, the overall oxidation rate is substantially decreased, as the growth rate of Fe\(_2\)O\(_3\) is slower than that of Fe\(_3\)O\(_4\). Subsequently, the growth of Fe\(_3\)O\(_4\) is decreased due to the lower effective partial pressure at the Fe\(_3\)O\(_4\)/Fe\(_2\)O\(_3\) interface. Thus, the oxidation of iron often shows a dependence on the oxygen partial pressure.
2.6.3 Oxidation of ferritic steels

Ferritic steels are usually used in lower temperature zones of superheaters and reheaters, wall membranes or in thick-section components such as headers and steam pipes and their preferential use is due to their high thermal conductivity. These steels are also characterised by a low coefficient of thermal expansion (CTE) compared to the oxide scales formed on them during service. This closer match in their CTE results in the oxides having good adhesion to the substrate, however, due to the rapid growth of the oxide scales and the additional oxide defects and growth stresses, the result is the formation of cracks in the oxides, which subsequently initiate oxide spallation. The resultant effect is that the spalled debris causes pipe blockages as well as being transported into the turbines where they cause blade erosion. Oxide spallation is highly detrimental for ferritic steels, as this exposes the underlying oxide, which is not protective, causing further rapid oxide scale growth. Ferritic steels are classified as either low or high alloyed steels, with the former consisting of the 2.25Cr steels whereas the latter are the 9-12Cr steels. Their resistance to high temperature corrosion and oxidation is attributed to the key alloying elements such as Cr, Si and Al. These elements form protective oxide scales on steels but this is dependent on the critical concentration in weight % of these alloying elements in the bulk composition. Furthermore, the type of oxidising environment will also determine whether protective or non protective oxides are formed on these steels.

According to Ernis and Quadakkers [8], Viswanathan et al.[45], and Zurek et al.[46, 47], ferritic steels can be classified into three groups depending on the oxidation behaviour, which is primarily determined by the Cr concentration in weight % in the bulk of the alloy composition:

i. For steels with chromium levels below 3%, the oxide scales formed have a duplex structure consisting of an outer scale layer composed of Fe₃O₄ (including a small amount of Fe₂O₃) and an inner scale composed of (Fe,Cr)₃O₄ each with approximately the same thickness. The types of oxides formed are dependent on the alloy composition and the oxygen partial pressure. The oxidation kinetics observed for these ferritic alloys range from parabolic to linear kinetics under isothermal oxidation tests. Bueno and Marino’s [48] work on 2.25cr steels showed parabolic growth kinetics for samples oxidised in air at temperatures ranging from 600 – 800°C. For ex-service oxidation kinetics, the results suggest a cubic, linear or mixed kinetics for temperatures up to 700°C. Sumida et al.[49] working on 2.25Cr steels used in superheaters and reheaters also reported parabolic growth kinetics with the scales formed have a duplex oxide structure.
i. Steels with chromium levels around 9-10% form thick oxide scales with the main constituent being magnetite. These steels at 550°C show minimal or slow diffusion of Cr (as well as other scale forming elements) and that its incorporation into the scale mainly occurs by embedding of Cr-rich carbides in the inner part of the scale due to the inwardly moving scale/alloy interface. This is such that there is hardly any selective oxidation of Cr. Therefore, in the inner scales, the oxidised carbides occurs as particles of (Fe,Cr)\(_3\)O\(_4\) spinel and their distribution within the inner scales exhibits a similarity with the carbide distribution in the steel. The scale observed at the interface with metal has been shown to be a mixture of wüstite and Cr-rich precipitates of chromia and Fe/Cr spinel. An increase in temperature to 600/650°C causes an increase in oxidation rate but the tendency of selective oxidation of Cr increases resulting in the formation of a Cr-rich zone of Fe/Cr spinel in the inner parts of the scale as well as causing a Cr depletion zone in the underlying metal matrix. At higher test temperatures and longer exposure times, the kinetics of the surface reaction is seen to affect the oxide scale layer with the absence hematite, which would otherwise exist in thermodynamic equilibrium with the gas atmosphere. Hematite’s absence could be attributed to spallation effects during cooling or due to low oxygen partial pressure. For these types of steels, parabolic kinetics are the dominant growth rates observed as corroborated by several authors [37, 50, 51]

ii. Steels with chromium levels around 10-12% exhibiting highly variable steam oxidation behaviour with the thickness, morphology of the scales differing as a function of test duration, temperature, minor alloying additions, grain size and surface treatment. The scales formed are characterised by Cr-rich spinel layers and subsequent magnetite formation. For these steels, an increase in temperature to 650°C can lead to an increase as well as a decrease in oxidation rate depending on the exact Cr content and the incremental temperature employed. The work of Tan et al.[52, 53] on 9-12Cr steels in supercritical water showed improved oxidation resistance on 12Cr steels with the oxidation kinetics also exhibiting a parabolic growth profile.

iii. Steels with more than 12.5%Cr possess excellent steam oxidation resistance and the scales consist of mainly Cr\(_2\)O\(_3\), (Cr,Fe)\(_2\)O\(_3\) or Cr-rich (Cr,Mn,Fe)\(_3\)O\(_4\) with an outermost layer of Fe\(_2\)O\(_3\). The high levels of Cr in these steels stabilize the protective oxide scale formed. Huczkowski et al.[54] working on high Cr ferritic steels further showed the importance of Cr concentration levels in the scale, which were instrumental in determining the lifetime of the alloys as opposed to the Cr levels in the bulk of the alloy. The oxidation rates are determined by
transport processes and the rate increases with increasing temperature. It is important to remember that temperature has an effect on Cr forming protective oxide scale as chromia volatilisation occurs with higher temperatures. The studies of Peraldi and Pint [55] on the oxidation behaviour of ferritic steels were in good agreement with the observations made above, with their results showing the formation of Cr-rich corundum (Cr,Fe)$_2$O$_3$ during growth of protective oxide scale and specimen mass loss occurrence, which they attributed to volatilisation of Cr species by changing the protective Cr-rich layer to non-protective $\alpha$-Fe$_2$O$_3$ layer.

Early oxidation studies involved weight gain measurements, however, there is an increasing trend towards oxide scale thickness measurement as used in this study. For low Cr ferritic steels, the assumption used is that the interface between the outer and inner oxide layer represent the original metal surface, such that the thickness of the inner oxide layers is a good measure of metal loss [56]. Caution must be taken for ferritic steels, where the oxide becomes more protective with time, as the relative thickness of the outer oxide layer may decrease.

2.6.4 Oxidation of austenitic stainless steels

Austenitic stainless steels are increasingly being used in the superheater and reheater components of boilers in power plants. This is attributed to their excellent creep properties and resistance to high temperature oxidation on both the fireside and steam-side surfaces of these boiler components. Furthermore, the expected thermal efficiency improvements of conventional power plants by increasing the steam temperature to $\sim$ 700°C by 2030 present new challenges to existing ferritic based materials, which favours austenitic stainless steels as the preferred candidate materials for the high temperature piping [10]. Austenitic stainless steels, with their excellent thermomechanical properties, are characterised by a high coefficient of thermal expansion (CTE) compared to the oxide scales formed during service. This mismatch in CTE results in the tendency of the oxides to crack and to spall off, with the spalled debris causing pipe blockages or blade erosion in the turbines. However, when spallation occurs in austenitic steels, it leaves a highly protective inner oxide scale, which becomes the rate controlling scale as opposed to the non-protective iron oxides that are formed on low Cr ferritic steels.

These steels typically fall into four categories; 15Cr, 18Cr, 20-25Cr and higher Cr ASS [57]. Their initial development consisted of mainly variations in the Ti and Nb contents for stabilisation from a corrosion point of view, then reducing Ti and Nb (under stabilisation) for improved creep properties. In this study, the austenitic stainless steels studied were E1250
and 347HFG which fall in the 15Cr and 18Cr categories respectively and have no Ti but contains appreciable Nb and Mo contents, with the addition of other alloying elements such as Cu for increased precipitation strengthening [58]. Literature reports [45, 59, 60] that the high temperature oxidation behaviour of these steels follows a parabolic growth rate in water vapour containing environments with the resultant oxide scales formed exhibiting an outer layer consisting of Fe rich oxides and an internal oxidised zone consisting of a mixture of Fe-Cr rich spinel type oxides. The presence of Ni in the alloy matrix has been proposed to improve their corrosion resistance compared to the ferritic low alloy steels in addition to stabilising the austenite phase. They also have a high Mn content with N content occasionally used to replace Ni as an austenizer as well as Mo, with concentration levels of up to 6 wt.% in some alloys [58]. The elements making up these alloys have a significant effect on the observed oxidation behaviour among other external factors [61].

Huntz et al. [62] studied the oxidation behaviour of austenitic stainless steel 304 and showed that parabolic kinetics occurred at low oxygen partial pressures for temperatures ranging from 850°C-950°C with chromia oxide scale formation. At high oxygen partial pressures and for temperatures above 850°C, the oxidation kinetics changed with the initial chromia formation followed by the growth of iron oxides inducing high oxidation rates. In the presence of water, whiskers rich in Cr and Mn were also observed on the substrate grain boundaries as well as the internal oxidation of silicon. Hanson et al. [63, 64] looked at steam oxidation of austenitic stainless steel 347 HFG, where they observed slower oxidation rates on grain boundaries than the rates by which the bulk substrate grains oxidised internally to form FeCr₂O₄. They also observed the formation of the chromia layer, which together with the FeCr₂O₄ controlled the oxide growth rates. Sun et al. [65] studying the scales formed on austenitic stainless steel 316 exposed to supercritical conditions reported that multi-layer oxide scales were formed on the substrate. These were identified from the outer to inner oxide layers as (Fe,Cr)₂O₃ / (Fe,Cr)₃O₄ and Cr₂O₃, with the substrate region adjacent to the Cr₂O₃ layer exhibiting a Ni-rich zone. They attributed the outer scale, (Fe,Cr)₂O₃, growth to Fe, which has a higher diffusion coefficient than Cr in oxides formed and through the steel substrate. The basis of their proposition was that the Cr content in the (Fe,Cr)₂O₃ layer decreased from 8 at.% in the inner areas of the oxide to 2at.% in the outer area. These steels are used for thin section heat transfer piping at temperatures above the temperature limits for ferritic steels and are characterized by a composition primarily of Cr (15-26%wt) and Ni (5-37%wt).
2.7 OXIDATION IN AIR AND STEAM ENVIRONMENT

Several authors [21, 66-69] have observed that water vapour has a detrimental effect to high temperature oxidation of steel alloys, but this was dependent on other factors such as the oxidation time, testing conditions and the Cr alloy contents. Under dry atmospheres, ferritic steels are known to form protective Cr₂O₃ oxide scale but this is subject to the Cr concentration levels within the bulk of the alloy. Othman et al. [69] showed water vapour causes accelerated or catastrophic oxidation behaviour, where a non-protective, iron rich oxide scale forms reducing dramatically the performance life of an Fe-9Cr alloy. They also showed an accelerated chromia scaling for Fe-17Cr steel with additions of water vapour. A change of environment to water vapour containing atmosphere results in dramatic changes in the oxidation behaviour of steel with the resultant oxide scales being less protective than Cr₂O₃ [21]. Sanchez et al. [70] working on steam oxidation of P91 showed that different scale structures formed on the surface as a function of temperature but the presence of water vapour had a significant effect on the stability of protective oxide phases. Porosity in the outer scale was associated with the formation of volatile species, Fe(OH)₂, from a higher reactivity of the scale with steam. Oxidation of P91 at 650°C and 800°C, showed Fe₂O₃, Fe₃O₄, (Fe,Cr)₃O₄ and Fe₃O₄, (Fe,Cr)₃O₄ phases respectively, with the latter being the thermodynamically stable phases at 100% water vapour levels. Similarly, Ehlers et al.[71, 72] working on 9Cr steels also showed the detrimental effect of water vapour on oxide scale formation of P91 steel and its relation to the breakaway oxidation occurrence and oxide scale spallation.

Essuman et al. [73] studied Fe-Cr alloys and showed that the oxidation mechanism occurring when changing from gas to water vapour containing atmospheres enhanced the tendency for Cr to become internally oxidized causing a rapidly growing non-protective iron rich scale. However, there were problems associated with the protective Cr₂O₃ stability at high temperatures [14, 20]. At temperatures above ~1200°C, Cr₂O₃ was shown to undergo volatilisation to CrO₃ in dry atmospheres and in the presence of water vapour chromium is lost from the scale by the formation of CrO₂(OH)₂ (a gas). Othman et al. [69] further showed a loss in chromium due to volatilisation but since they used low partial pressures of water vapour and oxygen, low gas flow rates and short reaction times, the levels of Cr loss noted were negligible but the results pointed out the importance of these parameters on the oxidation of Fe-Cr alloys. Segerdahl et al.[74] showed the effect of flow rate on the loss of chromia, and proposed that any volatile species formed diffuses through a layer of stagnant gas separating the oxide surface from the bulk of the flowing gas. This stagnant layer decreases with increasing flow rates, which exacerbates the subsequent loss of the Cr rich species. The loss of important alloying elements such as Cr in chromia forming alloys has a
direct effect on the formation of the protective oxide scales and subsequently affects the onset of non protective oxide scales through breakaway oxidation phenomena.

2.8 BREAKAWAY OXIDATION

Breakaway oxidation occurs in metal alloys when a protective scale of a slow growing oxide can no longer be maintained due to selective oxidation causing other alloying components to start oxidising resulting in accelerated alloy consumption. It can also occur when the oxide parabolically grows to a critical thickness above which cracking and rupturing of the protective scale occurs. Several authors [73-77] have shown the effect of water vapour on the oxidation of chromia forming alloys, such that with increasing water content and flow rates, localised breakaway oxidation occurred on the surface resulting in the formation of Fe rich oxides and Fe rich Fe-Cr spinel oxides. This localised breakaway oxidation occurs due to the formation and loss of volatile Cr rich phases, which leaves behind a Cr depleted oxide. Further oxidation results in Fe diffusing through to replace the lost Cr in the oxide thus forming Fe rich Fe-Cr rich oxides and with increasing exposure time, nodular growths also occur above the Fe rich Fe-Cr rich oxide phase as Fe-O rich oxide phases. Furthermore, the depletion of the key alloying element such as Cr in the alloy matrix, means upon crack formation in the scale, no crack healing occurs and the base metal is exposed to oxidising gas causing linear oxidation kinetics as illustrated in Figure 12. Essuman et al. [73] also concluded that for low alloy ferritic steels, internal oxidation had a profound effect on the breakaway oxidation by modifying the transport processes in the metallic matrix. Similarly, Evans et al. [78] showed that breakaway oxidation occurred due to the depletion of chromium arising from selective oxidation, but they also related other effects such as decreasing grain size and increased temperatures as the onset of this phenomenon.

Figure 12 schematic representation of breakaway oxidation kinetics, there is an initial parabolic oxide growth before linear or accelerated oxidation of the substrate occurs [11]
2.9 INTERNAL OXIDATION PHENOMENA

Internal oxidation occurs in alloys when the oxidant gas dissolves in the alloy and diffuses inwards to react with the solute metal to form dispersed precipitates of metal oxide or metal carbides. It is dependent on the gas-solid interaction and the formation of a reaction product zone adjacent to the alloy surface. The thickness of the internally oxidised zone depends on the depth at which the concentration of dissolved oxygen becomes too small for oxide formation. The process is considered highly destructive as the internally oxidised zone exhibits embrittlement and dilation of the subsurface region of the alloy, which can cause oxide scale flaking. This is considered to be the main cause of high temperature corrosion failures. Essuman et al. [73] showed that temperature changes affected internal oxidation by changing the steady-state diffusion gradients hence affecting the growth rate of the internal oxidised zone.

Goncharav and Kanunnikova [79] studied Fe-Cr alloy oxidation using XPS scans on the surface scale and developed a phase composition-depth profile in which the oxide scale consisted of Fe and Cr rich oxides as would be expected of ferritic alloys with an internal oxidation region composed of chromium oxides and nitrides. Essuman et al. [68, 73] also had similar observations for Fe-Cr alloy with preferential internal oxidation of Cr when the conditions were changed from gas to water vapour containing atmospheres. Hansson et al. [64] studied the microstructure evolution of a Nb stabilised austenitic 347 HFG steel and showed that internal oxidation occurred with the formation of Fe-Cr spinel in an Fe-Ni matrix. They also concluded that the presence of water vapour induced the inward anion species transport at 600°C resulting to internal oxidation.

Another phenomenon related to internal oxidation is the transition from internal to external (selective) oxidation. This occurs when the concentration of the less noble alloying element, Cr, Al or Si is increased such that a critical level is reached above which the alloy no longer oxidizes internally. The alloy thus forms a protective scale, such as Cr$_2$O$_3$, Al$_2$O$_3$ or SiO$_2$ on the surface - a process termed as selective oxidation. Furthermore, changing the oxidation conditions or presence of a second solute in the alloy matrix, whose oxide has a stability intermediate between the less noble and parent alloy components will affect the transition from internal to external oxidation. The latter case if often instrumental in high temperature alloy design, where the element giving protective scale through selective oxidation, such as Al, may have a deleterious effect on other alloy properties. Its concentration therefore should be held as low as possible by the addition of a second solute element leading to the development of the infamous M-Cr-Al alloys (M = Fe, Ni or Co)[14, 20].
2.10 EFFECT OF ALLOYING ELEMENTS ON OXIDATION BEHAVIOUR

Alloying elements are generally used in steels for purposes of solid solution and precipitation strengthening. These elements do form second phase particles such as $M_{23}C_6$, carbo-nitrides such as Nb(C,N) and (NbCrN) which confer strength through their stability in the alloy microstructure. These second phase particles do accommodate substantial Cr concentrations and since Cr participates in the formation of the protective Cr rich oxides, the amount and distribution of these second phase particles can play a key role on the formation of protective oxide scales [10]. The alloying additions considered include Cr, Ni, Si, Mn, Mo, W, Al, C and Co, which have an influence on the oxidation behavior of most alloys. Steels have Ni and Cr as the main alloying elements in heat resistant alloys attributed to their well known oxidation resistance properties. Other elements present include Al and Si, which, depending on their concentration (weight %) in the bulk matrix, can have adverse effects on the mechanical properties of these alloys but also offer good oxidation resistance. Several authors [56, 80, 81] have shown interrelations (joint effect) between the main alloying elements (Cr, Si, Mn, Mo, S and W) in providing oxidation resistance to heat resistant alloys Lepingle et al. [82] work on steam oxidation of 9-12%Cr steel showed complex interrelations between the main alloying elements (with varying concentrations in weight %) and emphasised the need to consider their joint influence on steam oxidation behaviour.

2.10.1 Effect of chromium

Chromium has been extensively researched in Fe-Cr alloy systems. Increasing its content in steels leads to iron chromium spinels formation and for the iron oxides present, the wüstite layer becomes thinner relative to magnetite and this is attributed to $\text{Fe}^{2+}$ blockage by the spinel structure. A further increase in Cr, results in a mixed spinel of $\text{Fe}(\text{Fe,Cr})_2\text{O}_4$ which further decreases the oxidation rates leading to the observed parabolic oxidation kinetics [14-16, 18, 45, 69, 70]. When the Cr level exceeds a critical concentration (12%wt) an initial outer layer of pure chrome is formed. Its stability over longer exposure times means a larger amount of Cr is required of about 20% and 25%wt at 900°C and 1000°C respectively. The high chromium containing steels has been shown to exhibit good scale adhesion compared to the low Cr containing steels [29, 83, 84]. Meir et al.[85] investigated the effect of Cr content and exposure environment on the selective oxidation of Fe-Cr alloys, the results of their study showed that there was a critical Cr content required to support continued growth of chromia scale in air in the temperature range 550-650°C corresponding to approximately 10% Cr. In addition, the oxidation experiments carried out in either CO$_2$ or H$_2$O disrupted the selective oxidation process such that substantially higher Cr concentrations are required to develop a protective chromia scale.
2.10.2 Effect of nickel

Nickel is mainly added in ferritic steels to transform it to austenitic with an FCC structure, which is more stable at high temperature. Its addition, however, results in significant reduction in oxidation rate at various temperatures, for example, nickel contents of 20%, 30% and 50% are effective at 870°C, 980°C and 1200°C levels respectively. Peraldi and Pint [55] proposed several mechanisms of how Ni supplements the oxidation resistance such as affecting the Cr diffusivity in the alloy, lowering oxygen solubility/diffusivity in the alloy or by affecting the activity of Cr (by increasing it) and/or Fe (decreasing it) at the oxide/alloy interface, a condition for chromia scale growth. Botella et al. [86] looked at austenitic stainless steels with 2% (with high Mn) and 8% Ni (with low Mn) contents with the results showing that both had similar weight gains during high temperature oxidation. The low Ni steel mainly exhibited the Mn-Cr rich spinel and chromia scale, whereas the high Ni steel had a chromia scale as the protective oxide scale.

2.10.3 Effect of silicon

Silicon additions have been shown to slow oxidation rates in steels, however, when silicon amount exceeds 2-3%, a marked embrittlement is observed in the parent alloy. When used with other beneficial elements such as Cr, silicon is quite effective in providing oxidation resistance, its effect has been studied extensively and demonstrated in various environments; carbon dioxide rich, humidified H₂-H₂O/Ar atmosphere for various austenitic steels. It has been shown to retard breakaway oxidation in water vapour containing atmospheres as well as aiding repassivation after breakaway oxidation occurred.

![Figure 13 Showing effect of Mn, Si and Co on critical Cr content from 550-650°C](image-url)
The work of Vaillant et al. [9] on new grades of steel for advanced coal fired plant showed the effect that Si, Co and Mn additions had on the critical Cr concentration level that dictates the steel oxidation behaviour. They found that the addition of Si and Co had a joint effect by lowering the critical Cr content but Mn had a negative effect, Figure 13.

Liu et al. [87] studied the oxidation of Ni-Cr-Fe based alloys and showed that Si affected oxidation rates such that alloys with low Si content had the highest weight gain over a wide range of temperatures, but its effect is prominent at higher temperatures, 800-950°C. For low or high Si contents and at temperature ranges of 800-850°C, oxide formation was inhomogeneous and took the morphological pattern inherited from the alloy substrate and was primarily observed on alloy carbides as opposed to the austenite regions within the austenitic structures. This effect diminished for low silicon alloys, which they attributed to low Si availability in forming a continuous SiO₂ sub-layer which acted as a diffusion barrier on both the eutectic and austenitic structures. For high Si contents, the oxide ridges were present up to 950°C as the continuous SiO₂ sub-layer on the austenitic area acted as an effective diffusion barrier to cation outward diffusion. Griess and Maxwell [88] also reported that Si additions of up to 0.5% had an effect on the oxidation kinetics by reducing it. Furthermore, they concluded that in the long term oxidation studies of the 2.25Cr and 9Cr steels with high Si contents, the presence of Si retarded the onset of oxide scale spallation. Mikkelsen et al. [89] also showed how Si affects the oxidation behaviour of Fe-22Cr steel oxidised at 900°C. Si formed silica precipitates beneath a chromia layer, which over longer exposure times and high Si content in the alloy matrix coalesced to form a protective silica layer beneath the chromia layer. The overall effect of Si on the oxidation behaviour of steels is such that it segregates beneath an external Cr rich oxide phase, where it inhibits the outward diffusion of cations [61]. This occurs by reducing the area of direct contact between the outwardly growing oxides and the substrate [90, 91].

2.10.4 Effect of aluminium

Aluminium addition in steels significantly reduces the oxidation behaviour but has a detrimental effect on the mechanical properties of the substrate. For alumina forming steel, Brady et al. [92] observed that its effectiveness depended on Cr effect, as a third element effect through Cr enrichment in austenite matrix, which aided the establishment of a protective alumina scale. The work of Hussain et al. [93, 94] on high temperature oxidation of nickel superalloys showed Al and Ti additions significantly improved oxidation characteristics in the absence of Mo and smaller amounts of Mn in Inconel 690, Hastelloy C-4. For Incoloy 825 these elements had minimal effect due to presence of Mo which dominated the beneficial effect of Al and Ti additions.
2.10.5 Effect of manganese

Manganese is a common alloying element in iron-chromium based alloys and has been used as an alternative to nickel as an austenite stabilizer, however, its concentration has to be monitored to prevent the formation of undesirable sigma phase in the alloy microstructure. For high temperature oxidation, manganese behaves like Fe such that it forms three oxides with the most notable one being MnO, which has similar free energy of formation as Cr₂O₃. For ferritic steels, Mn has a positive effect towards the oxidation behaviour in steam environments due to its participation in the protective oxide scale formation and in impeding the loss of Cr through volatilisation [10]. Small additions of Mn have been reported to affect oxidation resistance due to the formation of the less-protective MnCr₂O₄ spinel rather than Cr₂O₃. The oxidation rates are faster in the MnCr₂O₄ spinel, in addition to manganese promoting scale blistering and cracking [95, 96]. On superalloys, similar effects have been reported on the formation of Mn-Cr spinels together with chromia, however, this did not affect the scale growth rate but did reduce the formation of the volatile CrO₃. Schutze et al. [37] showed that Mn had a positive effect on slowing down the evaporation rate of Cr containing hydroxyl species due to formation of an outer Cr-Mn spinel layer. Stott et al. also reported similar results working on a high Cr steel with Mn varying from 0 – 5 weight % [97].

2.10.6 Effect of molybdenum and tungsten

Viswanathan et al. [45] also showed that variations in W had minimal effect but Mo was seen to have a negative effect on oxidation behaviour; hence its replacement with W. Osgersby and Fry [83] showed the beneficial effect from Mn and Si on 9-12%Cr steels but their studies also indicated a detrimental effect of W above certain concentration levels. Osgerby and Fry [98, 99] also looked at low alloy ferritic steels, T22 and T23, and concluded that no significant difference occurred in the oxidation behaviour of T23 due to the addition of Nb and W. Buscail et al. [100, 101] showed the role of Mo on austenitic stainless steels oxidised at 900°C, with the results showing that Mo played a protective role through the formation of NiMoO₄ phase but Mo volatilisation was also observed due to its presence on the outer oxide layers. Furthermore, their results showed good scale adherence which was attributed to the Mo rich phase occurring at the substrate/oxide interface in what they described as a keying effect at the interface.

2.10.7 Other alloying elements

There other minor elements present in metal alloys that affect their oxidation behaviour of metallic alloys. The addition of rare earth elements, in small concentrations, improves not only oxidation behaviour by changing the transient oxidation stage of reaction which promotes selective oxidation of Cr, but also enhances scale adherence and reduces scale
spallation. They act as oxygen getters, which assist in the formation of Al₂O₃ and Cr₂O₃ healing layers and these include Y, Ce, Hf, Zr, and La among others [14, 17, 89]. Their concentration (wt%) in the bulk alloy need to be monitored as high levels, for instance Y, has been shown to cause hot cracking of the substrate. Brady et al. [92] studies on alumina forming austenitic steels showed that Nb addition significantly improved oxidation resistance. With high levels of Nb, the volume fraction of B2-NiAl precipitates increased which acted as an Al reservoir for long term oxidation. They also showed the effect of C on 9Cr1Mo steels, where the oxidation rate increased with increasing C content and they suggested this occurred due to C tying up Cr in the form of carbides, which would have been available for oxidation resistance.

In summary, the reliability of materials at high temperature is vital for power generation where conditions of operation are highly corrosive (steam) and involve materials operating at their absolute limit. Water vapour effects (or steam conditions) have been shown to affect the oxidation behaviour of metals and their alloys at high temperatures for alumina, chromia, silica, titania, iron and nickel oxide forming materials. It has been shown how water vapour influences the scale morphology with whisker formation, the porosity/void formation in the scales. Volatilization effects due to the formation of oxyhydroxides, hydroxides in existing oxides resulting to the loss of protective ceramic scales. Oxide growth kinetics and mechanisms have also been shown to change dramatically. Steam oxidising conditions have also been shown to affect the mechanical properties of the scale such as scale adhesion where, for iron oxides, adhesion to the substrate improved but was made worse for alumina and chromia layers.

2.11 EFFECT OF COLD WORKING ON OXIDATION BEHAVIOUR

Cold working of surfaces of metal alloys can promote oxidation resistance, which is generally attributed to the enhancement of diffusion of Cr to the alloys surface due to the increased number of diffusion paths (dislocations) in the cold worked surface region. This results in the formation of Cr rich oxide scale that is rapidly formed when the alloy is exposed to oxidising environment, which subsequently becomes the rate controlling oxide scale. Several authors [102-104] have shown the effect of cold working and its improvement on the oxidation resistance of various steels.

Khanna and Gnanamoorthy [105] showed that cold working had a negligible effect on the 2.25Cr steels for temperatures of up to 700°C, however, beyond this temperature, the results of the study showed a general reduction in oxidation with the effect pronounced at 900°C. The increased oxidation resistance was attributed to the faster diffusion of Cr in the cold worked material compared to the annealed alloys resulting in the formation of Cr rich
spinels, which slows down the oxidation of the alloy. Langevoort et al. [106] working on the effect of cold work on austenitic stainless steels and nickel alloys, showed that cold work improved the oxidation resistance of 304 and 321 steels but had a slight negative effect on 314 and 800H alloy. They attributed this to the microstructural changes occurring in 304 and 321 due to cold work, whereas for 314 and 800H, these alloys had a more stable microstructure and were only marginally affected by cold working. On the other hand, Tan et al. [107] working on the effect of shot peening of alloy 800H showed improved oxidation resistance by creating an outer fine grained morphology that aided outward Cr diffusion. In addition, their study suggested that oxide scale spallation was reduced by preventing the formation of magnetite on the shot peened alloy, which if present would cause exfoliation due to magnetite’s higher volume thermal expansion in comparison with the Cr rich oxide oxides and the substrate, with the latter two having approximately the same thermal expansion rates.

Trindade et al. [108] working on the effect of grain size on high temperature oxidation of austenitic steel TP347 concluded that smaller grain sizes resulted in a predominantly protective chromia scale, whereas a coarse grain size resulted in an iron oxide as the main oxide. Formation of chromia was attributed to a high density of fast grain-boundary diffusion paths which is the case for fine-grained materials. Similar observations on the grain size effects were confirmed by Evans et al. [78] on the mechanisms of breakaway oxidation on chromia forming steel, they concluded that a small grain size (~5μm) increased Cr diffusion rates on the substrate to form a protective oxide scale which allowed even a higher temperature before the onset of breakaway oxidation occurred. Caplan et al. [109, 110] showed the effect of grain size on the oxidation behaviour, where a cold worked nickel oxidized faster than an annealed nickel. They attributed the fast oxidation rates of cold worked nickel to fine grains, which allowed the rapid diffusion of Ni through the substrate to form a NiO layer. The observed fine grained morphology of cold worked surfaces could have provided a basis for the development of the fine grained steels such as 304H and TP 347HFG, which were developed with the intention of providing improved resistance to steam oxidation.

In summary, coldworking has been shown to improve the oxidation characteristics of different steel and nickel alloys. The effect has been attributed to changes in substrate grain morphologies and the associated increase in short circuit diffusion paths allowing faster diffusion of Cr to the surface for the formation of Cr rich protective oxide scales.
3 EXPERIMENTAL PROCEDURES

3.1 INTRODUCTION
In this chapter the materials selected, the reasons for their choice, the methods of sample preparation (both pre and post oxidation), and the techniques used to examine the oxides scales formed will be described. The oxidation experiments were carried out at temperature ranging between 500 - 750°C. The exposure times used ranged between 1,000 and 5,000 hours, no short time oxidation experiments were carried as the aim of this study is to investigate longterm exposure of existing and proposed materials at elevated temperatures, for conditions approximating those expected in supercritical and advanced supercritical boilers.

3.2 MATERIALS
The materials under investigation are the 2.25Cr and 9Cr ferritic steels and the 15Cr and 18Cr austenitic stainless steels as presented in Table 1, with their corresponding nominal chemical compositions in weight %.

Table 1 showing the average nominal compositions in weight % of the ferritic and austenitic stainless steels under investigation, ASTM standard [111]

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Nominal composition % wt (balance is Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>T22</td>
<td>0.10</td>
</tr>
<tr>
<td>T23</td>
<td>0.07</td>
</tr>
<tr>
<td>P91</td>
<td>0.11</td>
</tr>
<tr>
<td>P92</td>
<td>0.10</td>
</tr>
<tr>
<td>E1250</td>
<td>0.10</td>
</tr>
<tr>
<td>347HFG</td>
<td>0.08</td>
</tr>
</tbody>
</table>

For the steam oxidised samples, Table 2, the 2.25Cr steels were supplied by Doosan Babcock, UK, as rectangular coupons, which were machined off from virgin tubular sections, these were oxidised in a 100% flowing steam from 500°C to 700°C at atmospheric pressure for 1,000 hours of oxidation.

Table 2 showing the material matrix of the samples oxidised in steam conditions for 1000 to 3000 hours from Doosan Babcock (blue) and National Physical Laboratory (red)

<table>
<thead>
<tr>
<th>Materials</th>
<th>Temperature (°C)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>510</td>
<td>568</td>
</tr>
<tr>
<td>T22</td>
<td>T22</td>
<td>T22</td>
</tr>
<tr>
<td>T23</td>
<td>T23</td>
<td>T23</td>
</tr>
<tr>
<td>P91</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P92</td>
<td></td>
<td></td>
</tr>
<tr>
<td>347HFG</td>
<td>347HFG</td>
<td></td>
</tr>
<tr>
<td>E1250</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
For the 9Cr ferritic steel, the 15Cr (E1250) and 18Cr (347HFG) austenitic stainless steels, these were supplied by the National Physical Laboratory, UK, also as rectangular coupons. The samples from NPL were exposed to 100% flowing steam at exposure temperatures of 650°C and 700°C at atmospheric pressure. After the oxidation experiments, all the samples were allowed to cool to room temperature before subsequent post oxidation preparation and analysis.

For the static air oxidised samples, the oxidation experiments were carried out at Loughborough University using boiler tubing supplied by Cranfield University. The tubes were the 2.25Cr (T23) and the 9Cr (P92) ferritic steels and the austenitic stainless steel 347HFG. For air oxidised E1250 austenitic stainless steel, these were supplied as tubular sections by RWE Npower, UK. Smaller coupons were machined off from the tubular sections before oxidation experiments were carried out as presented in Table 3.

Table 3 showing the material matrix of the samples oxidised in static laboratory air conditions at 650°C and 750°C for 250 to 5,000 hours of oxidation

<table>
<thead>
<tr>
<th>Material</th>
<th>Temperature (°C)</th>
<th>Exposure Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>650</td>
<td>750</td>
</tr>
<tr>
<td>T23</td>
<td>T23</td>
<td></td>
</tr>
<tr>
<td>P92</td>
<td>P92</td>
<td></td>
</tr>
<tr>
<td>347HFG</td>
<td>347HFG</td>
<td></td>
</tr>
<tr>
<td>E1250</td>
<td>E1250</td>
<td></td>
</tr>
</tbody>
</table>

3.3 OXIDATION EXPERIMENTS

3.3.1 Sample preparation

Sample preparation involved pre-oxidation and post-oxidation procedures. For the steam oxidised samples, the rectangular coupons were prepared from tubular sections and were mechanically ground using progressively finer SiC paper, finishing with the 600 grit paper and ultrasonically cleaned in ethanol before oxidation in steam rigs.

For the air oxidised samples, pre-oxidation procedures involved machining off coupons, Figure 14(a), from the boiler tubes and marked by punching numbers and introducing indents for ease of identification during post oxidation examination. The coupons were prepared by mechanical grinding using progressively finer SiC paper on the adjoining surfaces, finishing with 600 grit paper, and ultrasonically cleaned in ethanol before being placed in box furnaces for the oxidation experiments. The procedure involved oxidising the sample coupons with one surface ground to 600 grit finish (B), and the adjoining surface without any grinding also referred as the ‘as-received or ID side’ surface (A), Figure 14(b). Its worth noting that curved surfaces do affect the high temperature oxidation of metals. The effect is such that if a flat surface is being oxidised with the ratio of the volume of the oxide to that of the metal ~ 1, as the metal is consumed, the oxide/metal interface recedes deep into the substrate.
The oxide scale formed is still bonded to the surface and move with the retreating metal. If the scale growth occurs mainly by cationic transport, then no stress is developed in the oxide. If the sample geometry is convex in nature and the metal is receding, as the oxide follows it, compressive stresses will be generated that are tangential into a smaller volume formerly occupied by the metal. For a concave surface, radial stresses are developed. The resultant effect is crack development with subsequent oxide scale spallation effects. The effect is further worsened if there are large variations in coefficient of thermal expansions [17]. However, in this study, for the air oxidised samples, the effect of curvature on crack development was not observed on the convex surface of the austenitic steels or on the ferritic steels, as the scale was intact without the loss of the outer oxide. Where cracks had developed this were presumed to have occurred due to thermal expansion differences between the substrate and the oxide.

**3.3.2 Laboratory air oxidation experiments**

For the air oxidised samples, the experiments were carried out in laboratory air in box furnaces. This involved placing the prepared samples on a ceramic holder with the 600 grit finished surface facing upwards, with the “as-received” surface perpendicular to the ceramic holder. The number of samples on each ceramic holder was 5 with a minimum separation distance of 10mm and these were placed in the middle of the box furnace for the exposure times studied. If more than one ceramic holder was placed in the box furnace, these were positioned close together with a minimum spacing of 10mm. After oxidation, the samples were removed from the furnace and allowed to cool to room temperature in air before the post oxidation examinations.

**3.3.3 Post-oxidation sample preparation**

For post-oxidation procedures, standard metallographic sample preparation was carried out for the steel substrates and the oxide scales formed. Surface preparation involved mounting the samples in conductive polymer resin (Bakelite) for ease of handling and to avoid charging effects during analysis in a scanning electron microscope (SEM), followed by grinding and
polishing. The grinding process entailed grinding on progressively finer grades of SiC paper (from 400 to 1,200 grit levels). For the polishing procedure, this ensured that the resultant surface was both flat and devoid of topographical features unrelated to the bulk microstructure. With each polishing stage, removal of damaged material from the previous stages of surface preparation was achieved by progressively using finer grades of polishing diamond paste, 6µm, 3µm and 1µm respectively. It is important during post oxidation preparation to ensure that both the metal and the oxide scales are ground and polished. Oxide scales tend to be delicate and demand longer and gentler grinding to avoid cracks or loss of the scales at each stage of preparation. For the advanced analytical techniques, such as electron backscatter diffraction (EBSD), a further preparation procedure was carried out as will be discussed in Section 3.4.2.1

For the substrate microstructural analysis, chemical etching was carried out to reveal the underlying microstructure. Picral and/or 2% nital reagents were used for the 2.25Cr steels, Vilellas’s reagent for the 9Cr steels, and a solution consisting of 50ml H2O, 10ml HNO3 and 50ml HCl solution for the austenitic stainless steels grades. The exposure times used during the etching procedure ranged from a few seconds to minutes, but this was dependent on when the microstructure was revealed.

### 3.3.4 Oxide scale thickness measurements

For the steam oxidised samples, the oxide scale thickness measurements were carried out by analysing 10 SEM micrographs of different regions covering the whole oxide formed and getting the average oxide scale thickness as presented. For the air oxidised samples and for each of the material grades studied, two samples were analysed by taking 10 SEM micrographs on each sample covering the whole oxide formed and averaging the results with the aid of Image pro-plus analytical software. For the actual thickness measurements, the software uses a script that measures distances between two lines overlaid on the oxide scale per pixel stepwise movement. The software outputs the average distance between the two lines with their corresponding standard deviations, which have been used to plot the oxide scale thickness measurements. This technique was used whenever oxide scale thickness measurements were carried out.

### 3.4 CHARACTERISATION TECHNIQUES

#### 3.4.1 Optical microscopy (OM)

The samples prepared were examined using Reichert MEF-3 optical microscope with a 10 mega pixel digital camera attachment and Qimaging Qcapture imaging software. OM technique was used mainly for substrate microstructural analysis.
3.4.2 Scanning Electron Microscopy (SEM)

The SEM used to examine the samples was LEO1530 VP Field Emission Gun (FEG) SEM fitted with an EDAX Pegasus Energy Dispersive Spectrometer (EDS) system and a TSL Electron Backscatter Diffraction (EBSD) attachment. To differentiate elements with closely matched energies in the EDS spectrum, the Cambridge S360 SEM fitted with Microspec wavelength dispersive (4 crystal) spectrometer (WDS) using Oxford instruments INCA wave software was used. The working distances, operating voltages, apertures and currents were varied accordingly to give optimum conditions for imaging, chemistry collection and EBSD analysis. Sample examinations were carried out using secondary electron imaging (with conventional secondary electron detector and an inlens detector) and back scattered electron imaging. Working distances employed ranged from 4-18mm depending on the imaging mode used, that is, inlens secondary electron, electron backscatter mode or conventional secondary electron mode.

3.4.2.1 EBSD

For EBSD analysis, stringent surface requirements demanded for an additional sample preparation technique to obtain good diffraction patterns. This involved a final polish for an additional 20-30 minutes using colloidal silica solution. Figure 15, illustrates the effect of sample preparation technique on the quality of the diffraction patterns obtained.

![Figure 15 illustrating the effect of sample preparation techniques on the quality of EBSD diffraction pattern, (a) preparation after 1200 grit (b) after 1µm, (c) after 10 minutes with 0.05µm colloidal silica and (d) after 30 minutes of polishing with colloidal silica](image)

The results show that a finish using 0.05µm colloidal silica results in good diffraction patterns. The samples are then mounted in a stub at a tilt angle of 70° before analysis in the SEM chamber. The operating voltage used was 20kV and a high current selected (minimum aperture – 60µm) to obtain good diffraction patterns and the compositional chemistry of the oxide. The ideal working distance used was between 15-18mm. The software used for the
collection and the manipulation of the EBSD data obtained was the TSL OIM 4.5 analysis package (OIM, EDAX UK, Cambridge, UK). The software also enabled the use of the data collected via energy dispersive X-ray spectroscopy (EDS) to be used as a filter to aid in the phase identification. This was particularly useful when dealing with the spinel oxide phases, which have identical crystal structures but different chemical compositions.

### 3.4.2.2 Energy and Wavelength dispersive spectroscopy

For the energy dispersive spectroscopy (EDS), the LEO1530 FEGSEM is equipped with an EDAX EDS system that allows simultaneous collection of chemical composition data while carrying out EBSD or under normal SEM mode. This allowed points of interest analysis, elemental line analysis and the compositional mapping of selected regions of interest. Similarly, for the Wavelength Dispersive Spectroscopy (WDS), the Cambridge S360 SEM was used, which assisted in identifying elements with closely matched energies, such as differentiating between the Nb L and Mo L lines that have nearly identical kinetic energies, which the EDS system could not easily differentiate. Systems with WDS attachments have good energy resolutions, such that the amount of overlap between peaks of similar energies is much smaller. It also has a characteristically high count rate, by a factor of 10, compared to the EDS system making WDS system good for elemental tracing.

### 3.4.3 Focused Ion Beam and Scanning Electron Microscopy – Dual Beam System

This system consists of a conventional field emission gun scanning electron microscope and a liquid metal (gallium) ion source. Due to the machine having both of these sources, it is referred to as a dual beam focused ion beam. The machine used was a FEI Nova Nanolab 600 dual beam FIBSEM and was used to produce site specific cross-sections and TEM thin foils of features of interest on the oxide scales and within the substrate. Its advantage over conventional SEM is the site specificity, a reduction in mechanical damage and the speed of specimen production. Its limitation is the associated ion induced damage it causes to the surface.

#### 3.4.3.1 Cross-section preparation

Cross-sections were prepared in the dual beam system by first selecting the area of interest using conventional SEM. The sample was tilted to 52° to ensure its surface was perpendicular to the ion source. Rough milling was carried out with the ion beam current set at 20nA. After rough milling, the cross-sections were polished by using progressively lower probe currents finishing off with a 0.5nA. The finished cross-sections were viewed using the ion and electron beams for morphological information. Serial sectioning was also carried out by repeatedly
micromachining away layers from a solid sample allowing a composite three dimensional image from the two dimensional image data collected from each of the layers separately.

3.4.3.2 Transmission Electron Microscopy sample preparation

TEM sample preparation was carried out in a similar way as the cross-sections by first selecting the area of interest using conventional SEM and marking it out with platinum deposition, Figure 16(a). Rough milling was carried out from either side of the region of interest, which had been platinum deposited to prevent high energy ion beam surface damage, Figure 16(b). The remaining part of the feature was then polished on either side using a lower probe current. After polishing, the TEM sample was cut from the bulk of the sample by ion milling small boxes on either side and on the lower edge, Figure 16(c) and (d). The sample was extracted using a micromanipulator attached to it by a platinum weld and transferred onto a TEM grid where the sample was finally welded and freed off the micromanipulator by ion milling the weld, Figure 16(e). Final ion thinning was carried out to reach the required specimen thickness as illustrated in Figure 16(f).

Figure 16 FIBSEM - TEM sample preparation procedure of the oxide scale formed on P92 steel starting with (a) Pt deposition on the region of interest, (b) milling of both sides of the region of interest, (c) U-shape cut to free the specimen and the attachment of the micromanipulator to specimen, (d) lift-out and (e) attachment to TEM grid and (f) final ion thinning of the TEM lamella with voids clearly observed.
3.4.4 Transmission Electron Microscopy

A JEOL 200FX TEM was used with an accelerating voltage of 200keV for all the analysis. This machine was also equipped with an Oxford Inca EDS analysis system for chemical composition analysis. For EDS mapping of TEM thin foils, these were mounted on a TEM-SEM sample holder and conventionally analysed on the LEO1530 FEGSEM with its EDAX genesis EDS system.

3.4.5 X-ray Diffraction (XRD)

X-ray diffraction (XRD) measurements were performed on the surface oxides using a Bruker D8 X-ray diffractometer with Cu Kα radiation between 20°- 80° at step values of 0.02°. This technique was used to identify the oxide phases present on the surface as well as providing qualitative information on the oxide phase changes attributed to the increase in oxidation time. The resultant diffraction spectra were analysed with the powder diffraction files reported in the Joint Committee on Powder Diffraction Standards - International Centre for Diffraction Data (JCPDS-ICDD) [112] database using XPowder software [113].
4 THERMODYNAMIC PHASE CALCULATIONS

4.1 INTRODUCTION

This chapter discusses the equilibrium thermodynamic phase calculations carried out using Thermocalc software with the TCFE 6 database for the materials considered in this study. The calculations were based on the nominal compositions as shown in Table 1. The results are presented starting with the predicted substrate phases, the observed alloy microstructural changes and finally the equilibrium oxide phase predictions. For the substrate phase predictions, the thermodynamic calculations were carried out as a function of temperature whereas for the oxide phase predictions, these were carried out as a function of oxygen partial pressure, \( \text{PO}_2 \), at the set temperatures of interest.

4.2 T22 AND T23 FERRITIC BAINITIC STEELS

4.2.1 Substrate phase predictions

For the T22 steel substrate, the predicted equilibrium stable phases are Ferrite, \( \text{M}_{23}\text{C}_6 \) and \( \text{M}_6\text{C} \) carbides. The \( \text{M}_6\text{C} \) carbide was predicted not to be stable above 660°C, implying that the samples exposed at 700°C will only exhibit the \( \text{M}_{23}\text{C}_6 \) carbides as the stable secondary phase particles. For the T23 steel substrate, the predicted equilibrium stable phases were Ferrite, \( \text{M}_{23}\text{C}_6 \) that disappears at around 580°C leaving \( \text{M}_6\text{C} \) and MX/MC phases as the thermodynamic stable phases for exposures of up to 700°C.

Figure 17 showing the equilibrium thermodynamic phase predictions for (a) T22 and (b) T23 steel substrates in the temperature range 500-1,000°C

Literature reports that [57, 114] the presence of fine carbonitrides and carbides, which occur as the MX/MC phases in the T23 steel substrate serve to further strengthen and stabilise the alloy microstructure. The MX/MC particles in the T23 steel substrate were predicted to consist of Ti, Nb and V, and with small mass fractions compared to the other phases. Other carbides such as the \( \text{M}_6\text{C} \) carbides also confer strength to these low alloy ferritic steels, which for the
T22 steel substrate were identified as the Fe-Mo rich carbides, and for the T23 steel substrate as the Fe-W rich carbides. The Fe-W rich carbides were more stable over a wider temperature range compared to the Fe-Mo rich carbides found on the T22 steel substrate.

These low alloy ferritic based alloys are mainly found in boiler components working at lower temperatures. Historically, these components were made from the 2.25Cr-1Mo (T22) steel before the development of the 2.25Cr-1.6W-V-Nb (T23) steels intended for the wall membranes of ultra super critical boilers [51]. It is worth noting that the main difference between these two alloys is the W addition, which as predicted forms the M$_6$C carbides that are stable over a wide temperature range, and also accounts for the higher allowable stresses (up to 1.8 times) than the conventional T22 steel substrate at 580°C [115]. The T23 steels are increasingly finding use as retrofits in the superheaters and reheaters of conventional boilers and heat recovery steam generators [9].

### 4.2.2 Substrate microstructural changes

For both the T22 and the T23 steels, the second phase particles were observed to coarsen with increasing temperature, and the coarsening effect primarily occurred along the substrate grain boundaries and to a lesser extent within the substrate grains, Figure 18 and Figure 19. The coarsening of the second phase particles was more pronounced on the T22 steel substrate, Figure 18(a) to (d), which resulted in the disappearance of the bainitic/pearlite grain rich areas observed at temperatures below 600°C. For temperatures above 650°C and particularly at 700°C, the T22 steel substrate microstructure exhibited annihilation of the bainite microstructure resulting in the formation of an equiaxed ferrite matrix, Figure 18(d). The observed coarsening effect relates to the growth of the second phase particles, which cause the depletion of key alloying elements, such as Cr, Mo and W in regions where these particles occur. Thus the second phase particles act as sinks or reservoirs for these elements, which subsequently affect the high temperature oxidation behaviour of these alloys [10].

The preference of these particles to primarily nucleate along substrate grain boundaries serves to pin the grain boundary movement with the resultant effect of a stable substrate microstructure as seen on the T23 steel substrate, Figure 19, for temperatures above 650°C. Furthermore, because of the observed substrate stability, the T23 steel exhibited a high density of substrate grain boundaries. The relation between the microstructural stability and the observed high density of grain boundaries in T23 steel substrate was associated with its tempered microstructure during initial alloy heat treatment, which exhibited both the prior austenite grain boundaries and the intra-granular lath boundaries [114, 115]. During long-term aging or by increasing the exposure temperature, the second phase particles, M$_{23}$C$_6$, M$_6$C, and MX/MC precipitate, grow and coarsen on both grain boundaries and thus confer the
Results and Discussion – Thermodynamic Phase Calculations

observed microstructural stability of the T23 steel substrate compared to the T22 steel substrate.

Figure 18 Optical micrographs showing the substrate microstructural changes of T22 steel substrates exposed for 1,000 hours at (a) 510°C (b) 570°C (c) 650°C and (d) 700°C

For temperatures <600°C, both substrates exhibited a ferrite/bainitic microstructure, except for the T23 steel substrate, which had a tempered ferritic/bainite microstructure. Therefore, from microstructural stability and considering the observed high density of substrate grain boundaries on the T23 steel, Harts equation for the diffusion coefficient of materials would suggest faster oxide growth kinetics on the T23 steel substrate [27, 108].

\[ D_{\text{eff}} = fD_{\text{gb}} + (1-f)D_{\text{v}} \]

Where \( D_{\text{eff}} \) is the effective diffusion coefficient, \( D_{\text{gb}} \) is the grain boundary diffusion and \( D_{\text{v}} \) is the volume diffusion with \( f \) denoting the volume fraction of grain boundaries in the substrate. Furthermore, the effective diffusion \( D \) is also dependent on the temperature and obeys an arrhenius equation of the type

\[ D = D_0 \exp \left(\frac{-Q}{RT}\right) \]

Where \( D_0 \) is the temperature independent constant, \( Q \) is the activation energy of the diffusion process, \( R \) is the molar gas constant and \( T \) is the absolute temperature. This means that increasing the temperature will result in an increase in the flux of migrating species through
bulk diffusion, however, the presence of short circuit paths, such as dislocations, grain boundaries, which are also thermally activated and with lower activation energies will be preferred sites for migrating species diffusion [25, 27, 28, 116]. This is supported by Atkinson’s [26] work on diffusion along grain boundaries and dislocations, which showed that short-circuit diffusion in metals, attributed to grain boundaries and dislocations was several magnitudes higher $10^4-10^6$ than for bulk diffusion, and this was true for metals that exhibited fast lattice diffusion such as Ag in Cd. Furthermore, the activation energy for the short-circuit diffusion was 0.5 to 0.7 times that for lattice diffusion and is even greater for dislocation than for grain boundaries.

Raman’s work [117] on grain size effects on the 2.25Cr-Mo concluded that a decrease in oxidation rate was observed with increasing grain size and attributed this to the decrease in grain boundary area and hence a decrease in the short circuit diffusion paths. Literature reports [26] that grain boundary diffusion rate has a magnitude of up to $10^4-10^6$ compared to the lattice diffusion rates. Thus one would expect that the oxide scale formed on the T23 steel should be significantly thicker compared to the oxide scale formed on the T22 steel substrate.

Figure 19 Optical micrographs showing the substrate microstructural changes of T22 steel substrates exposed for 1,000 hours at (a) 510°C (b) 570°C (c) 650°C and (d) 700°C.
4.2.3 Oxide phase predictions

Oxide phase predictions were carried as a function of the oxygen partial pressure $P_{O_2}$ at set temperatures of interest. Since the samples were oxidised in steam, the oxide phases predicted at low oxygen partial pressures should have a good correlation with the experimentally observed oxide phases formed under steam environment. This was attributed to steam oxidising environments having low oxygen partial pressures compared to oxygen rich environments. The oxide phase predictions, Figure 20(a) and (b), were carried for all the exposure temperatures investigated, with the results showing similarities for the predicted oxide phases.

Figure 20 Oxide thermodynamic phase prediction as a function of oxygen partial pressure $P_{O_2}$ for (a) T22 and (b) T23 exposed at 700°C
The main difference observed in the thermodynamics phase diagrams for all the exposure temperatures studied was the shift of the phase diagrams towards higher PO$_2$ levels. This suggests that with increasing exposure temperature, there was an increased activity of oxygen species and hence an increase in its transport to the metal/oxide interface. This marginally increases the oxygen partial pressure levels at the metal/oxide interface causing the shift to the right in the equilibrium phase diagrams. For both the T22 and T23 steel substrates, the equilibrium predicted oxide phases were an outer corundum Fe-O phase at the scale/oxidant interface, followed by an inner Fe-O rich spinel. At temperatures $>600^\circ$C a thin Fe-O rich halite phase was predicted to form adjacent to the proposed inner/outer oxide interface whose stability appeared to increase with increasing exposure temperature. For the inner oxides, the oxide phase predictions showed the presence of Fe-Cr-O rich spinel with trace levels of Mn. There should also be traces of corundum Cr-O rich oxide, which is predicted to occur at low PO$_2$ levels, and since at these levels the ferrite phase mass fraction was high, the Cr-O rich phase was related to the formation of internal oxides along substrate grain boundaries.

Fe-Si-O rich phase was also predicted to occur as internal oxides but this preferentially at the metal/oxide interface. For the T23 steel substrate, Figure 20(b), the oxide phase predictions showed that the $M_6$C and MX/MC particles were stable and would be incorporated into the inner oxide layers up to the inner/outer oxide interface. This could be related to their microstructural stability over a wide range of temperatures as discussed in section 4.2.1, and they appear not to be strongly affected by oxidising environment.

**4.3 P91 AND P92 FERRITIC MARTENSITIC STEELS**

**4.3.1 Substrate phase predictions**

For the 9Cr ferritic martensitic steels, similar to the 2.25Cr steels the main difference between the P91 and the P92 steel was the W addition, although other constituent elements such as Si, Mo, Mn, Nb and V, as shown in Table 1, show minimal variation in weight %. The thermodynamic equilibrium stable phases in the P91 and the P92 steel substrate are presented Figure 21(a) and (b), which shows the mass fraction of the phases present as a function of temperature. The stable phases predicted at the temperature of interest were the $M_{23}C_6$ enriched with Cr, Fe and Mo, and MX ($M=$Nb and V, $X=$ C and N) in P91 steel whereas for the P92 steel, the substrate was predicted to have $M_{23}C_6$ with Cr, Fe and W (replacing Mo) and an additional Laves phase, $(\text{Fe,Cr})_2(W, \text{Mo})$, which was predicted to be stable up to about 720°C. These second phase particles have been shown [118] to occur along prior austenite grain boundaries and along the martensite lath boundaries in the substrate where they coarsen as a function of long-term ageing at elevated temperatures. Furthermore, the stability of the martensitic matrix in these steels is generally dependent on these particles and how they are distributed along the substrate grain boundaries.
The ferritic martensitic microstructure is normally characterised by a high density of substrate grain boundaries consisting of prior austenite and martensite lath boundaries. Thus, the presence of the second phase particles along substrate grain boundaries do affect the high temperature oxidation behaviour of 9Cr steel alloys, as they provide a source of Cr, Mn, Mo and W, and as discussed in Section 4.2.2. In addition, the stability of these second phase particles over a wider temperature range do play a significant role by ensuring a high density of substrate grain boundaries by pinning their movement during high temperature oxidation, which subsequently has an effect on the oxide growth morphology and chemistry.

4.3.2 Substrate microstructural changes

For both P91 and P92 steel substrates with exposure times of up to 1,000 hours, there was minimal microstructural changes and the substrates mainly exhibited a ferritic martensitic microstructure as shown in Figure 22(a) and Figure 23(a) respectively. However, after 3,000 hours of exposure time, the P91 steel substrate showed a localised equiaxed ferrite phase formation ($\alpha$) adjacent to the metal/oxide interface, Figure 22(b), approximately 10-15µm thick. This was not observed on the P92 steel substrate as shown in Figure 23(b). For the P92 steel substrate, its stable martensite microstructure at elevated temperature and over long-term ageing was attributed to the combined effect of W and Mo (at a lower weight %) [118, 119]. The predicted laves phase provided the strengthening mechanism for the P92 steel substrate analogous to the effect of M6C carbide phase observed on the W strengthened T23 steel substrate discussed in Section 4.2.1. The stabilising effect from the laves phase ensured that there was a high density of substrate grain boundaries close to the metal/oxide front in P92 steel substrate compared to the P91 steel substrate.

From the observed microstructural stability and the Harts equation for diffusion discussed in Section 4.2.2, the results would suggest that a higher effective diffusion coefficient would be
expected on the P92 steel substrate due to a higher volume/area fraction (f) of grain boundaries adjacent to the oxide. For the P91 steel substrate, the observed localised ferrite formation ~10-15 µm would have an effect on the effective diffusion coefficient due to the reduced fraction (f) of grain boundaries adjacent to the substrate/oxide interface.

![Figure 22 EBSD image quality maps of the substrate and the scale formed on the P91 steel substrate after (a) 1,000 hours and (b) 3,000 hours of exposure time](image)

![Figure 23 EBSD image quality maps of the substrate and the scale formed on the P92 steel substrate after (a) 1,000 hours and (b) 3,000 hours of exposure time](image)

The net effect of a higher diffusion coefficient for the P92 steel substrate would be an increased outward diffusion of cationic species from the substrate resulting in continued oxide growth. For P91 steel substrate and from the viewpoint of the density of substrate grain boundaries adjacent to the metal/oxide interface, the localised ferrite band would be expected to impede outward cationic transport resulting in slower growth rates. The additional effect that would be expected to occur is the enrichment of the cationic species at the interface of the localised ferrite zone and the martensitic substrate grain regions adjacent to it. This would be attributed to the high fraction of grain boundaries, typical of a martensite microstructure, which would allow faster cationic transport to the interface causing a cationic enriched region. This interface would be laden with Cr and Mn cations, such that as the localised ferrite region is
consumed, a band of Cr rich oxide phase would then preferentially occur at this region as the metal/oxide moves inwards.

### 4.3.3 Oxide phase predictions

Similar to Section 4.2.3, the oxide phase prediction was carried as a function of oxygen partial pressure $PO_2$ at the set temperature of interest, 650°C, as shown in Figure 24(a) and (b).

For both the P91 and P92 steel substrates, the equilibrium predicted oxide phases were an outer corundum Fe-O rich phase at the scale/oxidant interface, followed by Fe-O rich spinel. Inner oxides should also be expected to consist of Fe-Cr-O with trace levels of Mn, which also

![Figure 24](image-url)
occur as internal oxides within the substrate at low PO\textsubscript{2} levels. For both P91 and P92 steel substrates, the internal oxides also consisted of Cr-O rich phases and low mass fraction of Si-O phase. At the substrate/oxide interface, Fe-Si-O rich phase was also predicted to occur. The main difference between the two steels was the presence of the second phase particles within the inner oxides. For P91 steel substrate, there were traces of M\textsubscript{23}C\textsubscript{6} particles but these were at extremely low oxygen partial pressure, \(<10^{-16}\) atmospheres. For the P92 steel substrate, M\textsubscript{6}C particles were predicted to occur at low PO\textsubscript{2} levels \(\sim10^{-18}\) atmospheres and were stable up to \(10^{-13}\) atmospheres. From the substrate phase predictions, Section 4.3.1, M\textsubscript{6}C phase was not predicted to occur for the studied exposure temperatures, however, it was predicted to within the inner oxides and could be attributed to the consumption of the predicted laves phase. Similar to the 2.25Cr steels, the stable oxide phases predicted at low oxygen partial pressures relate to internal oxidation along substrate grain boundaries and these phase are likely to be Cr-O rich, Si-O rich and the Fe-Cr-O rich spinels with the later occurring in small mass fractions compared to the former two phases.

4.4 AUSTENITIC STAINLESS STEELS E1250 AND 347HFG

4.4.1 Substrate phase prediction

The equilibrium thermodynamic calculations were carried out for E1250 and 347HFG steel substrates as illustrated in Figure 25 (a) and (b), showing the mass fraction of the phases present as a function of the oxygen partial pressure PO\textsubscript{2}. It is worth noting that low oxygen partial pressures, less than \(10^{-17}\) atmospheres, represent conditions where the activity of oxygen is negligibly low to cause any oxide scale formation. In these conditions, the predicted phases are those found within the bulk of the alloy matrix. Therefore, the phases predicted at the temperatures of interest were austenite, sigma, MX/MC and laves phase. The sigma, MX/MC and laves phase have been reported to occur on the austenite grain boundaries, at triple junctions and within the substrate grains as second phase particles where they undergo coarsening as a with long-term ageing at elevated temperatures [58].

The presence of these second phase particles within the substrate matrix affect the oxidation behaviour of these steels given that they are rich in elements that have a direct effect on oxide scale formation. These second phase particles are an abundant source of the constituent elements, Cr, Mo, and Mn, by acting as alloying element reservoirs. The sigma phase predicted was identified as the Fe-Cr-Ni-Mo-Mn rich from EDS spot analysis, Figure 26, and had approximately the same composition to the predicted sigma phase composition. For the predicted MX/MC phase, this was identified as consisting of Nb rich carbonitrides, whose size averaged between submicron to tens of microns and had approximately the same composition to the predicted Nb(C,N). The Nb(C,N) particles were observed to occur on substrate grain
boundaries as well as intra-granular particles. The NbC particles occurred in a unidirectional manner and were related to the tube rolling direction.

![Graph showing the mass fraction of phases present as a function of oxygen partial pressure (PO2) for (a) E1250 and (b) 347HFG steel substrates.]

Figure 25 Equilibrium thermodynamic phase prediction for (a) E1250 and (b) 347HFG steel substrates and the corresponding stable oxides at the temperature of interest, 700°C as a function of oxygen partial pressure.

The stainless steel grades investigated were the 15Cr steel Esshete 1250 (E1250) and the 18Cr steel 347HFG. The main differences between these two steels was their Cr and Mn content, with E1250 steel substrate having a high concentration of Mn. Mn in E1250 steel was added as an austeniser, which allowed a reduction in the Cr and Ni concentrations in the alloy matrix. For 347HFG, this had a high Cr and Ni content but did not contain Mo observed in E1250 steel of up to 1 weight %.
Results and Discussion – Thermodynamic Phase Calculations

Figure 26 EDS spot analysis of second phase particles observed on E1250 steel substrate confirming the presence of phases with compositions consistent with both sigma and Nb(C,N).

For the substrate microstructure, 347HFG steel exhibited a fine grained microstructure with a bimodal grain profile compared to E1250 steel substrate which had a large grained profile. Literature reports[103, 120] that a fine grained morphology has beneficial effect towards high temperature oxidation resistance of high Cr containing steels. The predicted laves phase was the Fe₂Nb, which occurred along grain boundaries and within the substrate grains [121]. For the two austenitic stainless steel grades, the differences observed on the oxide phase predictions was in their mass fraction of the phases present. For the 347HFG steel, it exhibited a higher mass fraction of sigma second phase particles compared to the E1250 steel substrate. This was attributed to the higher Cr content in the alloy, a prerequisite for a higher mass fraction of sigma particle formation. The formation of the second phase particles had an effect on the predicted oxide phases, such as the NbC phase and its relation to the Nb rich oxides and sigma phase with Cr rich internal oxides formation along substrate grain boundaries.

4.4.2 Oxide scale phase prediction

For the equilibrium oxide phase predictions, Figure 25(a), with increasing oxygen partial pressure, greater than 10⁻¹⁷ atmospheres, internal oxidation occurred, which according to Ellingham Richardson diagram in Figure 7, phases that are stable at low oxygen partial pressure, such as alumina, silica and chromia will occur. This as shown from the predicted oxide phases was highly dependent on the substrate alloy composition and in particular the concentration of the elements Si, Cr and Al within the substrate. For E1250 steel substrate, Thermocalc phase predictions showed that the oxide phase formed with a higher mass fraction was the Cr and Mn rich spinel phase. For E1250 steel substrate, the predicted spinel phase exhibited a higher mass fraction up to the substrate/oxide front. The chromia phase was also predicted to occur as internal oxides preferentially at the substrate/oxide interface.
and this had a lower mass fraction compared to that predicted on high Cr containing 347HFG steel substrate. This suggests that its formation on 347HFG steel was favoured at low oxygen partial pressures and was attributed to the high Cr content and low Mn content in the alloy matrix. SiO₂ was also predicted to form, but due to the lower Si content, 0.6 weight %, within the alloy matrix of E1250 steel substrate, the phase had a lower mass fraction compared to that formed on 347HFG with a 1 weight % Si. However, the phase was stable at low and high oxygen partial pressures. Si was also predicted to form fayalite (Fe-Si-O) and this occurred at considerably higher oxygen partial pressures than the Cr rich corundum phase formation.

The phase prediction also exhibited the presence of Fe-Nb-O rich phase. This phase was predicted to be stable at low ∼ 10⁻¹⁴ and at high, up to 10⁰ atmospheres, oxygen partial pressures, and had a strong relation with the consumption of the NbC second phase particles. With increasing oxygen partial pressure of the system, the substrate and its second phase particles were completely consumed resulting in the formation of the spinel phase with a higher mass fraction. The phase constitution of the spinel is Fe-Cr-Mn rich oxide phase within which the Nb rich and Si rich oxide phases existed. For the spinels found between partial pressures of 10⁻¹¹ and 10⁻⁵ atmospheres, the phase constitution also exhibited an increasing Ni enrichment. At higher oxygen partial pressure, corundum oxide was also predicted to occur, which from the predicted phase constitution was Fe rich oxide phase with an appreciable Mn concentration.

Based on the substrate and oxide phase predictions of the austenitic stainless steels, the surface oxides were investigated by studying their morphology and chemistry. In addition, oxide cross sections were carried out to confirm the presence of the predicted oxide phases and their associated chemical distributions as presented in the following sections.
5 OXIDE SCALE FORMATION ON FERRITIC-BAINITIC STEELS

5.1 INTRODUCTION

This chapter addresses the oxide growth and the microstructural changes occurring on the T22 and the T23 ferritic/bainitic steel substrates exposed to air and steam oxidising environments. The steam oxidation experiments were carried out at 510, 568, 600, 650 and 700°C at a constant time of 1,000 hours. For the air oxidised samples, these were carried out at 650°C and 750°C from 1,000 to 3,000 hours. The main drivers for investigating these conditions are the beneficial boiler thermal efficiency improvements attributed to the increase in boiler operational temperatures. Furthermore, the thermal efficiency improvements have an effect on the CO₂ emissions from the boilers, such that reductions in the emissions per kWh of electricity generated are observed.

The discussion will highlight the role of the substrate microstructure, the alloying elements, the oxidation conditions and the effect of surface preparation on oxide scale development of the 2.25Cr ferritic stainless steels. Oxide growth models have also been developed and will be presented to explain the oxide growth behaviour of the T22 and T23 ferritic bainite steels.

5.2 STEAM OXIDATION

5.2.1 Oxide thickness analysis

For the steam oxidised samples, the oxide scale thickness analysis exhibited minimal difference in the growth kinetics for both the T22 and the T23 steel substrates, Figure 27. At temperatures below 600°C, both substrates exhibited minimal difference in oxide scale thickness, which ranged from 15 to 90μm thick with increasing temperature. For temperatures above 600°C, there was a marked increase in oxide scale thickness of ~ 1000μm, a factor of up to 100 times compared to the samples oxidised below 600°C, which suggest accelerated oxide scale growth with temperature increase. For high temperature oxidation studies, time and temperature are related in such a way that at constant time an increase in oxidation temperature results in accelerated oxide scale growth attributed to the increased activity of migrating species. Similarly, at constant temperature, increasing the exposure time will result in an increase in oxide scale thickness due to the availability of sufficient time for the migrating species to participate in oxide scale growth.

Thus, the profile of the plots of the oxidation results in Figure 27 can be related to the well known oxidation rates, such that for temperatures below 600°C, parabolic oxidation regimes are to be expected, however, for temperatures above 650°C, the linear oxidation regime would be expected. As previously observed on the T23 alloy steel, Section 4.2.2, one would
expect a thick oxide scale formation due to the high density of substrate grain boundaries. However, the results showed that the thickness measurements of the oxide scales formed on the T23 steel substrates were approximately similar to those of the T22 steel substrate.

5.2.2 Oxide cross-sectional morphology

The oxide cross-sectional analysis was carried out by classifying the growth morphology under two oxidation regimes. That is, for exposure temperatures below 600°C and those above 650°C as the oxide scales formed exhibited comparable oxide growth morphology.

Figure 27 Oxide scale thickness of the scales formed on (a) T22 and (b) T23 steel substrates oxidised in the temperature range 510-700°C in steam for a 1,000 hours
5.2.2.1 500-600°C oxidation regimes

For the T22 steel substrate, Figure 28, the oxide layer observed in this oxidation regime is a double layered structure consisting of an outer and an inner oxide layer. The inner layer had a compact microlayered profile similar to the growth profiles reported by Wright et al. [10], Figure 28(a) and (b). The inner oxide layer exhibited good adherence to the substrate and showed areas where internal oxidation had occurred along substrate grain boundaries as indicated with red arrows in Figure 28(b) and (d). At 600°C, Figure 28 (c and d), the scale exhibited voids occurrence towards the metal/oxide interface with the microlayered profile appearing disjointed but interconnected. Adjacent to the metal/oxide interface, voids were also observed ~ 10µm into the substrate. Internal oxidation was pronounced at 600°C and primarily occurred on prior austenite grain boundaries, which were revealed in the substrate after etching in nital and where the internal oxide stringers were observed. Furthermore, the internal oxide formed showed areas where they had occurred around the substrate grains (X) and encircled the substrate rich areas into the inner oxide layer, Figure 28 (c).

![Figure 28 SEM micrographs of the oxide cross-sectional morphology of the scales formed on the T22 steel substrate oxidised at (a) 510°C (b) 570°C and (c-d) 600°C for 1,000 hours respectively](image)

For the oxide scale formed on the T23 steel substrate, Figure 29, a similar growth profile was observed, however the microlayered growth profile was more pronounced with a higher periodicity than that formed on the T22 steel substrate. The inner oxide layer of the T23 steel
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exhibited bright particles (x), which occurred within the substrate microstructure along the substrate grain boundaries with a profile mimicking that of the substrate grain boundaries. These particles were related to the predicted second phase particles identified as W rich in Section 4.2.2. Voids were also observed within the substrate adjacent to the metal/oxide interface. Internal oxides were also observed on both the lath and prior austenite grain boundaries. At 600°C, Figure 29 (c-d), the voids/pores were observed to form a pore/void boundary zone about 5-10\(\mu\)m into the substrate. This boundary zone had a profile following that of the substrate/oxide interface and appeared to have a good correlation with the voids/pore zone observed between the microlayers in the inner oxide layer.

Figure 29 SEM micrographs of oxide cross-sectional morphology of the scales formed on the T23 steel substrate oxidised at (a) 510°C (b) 570°C and (c - d) 600°C for 1,000 hours respectively

5.2.2.2 650-700°C oxidation regimes

At 650°C, the T22 oxide scale exhibited a multi-layered growth profile, as annotated 1, 2 and 3 in Figure 30(a). The outer layer exhibited a two phase region; an outer zone (3) devoid of voids of approximately 80\(\mu\)m from the oxide/steam interface and an inner zone (2) of approximately 40\(\mu\)m exhibiting larger voids, which occurred at the inner/outer layer interface. The inner oxide layer had a characteristic microlayered appearance as observed in the 500-600°C regimes, but at 650°C the inner microlayered profile exhibited interconnectivity and an apparent larger pore/void zone between the microlayers, Figure 30(b) that was also less compact. The substrate also exhibited internal oxidation along substrate grain boundaries in
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addition to the pronounced incorporation of the substrate rich areas into the inner oxide, Figure 30(a) and (b), as was shown in Figure 28(c).

For the scale formed on the T23 steel substrate, Figure 31(a), a multilayered growth profile was also observed for the outer oxide layer, but for the T23 steel, there were differences in the inner oxide layer, Figure 31(b). The microlayers observed on the T23 oxide scale were compact, denser and with less microporosity compared to those formed on the T22 oxide scale. This is attributed to the microstructural stability of the T23 steel with its high density of substrate grain boundaries, which ensures a higher flux of cations from the substrate into the inner oxide layer for the formation of a compact oxide scale. Furthermore, the matrix stability of the T23 steel also resulted in the extensive internal oxidation observed along prior austenite and lath boundaries, ~ 10-15µm into the substrate.

Figure 30 SEM micrographs of the oxide cross-sectional morphology of the scales formed on the T22 steel at 650°C (a) and (b) and at 700°C (c) and (d) showing the inner microlayered growth profile and the internal oxidation zone (IOZ).

Figure 30(c) and Figure 31(c) show the oxide growth morphology formed at 700°C. The oxide scales formed had similar growth profiles for the outer oxide layer; this had a duplex structure consisting of a thin outer zone (3) ~ 50-80µm and an inner zone (2) ~ 400-450µm. For both
substrates, the oxide scale exhibited large voids that occurred at the original substrate/oxidant interface. The main difference between the two steels at 700°C was the growth morphology of the inner microlayered profile (1). The difference was on the periodicity of formation of the microlayers with the T23 oxide layer exhibiting a higher frequency of formation of the microlayers compared to the T22 oxide layer. The voids observed within the inner oxide layer were also different and appeared to have a larger area fraction than those observed on the T22 scale. Furthermore, the internal oxidation observed along grain boundaries was significantly higher on the T23 steel substrate ~ 30-40µm into the substrate compared to the T22 steel substrate, which only exhibited areas with marginal or no internal oxidation, Figure 30(d) and Figure 31(d).

Figure 31 SEM micrographs of the oxide cross-sectional morphology of the scales formed on the T23 steel at 650°C (a) and (b) and at 700°C (c) and (d) showing the inner microlayered growth profile and the internal oxidised zone (IOZ).

For the T23 oxide, it was easy to detect where the former substrate grain boundaries were positioned as they were marked by the W rich bright second phase particles within the inner oxide layer. For the T22 oxide, former substrate grain boundaries were not easily discernible but these occurred as ridges, with microcracks, within the inner oxide layer. The results for
both oxidation temperature regimes suggests that the extent of the microlayered periodicity formation, and whether the inner oxide layers are dense and compact or exhibit microporosity and the extent of internal oxidation are mainly related to the substrate microstructural stability.

5.2.3 Oxide chemical composition

EDS line scans analysis were carried out across the oxide scale as illustrated in Figure 32 for exposures at 600°C (a) and (b) and 650°C (c) and (d) for 1,000 hours of oxidation. The results show the component distribution profiles across the oxide scale, with the outer oxide layer identified as the Fe-O rich oxide phase, whereas the inner oxide layer is a spinel of Fe-Cr-O rich oxide phase. For the inner oxide layer of the T22 steel substrate (a) and (c), the EDS line profiles exhibited traces of Mo concentration, whereas for the T23 steel, both the substrate and the inner oxide layer exhibited traces of W observed as sharp peaks, Figure 32(d). Similar EDS component distribution profiles were observed for the samples exposed at 700°C, however, the inner oxide layer exhibited pronounced alternating Cr and Fe rich peaks associated with the microlayered profiles observed in Figure 30 and Figure 31 respectively.

For the outer oxide layers, these were mainly Fe-O rich oxides, which from the EDS elemental maps of the samples oxidised above 650°C, Figure 32(c) and (d), exhibited a two phase region, X and Y. The two phase region was visually identified from the backscattered micrographs showing image contrast changes and verified by the compositional change in the EDS line profiles of Fe and O starting at the interface of inner and outer oxide layers. For Fe the was a decrease of ~ 2.5%wt, whereas for O there was an increase of ~ 2%wt. Based on their corresponding component weight (%) distributions, the outermost layer was identified as Fe$_2$O$_3$ layer, whereas the inner layer as the Fe$_3$O$_4$ layer.

A further analysis was carried out at the substrate/oxide interface and in the bulk of the inner oxide as shown in Figure 33 and Figure 34. For the T22 steel, at the substrate scale interface, the results showed minimal internal oxidation, and where it occurred, the oxide phase formed was Fe-Cr rich oxide with trace levels of Mo. The substrate also exhibited Mo rich second phase particles, which occurred along substrate grain boundaries and associated with M$_{23}$C$_6$ phases as thermodynamically predicted as the stable phase in equilibrium with a ferrite matrix. The bulk of the inner oxide was Fe-Cr-O rich oxide phase, which also exhibited Mo-rich profiles that mimicked the former substrate grain boundaries where initial Mo rich second phase particles were observed, Figure 33(b). This suggests that the presence of the Mo rich second phase particles had a positive effect on the formation of the Cr rich oxide phases though Mo did not participate in oxide scale formation. Furthermore, the formation of the oxide ridges along the substrate grain boundaries can be attributed to the presence of Mo volatile species in high temperature water vapour containing environments. The Mo volatile species
have been reported to cause micro-cracks on the 9Cr steels [37] and could provide an explanation for the observed ridges, whose profile resembles that of prior substrate grain boundaries.

Figure 32 EDS line scans of the scale formed at 600°C for 1,000 hours for (a) T22 and (b) T23 and at 650°C for (c) T22 and (d) T23 steel substrates respectively.
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Figure 33 SEM and EDS maps of the oxide scale formed on the T22 steel exposed at 700°C for 1,000 hours with (a) showing substrate/scale interface and (b) showing an analysis of the inner oxide layer.

For the T23 steel, Figure 34 (a), the substrate shows significant internal oxidation extending ~ 40 microns into the substrate. The internal oxides formed are Cr rich Fe-Cr-O rich phases with the substrate exhibiting the W rich second phase particles along prior austenite and lath boundaries. The inner oxide chemistry was similar to that of the scale formed on the T22 steel. The observed bright particles in the substrate and extensively within the inner oxide layer were identified as W rich phases. The W rich phases were related to the M₆C phase which was thermodynamically predicted as a stable phase within the inner oxides. These particles marked out the position of the former substrate grain boundaries in the inner oxide layer confirming that oxide growth occurs inwardly at the metal/oxide interface, Figure 34(b). The outer oxide was identified as purely an Fe-O rich oxide, Figure 35, with the interface between the inner and outer oxide layers as the original substrate interface. For T22 oxide scale, the outer oxide layer had a similar phase to that observed on the T23 oxide scale.
Figure 34 SEM and EDS maps of the oxide scales formed on the T23 steel exposed at 700°C for 1,000 hours (a) showing substrate/scale interface and (b) showing the inner oxide layer with bright particles.

Figure 35 SEM, Image quality map and EDS maps of the scales formed on the T23 steel exposed at 650°C for 1,000 hours showing the interface of the inner and outer oxide layers, with the latter exhibiting equiaxed grains in the image quality map.
Figure 36 further shows the oxide growth morphology with the oxide grains growth in the outer layers (3) exhibiting an equiaxed zone followed by columnar growth for both T22 and T23 steel substrates. The inner oxide is observed darker due to the layer having fine oxide grains in addition to the extensive microvoids observed, which hamper indexing due to the shadowing effect during EBSD map collection. Its clear from both Figure 34 and Figure 36 where the original substrate interface is located, which supports the proposition of growth occurring due to inward and outward growing of oxides.
5.3 AIR OXIDATION

This section presents the results of the static air oxidation experiments carried out on the T23 steel substrates exposed at 650°C and 750°C, for exposure times ranging from 1,000 to 3,000 hours. The results consist of the oxide scale thickness analysis, the oxide growth morphology and the associated chemical composition.

5.3.1 Oxide thickness analysis

The scale thickness analysis showed accelerated oxide growth on the samples oxidised at 750°C compared to those oxidised at 650°C, Figure 37. After 1,000 hours of oxidation, the scale thickness observed in the low-temperature sample was approximately 32µm thick, whereas, for the samples oxidised at 750°C, these exhibited thick oxide scale formation of approximately 1,180µm thick. With increasing times, the samples oxidised at 650°C exhibited a parabolic growth profile with the thickness decreasing from 2,000 to 3,000 hours, whereas samples oxidised at 750°C, the oxide scale growth exhibited a linear growth profile with the scale growth after 3,000 hours at ~ 2 times that observed at 1,000 hours of oxidation.

![Figure 37 Oxide scale thickness analysis of the scales formed on the T23 steel substrate oxidised at 650°C and 750°C in air for 1,000 hours](image)

5.3.2 Cross-sectional oxide growth morphology and chemistry

For the samples oxidised at 650°C, the oxide growth morphology exhibited a layered growth profile after 1,000 hours of oxidation, Figure 38(a). The internal oxide layer exhibited the characteristic microlayered profile observed in steam oxidised samples, Figure 38(b), however, there were oxide stringers within the inner oxide layer attributed to the preferential
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Internal oxidation along substrate grain boundaries. Cracks were observed midway between the inner and outer oxide layers, which is the original substrate/gas interface. After 3,000 hours of oxidation, the substrate exhibited a multilayered growth profile as annotated 1, 2 and 3 in Figure 38(c). For the inner oxide layer (3), the former substrate grain boundaries were easily discernible, as these were laden with the bright particles associated with the second phase particles in the substrate, in addition to the formation microvoids within the boundaries, which acts as a sink vacancies generated during cationic migration, Figure 38(d). This suggests that the inner layer growth occurs by the inward transport of oxidant species whereas the outer layer forms by the outward cationic species diffusion.

![Figure 38 SEM micrographs of the oxide cross-sectional morphology of the scales formed on the T23 steel oxidised at 650°C for (a) 1,000 hours and (c) 3,000 hours with (b) showing the corresponding higher magnification of the inner layer/substrate interface and (d) bulk of the inner oxide layer.](image)

EDS map and line scans showed the outer layer consisted of an Fe-O rich oxide layer similar to steam oxidised samples with the inner oxide layer consisting of Fe-Cr-O rich with the bright particles identified as W-rich phases observed on the former substrate grain boundaries, Figure 39 and Figure 40. The internal oxides within the substrate were Cr-rich phases and these occurred along prior austenite and lath boundaries as shown in Figure 39, with the bright particles identified as W rich particles. It is also evident that voids occurred within the substrate and these coalesced into larger voids in front of the internal oxides along substrate grain boundaries.
For the samples oxidised at 750°C, the oxide growth morphology exhibited a multilayered growth profile, Figure 41, with the ratio of inner to outer oxide layers of approximately 1:1 suggesting that the inwardly and outwardly growing oxide had approximately the same growth rates. After 1,000 hours of oxidation, the outer layer exhibited pronounced void formation, which occurred close to the original substrate/gas interface with cracks also developing within this region, Figure 41(a). The inner oxide layer exhibited a faint microlayered profile similar to that observed at 650°C. At the substrate/oxide interface, Figure 41(b), internal oxidation occurred along substrate grain boundaries that resulted in the localised detachment of substrate grains (x) into the oxide. Furthermore, the depth of penetration of the internal oxides was clearly marked in the substrate with microvoids, which occurred in a profile parallel to and mimicking the substrate/oxide interface as shown in Figure 41(b).

Figure 39 SEM micrograph and EDS maps of the oxide / substrate interface of the scale formed on the T23 steel at 650°C after 1,000 hours of oxidation.

Figure 40 SEM micrograph and EDS maps of the outer / inner oxide interface of the scale formed on the T23 steel at 650°C after 3,000 hours of oxidation.
After 2,000 hours of oxidation, Figure 41(c), the oxide scale formed further showed a multilayered growth profile with the outer layer exhibiting pronounced void formation and crack development. For the inner oxide layer, this was intact and did not show cracking but exhibited the previously observed microlayered growth profile on steam oxidised samples. The inner oxide layer also had pronounced microporosity. At the substrate/oxide interface, Figure 41(d), voids were observed within the substrate as well as the formation of the internal oxides within the substrate.

Figure 41 SEM micrographs of the oxide cross-sectional morphology of the scales formed on the T23 steel oxidised at 750°C for 1,000 hours (a) and (b) and for 2,000 hours (c) and (d) showing the growth profile and the extent of internal oxidation.

![Microvoids](image1.png)

![Internal oxides](image2.png)

![Voids/Cracks](image3.png)

Figure 42 SEM micrograph and EDS maps of the outer oxide layer showing the duplex phases identified as hematite and magnetite on both the T22 and T23 steel substrates.

![Fe](image4.png)

![Hematite](image5.png)

![Magnetite](image6.png)

![O](image7.png)
For the outer oxide layer, its composition was similar to that observed at 650°C and consisted of Fe-O rich phases. These phases were identified as a thin outer hematite layer and the bulk of the oxide being magnetite as presented in Figure 42 and based on the approximate stoichiometric compositions for quantified EDS line scans. For the inner oxide layer shown in Figure 43, there were Cr rich internal oxides along substrate grain boundaries with the bulk of the inner oxide being Fe-Cr rich oxide phase. The localised detachment of the substrate rich areas was observed as high intensity Fe rich areas (X) within the inner oxide layer, and with either side of the detached areas exhibiting extensive void formation. This resulted in the region with localised detachment of the substrate adjacent to the substrate/oxide interface forming the observed Fe-Cr rich oxide areas.

Figure 43 SEM micrograph and EDS maps of the oxide / substrate interface of the scale formed on the T23 steel at 750°C after 1,000 hours of oxidation.

Figure 44 SEM micrograph and EDS maps of the oxide / substrate interface of the scale formed on the T23 steel at 750°C after 3,000 hours of oxidation.
After 3,000 hours of oxidation, the inner oxide layer was marked out by the Fe-rich phases with appreciable Cr concentration from the Fe and Cr maps, occurring in a microlayered growth profile partitioned with voids, Figure 44. The microlayered growth profile was more pronounced with its Fe-rich oxide phase attributed to the localised detachment effect observed in Figure 43. The combined effect of substrate detachment and void formation results in the partitioning of the Fe-rich microlayers. The former substrate grain boundaries are easily noticeable in the Cr EDS maps due to the preferential Cr rich oxide phase formation along prior austenite boundaries during growth. Furthermore, W rich particles were also observed within the inner oxide layer as bright particles as shown in the EDS maps, Figure 44.

5.4 DISCUSSION – T22/T23

5.4.1 Introduction

In Section 4.2, it was shown that due to the differences in the alloying compositions of the T22 and T23 steel alloys, substrate microstructural changes do occur as a function of long-term aging at elevated temperatures. These changes involve the precipitation and growth of second phase particles, M_{23}C_6 and M_6C [114], whose formation, growth and subsequent consumption is depended on the exposure temperatures and times. These second phase particles have been proposed to affect the high temperature oxidation behaviour of these alloy steels in a number of ways[10, 51]. These particles alter the Cr content of the alloy by causing denudation of Cr along grain boundaries where they predominantly occur and in regions adjacent to where they precipitate and grow. As the oxidation resistance of these materials mainly rely on the formation of protective chromium rich oxides, any process that consumes the available Cr will affect the oxidation resistance of the alloy. Furthermore, the stability of these second phase particles along substrate grain boundaries has been shown to affect the microstructural stability of these alloys. For alloys whose second phase particles are rapidly consumed and not stable at elevated temperatures, such as in the T22 alloy, the resultant effect was the formation of an equiaxed matrix with fewer substrate grain boundaries compared to the more stable T23 alloy steel. This substrate matrix stability had an effect on the resultant oxide growth morphology, oxide scale thickness and its chemical compositions as will be discussed in the following sections.

5.4.2 Oxide scale thickness

For the steam oxidised samples, there was minimal difference in oxide scale thickness between the T22 and T23 steel substrates as shown in Figure 27. This suggests that the stabilised substrate microstructure of the T23 steel, with a high density of substrate grain boundaries attributed to the M_6C phase discussed in Section 4.2.1, had minimal or no effect on the oxide growth kinetics in comparison to the T22 steel substrate. Similar results have
been reported in the literature for both substrates where they exhibited similar oxide thickness and/or weight gain measurements with the assumption that no oxide scale spallation occurred [98, 115]. Thus, the observed substrate microstructural changes could have another effect on the oxidation behaviour of the 2.25Cr alloys, and particularly on the oxide growth morphology of the oxide scales formed.

For the air oxidised samples, there was a marked increase in scale thickness with the change in temperature from 650 to 750°C. The observed change was significantly higher for the samples exposed below 1,000 hours of oxidation. This suggests that there is increased activity of the oxidant species for the outward and inward growing oxide phases that results in thicker oxide scale formation. The growth profile at 750°C was approximately linear whereas that at 650°C was parabolic, which correlate well with the discussion in Section 5.2.1, such that for temperatures above 650°C an approximate linear profile was observed in steam conditions. These results have a good correlation with the thermodynamic phase predictions in Figure 20, which showed that increasing the exposure temperature resulted in a shift to the right of the equilibrium phase diagrams towards the high oxygen partial pressures. A shift to the high oxygen partial pressure results in a considerable increase in the flux of oxidant species across the scale and towards the substrate/oxide interface. The increased flux of oxidant species results in rapid oxide scale formation as observed at 750°C compared to the samples oxidised at 650°C.

For comparisons between the steam and air oxidised samples, the T23 oxide scale formed at 650°C for 1,000 hours showed that steam oxidising environments resulted in thick oxide scales (~230µm) compared to the air oxidising environment (~32µm). This suggests that water vapour containing environments accelerate the rates of high temperature oxidation similar to reported literature [10, 21, 66, 69]. The oxide scale formed at 750°C for 1,000 hours in air (~1180µm) exhibited comparable scale thickness to that formed at 700°C for 1,000 hours (~1010µm) in steam. The results suggest that steam oxidised experiments can be related to the air oxidised experiments by increasing the oxidation temperature (for 2.25Cr steels), however, caution must be taken as the oxide morphology should be taken into account for a holistic view.

5.4.3 Formation of the inner microlayered growth profile and the oxide growth morphology

The formation of the microlayered growth profile was attributed to several mechanisms. First, the transport mechanisms resulting in the formation of second phase particles along substrate grain boundaries creates a Cr depleted zone adjacent to the substrate grain boundaries. With increasing aging time, further outward cationic diffusion (Cr) is enhanced towards the grain
boundaries wherein Cr rich internal oxides are formed by the reaction of Cr with the inwardly diffusing oxidant species, [122] as observed on the T23 substrate, Figure 29 and Figure 31. The resultant effect is further depletion of the alloying elements from the grains close to the metal/oxide interface with the development of cationic vacancies related to the outward cationic transport. These vacancies coalesce into microvoids which were observed within the substrate grains preferentially at the internal oxides/substrate interface front. Microvoids have also been reported to preferentially move to the nearest substrate grain boundaries, which act as a sink, where they further coalesce to form larger voids. Furthermore, the oxide scale adherence to the substrate during oxide growth results in the development of growth stresses, which develop due to the mismatch in the coefficient of thermal expansion between the substrate and the growing oxide scale [10, 123]. To relieve the developed growth stresses, localised detachment of the substrate occurs in the void laden grain boundaries or in regions within the substrate grains where significant alloy depletion occurred, Figure 29(d). This results in the formation of a weak boundary zone within the substrate ~ 5-10\(\mu\)m from the metal/oxide interface. With increasing exposure time at a constant temperature or increasing temperature at constant time, the combined effect of void formation and stress relief results in the periodic localised detachment of substrate grains into the inner oxide, as shown in Figure 29, Figure 31 and Figure 41, which slowly undergo oxidation to form the Fe-Cr rich oxide areas of the microlayers, whereas the porous or void laden regions form the Fe rich oxide areas. For the outer oxide layers of the scales formed on the T22 and T23, these exhibited voids and the occurrence of cracks midway from the oxide/steam interface. The cracking was attributed to the void formation from the coalescence of vacancies attributed to outward Fe ions transport for the outer oxide layer formation. The observed voids subsequently create a region of weakness, which easily propagates the cracks across the outer oxide layer and hence cause oxide scale spallation of the outer oxide layers.

### 5.4.4 Differences between steam and air oxidised samples

There were similarities in oxide growth morphology and chemistry for the T23 steel substrates oxidised in steam and air. Both oxides exhibited multilayered growth profiles consisting of an outer oxide layer with a characteristic two phase region consisting of a thin hematite and thick magnetite layers based on their thickness ratios. For the inner oxide layer of the T23 steel substrate, both steam and air oxidised samples exhibited the microlayered growth profile with comparable periodicity of formation of the observed microlayers. The main observable differences were on the compactness of the inner microlayers with the steam oxidised samples exhibiting denser microlayers as well as the apparent large void formation between the layers. The air oxidised samples exhibited considerably smaller voids but the microlayer growth profile was evident.
For the internal oxide formation along substrate grain boundaries, the steam oxidised samples exhibited pronounced oxide formation along prior austenite and lath substrate grain boundaries compared to the air oxidised samples. The effect was more pronounced at 700°C for the steam oxidised samples, due to water vapour effect on high temperature oxidation as well as the increased activity of migrating species with increasing temperature. This suggests that the depth of penetration of the oxidant species in steam is considerably higher than in air. This correlates well with literature reports [9, 10, 69, 85, 91, 124] that more oxidant species are involved in wet oxidising environments, which diffuse along oxide grain boundaries, on the developed microcracks and micro-fissures resulting in pronounced internal oxide formation with the outwardly diffusing cations.

5.5 OXIDE GROWTH MECHANISMS

5.5.1 Steam oxidised

Based on the analysis of the scales formed, the oxide growth mechanisms on the 2.25Cr steels were developed with the following assumptions taken into consideration. First, the reaction front occurs at the oxide/gas and metal/oxide interfaces. Secondly, the outer oxide layer forms by outward Fe ions and electron diffusion whereas the inner oxide layer forms by inward transport of gaseous H₂O molecules along microvoids and microcracks to the metal/oxide interface [125]. Work carried out by Tomlinson and Cory [126] illustrated the effect of hydrogen as a function of temperature, where they showed that hydrogen diffuses through the oxide and the substrates and affected oxidation by diffusing as protons across the oxide layer. This had an effect on the OH⁻ species by pulling them into the substrate/oxide interfaces for further oxide growth, whereas the hydrogen was desorbed as hydrogen gas at the oxide/gas interface into the steam by reacting with outward diffusing electrons. However, the effect of hydrogen was dependent on the concentration of protons in the oxide, which were also dependent on the amount of chemisorbed H₂O.

5.5.1.1 500-600°C oxidation regimes

During initial oxide growth, the Fe ions diffuse outwards reacting with the adsorbed water molecule to form the Fe-O nuclei, which in the early stages of oxidation uniformly cover the metal surface, Figure 45(a). Similarly, as the Fe-O rich nuclei are known to exhibit pores [44], the inward ingress of oxidant species occurs resulting in the formation of the subsurface Fe-Cr rich spinels. The outer Fe-O rich phase is reported [43, 95] to have lower permeability to Cr ions and these are left below the original metal surface. As the Cr concentrations in the T22 and the T23 steel substrates is below the critical level for the formation of the protective Cr rich oxides, the subsurface high Cr rich areas, together with the outwardly diffusing Fe ions, results in the formation of the Fe-Cr rich spinel phases. The newly formed subsurface Fe-Cr
rich spinel layer leaves behind a Cr denuded region, which also contains microvoids attributed to the cation vacancies formation and coalescence. The Cr deficient region that is also laden with microvoids attributed to the transport processes further forms larger voids where oxidant species (molecular gas, OH ions) accumulate contributing to further internal oxidation, Figure 45(b).

The effect of hydrogen proton effects discussed earlier play a key role in steam oxidised samples such that the proton effect aids the transport of the oxidant species via oxide grain boundaries and the observed microvoids. This results in further formation of the inner Fe-Cr rich phases. Since the oxidation rate at lower temperatures (< 600°C) is slow, the voids do not play a key role of pronouncing the Fe-rich microlayers observed at higher temperatures, but results in the microlayered appearance observed. At 600°C, or with increasing exposure time, more voids are formed between the microlayers causing localised partitioning of the Fe-Cr rich spinel layers.

Figure 45 Schematic illustration of oxide growth model of the 2.25Cr steels oxidised in the temperature range from 510-600°C in a 100% flowing steam with (a) showing early stage oxide growth (b) intermediate growth and (c) growth with increasing time.

The partitioning effect observed within the T23 steel substrate where detachment of the substrate occurred was related to the formation of the void boundary zone, Figure 45(c). The apparent increase in the voids area fraction with increasing temperature within the inner oxide
layers was attributed to the increased activity of diffusing species that are also responsible for voids formation. The T23 steel substrate exhibited this effect better, and was attributed to the high density of substrate grain boundaries compared to the T22 steel substrate.

5.5.1.2 650-700°C oxidation regimes

At these temperatures, the oxidation rates are much faster such that for the inner oxide layer the Fe-Cr rich phases are partitioned by the voided boundary zone, Figure 46(a) and (b). For the T23 steel substrate, the high diffusion rates attributed to the high density of grain boundaries resulted in the high periodicity of the microlayered growth profile and the apparent increase in the voids area fraction towards the metal/oxide interface Figure 46(b). The apparent increase in voids area fraction towards the substrate/oxide interface for the inner oxide layer is also proposed to occur by oxide dissociation within the voids formed (x), Figure 46(a). This dissociation mechanism thus provides a source for oxidant species which inwardly diffuse for more oxide formation, whereas the released cations from this mechanism outwardly diffuse for outer oxide growth.

Figure 46 Schematic illustration of the oxide growth model for the 2.25Cr steels oxidised in the temperature range from 510-700°C in a 100% flowing steam with (a) and (b) showing the growth morphology at the substrate/inner oxide interface.

For the outer oxide layer, the Fe-O rich oxide phase formed by Fe ions reacting with oxidant species to form the thick magnetite layer. The thin hematite layers are also proposed to occur by the conversion of magnetite to hematite at their interface as well as the Fe$^{2+}$ cations reacting with chemisorbed oxidant anions at the oxide/gas interface.
5.5.2 Air oxidised

For air oxidised samples, there were similarities in growth between the steam and air oxidised samples. The only observable differences in the growth model were in the inner oxide layer, such that the air oxidised samples have an apparent high density of microvoids compared to the steam oxidised samples. This was attributed to the presence of oxygen gas as the only available for oxidant species, whose transport inwards to the metal/oxide interface caused void creation. Furthermore, the increased activity of the oxidant species due to the presence of water vapour resulted in the pronounced internal oxide formation along the lath and prior austenite grain boundaries observed on the T23 steel substrate.
6 OXIDE SCALE FORMATION ON FERRITIC-MARTENSITIC P91 AND P92 ALLOYS

6.1 INTRODUCTION

This chapter addresses the oxide growth and the microstructural changes occurring on the P91 and P92 ferritic steel substrates exposed to air and steam oxidising environments. The oxidation experiments were carried out in steam at 650°C and in air at 650°C and 750°C for varying oxidation times. The results and discussion sections will highlight the role of the substrate microstructure, the alloying elements and the oxidation conditions on the oxide scale development of ferritic/martensitic steels. Oxide growth models have also been developed and will be presented to explain the observed oxide growth behaviour.

6.2 STEAM OXIDATION

6.2.1 Oxide scale thickness analysis

Figure 47 shows the oxide scale thickness measurements as a function of time on the P91 and P92 steels oxidised in 100% steam for 1,000 to 3,000 hours.

There was no indication of oxide scale spallation during the analysis of these samples, as supported by the comparison of Fe₃O₄ and the inner Fe-Cr rich layers thickness. Both layers had approximately a thickness ratio of approximately 1:1. The results showed that the P92 steel had a thick oxide scale, approximately 2-3 times thicker, compared to the P91 steel substrate for all the exposure times studied. The scale thickness plots showed that both steels exhibited the same growth profile, implying that the oxidation kinetics were similar.
6.2.2 Oxide scale morphology and chemistry

Figure 48 and Figure 49 shows the growth morphology of the oxide scales formed on P91 and P92 steel substrates. For P91 steel, Figure 48, the inner oxide layer had a compact structure that was also laden with microvoids. The observed microvoids appeared to decrease in size with increasing exposure time as the sample oxidised after 3,000 hours exhibited a denser and more compact oxide. There were microcracks observed within the inner oxide layer whose profile mimicked that of the prior austenite grain boundaries. These were particularly pronounced after 3,000 hours of oxidation. The inner oxide layer exhibited oxide banding, which after 1,000 hours of oxidation had a single band at the substrate/scale interface, however, after 3,000 hours of oxidation the formation of the bands extended 20-30µm from the interface. These bands were faint and appeared to be interconnected through the former ferrite grain boundaries attributed to the localised ferrite formation discussed in Section 4.3.2.

![Figure 48](image1.png)  
(a) Substrate  
(b) Inner oxide  
Outer

Figure 48 shows electron backscatter micrographs of the scales formed on P91 substrate at 650°C for (a) 1,000 and (b) 3,000 hours at the substrate/scale and the inner/outer oxide layers interfaces respectively.

For the P92 steel, Figure 49, the inner oxide layer exhibited a porous structure with extensive oxide band formation for the exposure times studied. These oxide bands occurred parallel to the substrate/oxide interface and showed interconnectivity through the substrate grain boundaries. With increasing exposure times, the banded appearance was more pronounced with a higher periodicity of formation. The inner oxide layer also exhibited bright particles, which were identified as the W rich particles, discussed in Section 4.3. The main differences
between the two substrates were in the formation of the inner oxide banding. For P92 steels the inner banding was more pronounced compared to the P91 steel, which for shorter times, showed no banding effect. Furthermore, the P91 inner oxide layer exhibited microcracks as shown by the arrows in Figure 48(b), which were absent on the P92 inner oxide layer, Figure 49, however, the P92 oxide scale exhibited bright particles that were related to the M₆C phase predicted as a stable phase within the inner oxide phases.

Figure 49 shows electron backscatter micrographs of the scales formed on P92 substrate oxidised at 650°C for (a) 1,000 and (b) 3,000 hours at the substrate/scale and the inner/outer oxide layers interfaces respectively.

For the outer oxide layers of P91 steel substrate, these were characterised by voids and pores that preferentially occurred midway in the outer oxide layer and appeared to increase in size with increasing exposure time. Within these voids for samples oxidised for longer exposure times, a new oxide phase was observed to occur as shown in Figure 50(a). This new phase had a sharp pointed tip growth profile emanating from the pores within the outer oxide layer into surrounding matrix. Furthermore, cracks were observed within the outer oxide layer and occasionally they occurred from the outer layer, across the scale and into the inner oxide layers. It was also observed that where the cracks had developed the sharp pointed phase occurred on either side of the crack into the bulk of the outer oxide. For P92 steel, this phase did not form within the voids but occurred where cracks had developed and as a thin surface oxide. This phase was identified as Fe₂O₃ from EBSD phase analysis as shown in Figure 50 (b), which suggests that oxidant species transport into the voids and cracks occurs.
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Figure 50 (a) shows an optical micrograph of voids in the outer oxide layer of the scale formed on P91 steel at 650°C after 3,000 hours of oxidation. The new phase, as shown in the EBSD phase map (b) taken around a pore from the image quality map, was identified as Fe$_2$O$_3$ in a bulk of Fe$_3$O$_4$ matrix.

Figure 51 and Figure 52 shows the oxide cross-section analysis of the scales formed on P91 and P92 steel substrate with the distribution of the main alloying elements starting from the substrate and across the scale.

For both alloys, starting with the substrate (1), there was a Cr depleted zone (2) occurring adjacent to the substrate and internal oxidised zone along substrate grain boundaries (3). This zone was less prevalent on the P92 steel substrate compared to the P91 steel substrate and also exhibited the Cr-O rich areas. This was followed by the Fe-Cr-O rich (4) inner oxide layer,
which exhibited the Cr-rich areas, with an appreciable concentration of Fe, occurring as alternating bands with Fe-O rich areas, with the Fe-Cr-O rich region extending outwards to the inner/outer oxide layer interface, Figure 51(b). For P91 oxide scale, the banding effect was less pronounced and appeared to have a correlation with the maximum depth at which the internal oxides formed within the substrate. This was related to the localised ferrite zone formation adjacent to the substrate/oxide interface. For P92 oxide scale, Figure 52, the banding effect was more pronounced with its intensity increasing towards the substrate/oxide interface, Figure 52(b). For the outer oxide layers (5), this was identified as the Fe-O rich phase with a stoichiometry approximating that of Fe₃O₄.

Figure 52 Shows electron backscatter micrographs with EDS line scans across the oxide cross-section of the scale formed at 650°C on a P92 steel for (a) 1,000 and (b) 3,000 hours of oxidation in a 100% flowing steam.

For detailed oxide compositional distribution, a EDS map scans were carried out as shown in Figure 53 and Figure 54. The maps showed the presence of Mn in the Cr-rich bands, which was not easily detected on the EDS line scans. Additionally, the Mo-Cr-rich second phase particles (X) on the P91 steel substrate and W-Cr-rich particles (Y) on the P92 steel, observed on the prior austenite boundaries and lath boundaries, promoted the formation of the Cr-rich oxide phases. Looking at the Mo EDS maps, Figure 53(b), its distribution after 3,000 hours had a profile mimicking the ferrite grain boundaries, attributed to the localised transformation of martensite to an equiaxed ferrite profiles, as well as where preferential formation of Cr-Mn-O rich phases occurred. However, from the oxide morphology there were no Mo second phase particles along former substrate grain boundaries but instead microcracks were observed. Similarly, for P92 scale, Figure 54, W EDS maps showed that the second phase particles occurred in both the intra and intergranular areas within the substrate, and within the bulk of the inner oxide layers as also illustrated in Figure 55.
Figure 53 showing image quality and EBSD EDS elemental map distribution at the substrate/inner scale layer interface of P91 steel oxidised for (a) 1,000 and (b) 3,000 hours at 650°C in a 100% flowing steam.

Figure 54 showing image quality and EBSD EDS elemental map distribution at the substrate/inner scale layer interface of P92 steel oxidised for (a) 1,000 and (b) 3,000 hours at 650°C in a 100% flowing steam.
Tungsten also occurred in the Cr-O rich bands and in Fe-O rich oxide phases. Its high concentration in the Cr-O rich phase suggests a strong relation with the $M_6C$ phase, as predicted in Section 4.3.3, from laves consumption, which previously occurred on the prior austenite grain boundaries.

Figure 55 EBSD IQ map and the elemental distribution of the bulk inner oxide showing a Cr rich band on P92 scale oxidised for 3,000 hours at 650°C in a 100% steam

Figure 56 Combined EBSD/EDS scan for phase identification of the scales formed on the P91 substrate oxidised for (a) 1,000 (b) 2,000 and (c) 3,000 hours respectively at 650°C in a 100% steam

Figure 56 shows a combined EBSD/EDS scans at the scale/substrate interface with corresponding composition analysis identifying the different oxide phases present on the scale. Within the pores observed in Figure 56(c), high Si content was detected but this was attributed to polishing artefact caused by the accumulation of Si from the conductive bakelite

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used to mount the sample. To further identify the oxide phases present and the presence of second phase particles, TEM analysis was carried out as shown in Figure 57. The presence of second phase particles (P) within the substrate, Figure 57(a), were identified from their EDS compositions as being the W rich particles related to the predicted laves phase in Section 4.3.3, whereas those found in the inner oxide layer were related to M₆C phase as shown in Figure 57(b). These particles were observed within the oxide grains and along former substrate grain boundaries.

Figure 57 TEM micrographs showing (a) analysis of the substrate/inner oxide interface and (b) the bulk of the inner oxide layer of the scale formed on the P92 steel substrate after 3,000 hours of oxidation.

The EDS maps, Figure 58, showed the oxide scales formed as consisting of the Fe-Cr oxide phases, which occurred within the inner oxide layer as bands, and the Fe-O rich oxide phases. The bright particles observed within the inner oxide relate to the W rich second phase particles as seen from the EDS maps. The corresponding oxide stoichiometry was confirmed from the TEM EDS point analysis, Figure 59 and related to the EDS maps of the same region highlighted in red in Figure 58, identified as Cr rich Cr-Fe rich band (1) and the Fe rich Fe-O rich areas (2) and (4), with a W rich particle (3).

Figure 58 shows SEM and EDS micrographs of a TEM thin-foil of the inner oxide layer of the scale formed on the P92 steel substrate after 3,000 hours of oxidation.
Figure 59 shows a TEM micrograph and the corresponding oxide composition of points 1 to 4 analysed from an area in Figure 58 (red) of the inner oxide formed on the P92 steel substrate.

For P91 steel substrate, Figure 60, Mo was observed in the oxide scale together with the Cr-O rich phase, which was observed to occur at former ferrite boundaries adjacent to the oxide/metal interface. Si was also observed within the oxide and its oxide phase preferentially occurred adjacent to the Cr-O rich oxide phase. The bulk of the inner oxide layer was Fe-O rich oxide phase with a considerable amount of Cr content. The inner oxide layer also exhibited voids that primarily occurred within the Fe-O rich oxide regions with the Cr-O rich areas exhibiting no voids. The microcracks observed in Figure 48 were also observed on the TEM thin foils and occurred within the Cr-O rich oxide phase.

Figure 60 shows SEM and EDS micrographs of a TEM thin-foil of the inner layer of the scale formed on the P91 steel substrate after 3,000 hours of oxidation.

Furthermore, a TEM analysis at the substrate/oxide interface, Figure 61, shows the presence of the Cr-O rich oxide phase adjacent to the substrate with varying concentrations of Mn and Si. The presence of these alloying elements within the Cr-O rich areas suggest the preferential
segregation to the substrate grain boundaries or to the substrate / oxide interface where they have been reported to form oxides at high temperature. Si was observed on the EDS maps as shown in Figure 60, and was seen to have a considerable concentration adjacent to the Cr-O rich phase as shown by its varying concentration in Figure 61. Its presence adjacent to the substrate at a considerable concentration suggests its involvement in oxide scale formation.

Figure 61 shows TEM micrograph and the corresponding oxide composition of points 1 to 4 at the substrate, annotated as 1, and inner oxide interface, 2 to 4, of the scale formed on the P91 steel substrate.
6.3 AIR OXIDATION

For air oxidation experiments, the P92 steel substrate was oxidised in air at 650°C and 750°C for 1,000 to 3,000 hours respectively for comparisons with the steam oxidised samples. The results presented in the following Sections show the oxide scale thickness analysis, oxide morphology and compositional analysis of the oxide phases formed on the T/P92 steel substrate.

6.3.1 Oxide scale thickness

The oxide scale thickness analysis exhibited faster oxide scale growth and hence thicker oxide scale formation on the samples oxidised at 750°C compared to those oxidised at 650°C, Figure 62. At 650°C, the oxide scale thickness measurements were below 100µm thick and exhibited a minimal change (~ 8µm) of oxide growth from 2,000 to 3,000 hours of oxidation, which suggested decreasing growth rate with time similar to parabolic growth profiles. For the samples oxidised at 750°C, these exhibited thick oxide scale formation ranging from 200µm to nearly 700µm after 3,000 hours of oxidation, and appears to increase proportionally with time, and from 2,000 to 3,000 hours the growth rate was slow that also indicated growth profiles approximating parabolic growth kinetics.

![Oxide thickness vs Time graph](image)

Figure 62 shows oxide scale thickness analysis of the scales formed on P92 steel substrate oxidised at 650°C and 750°C in air for 1,000 to 3,000 hours

6.3.2 Oxide growth morphology and chemistry

Figure 63 to Figure 66 shows the cross-sectional growth morphology and chemistry of the oxide scales formed on the P92 steel substrate oxidised at 650°C for 1,000 and 3,000 hours of oxidation. The oxide scales formed exhibited multilayered oxide scale consisting of an outer and an inner oxide layer with the interface of the two layers being the original substrate
surface. For the samples oxidised at 650°C for 1,000 hours, Figure 63(a), the outer oxide layer exhibited a single phase that had voids but was compact for all the samples examined. The inner oxide layer exhibited voids with needle like growth features, which occurred up to the inner/outer oxide interface. There was also significant oxide porosity within the inner oxide layer suggesting rapid vacancy formation during growth, which resulted in the formation of the voids. With increasing oxidation times, Figure 63(b), the voids within the inner oxide layer were not as pronounced as seen for low oxidation times, however, the inner oxide layer showed large voided regions adjacent to the substrate/oxide interface. Furthermore, a compact thin oxide was also observed, which occurred in a profile parallel with the substrate/oxide interface and appeared to be of the same phase with the observed needle like phase.

Figure 63 shows SEM micrographs of the scales formed on P92 steel substrate at 650°C after (a) 1,000 and (b) 3,000 hours of oxidation in air.

The former prior austenite substrate grain boundaries are also easily discernible after 3,000 hours of oxidation within the inner oxide layer, and these appear to be laden with microvoids, Figure 63(b). For the outer layer, the oxide exhibited an additional phase, black arrows, in
Results and Discussion – Ferritic Steels

addition to the phase observed after 1,000 hours of oxidation. The second phase particles were also observed within the substrate as bright (x) and greyish particles (y) deep within the substrate. The inner oxide scale composition showed that the scale consisted of Cr-O rich and Fe-O rich oxide phases, with the needle-like features observed after 1,000 hours of oxidation identified as the Cr-O rich oxide phase. The Fe-O rich phase also occurred within the inner oxide in a matrix of Cr rich and Fe-Cr rich oxide phase. The W EDS maps showed that the bright second phase particles observed on prior austenite grain boundaries in Figure 63(b), were W rich phases, whereas the greyish particles were identified as Cr rich phases. There appears to be a region (A) adjacent to the substrate/oxide interface where the Cr rich greyish particles were absent.

Figure 64 shows SEM micrographs of the scales formed on P92 steel substrate at 650°C after 1,000 hours of oxidation in air.

A further analysis of the substrate/oxide interface after 2,000 hours of oxidation as shown in Figure 65, showed that these particles had been consumed and these were prevalent in the substrate and occurred in both the prior austenite and martensite lath boundaries.

Figure 65 shows SEM micrographs at the substrate/ scales interface of P92 steel substrate oxidised at 650°C after 2,000 hours of oxidation in air.
The W rich particles were still present along the grain boundaries and were more pronounced for longer exposure times. The presence of the Cr-rich oxide phase at the substrate/oxide interface suggests that its formation could be attributed to the supply of Cr from the consumption of the second phase particles as well as through diffusion from grain regions adjacent to this interface. These Cr-rich oxide phases exhibited low or no traces of Fe, from the Fe EDS map in Figure 66, and could have a correlation with the thermodynamically predicted Cr rich corundum phases. For the main constituent elements of the oxide scale formed on P92 steel substrate, Figure 66, the outer oxide layer was identified as primarily Fe rich oxide phase with the outer most oxide grain regions exhibiting traces of Cr. For the inner oxide layer phases, these consisted of the Fe and Cr rich oxide phases, with the Cr rich oxide having a banded appearance whose intensity and Cr concentration profile increasing towards the substrate/oxide interface. The Cr depleted zone, shown in Figure 65, also occurred adjacent to the substrate/oxide interface.

![Figure 66](image_url)

Figure 66 shows SEM micrographs and the corresponding EDS maps of the oxide scale formed on P92 steel substrate oxidised at 650°C after 3,000 hours of oxidation.

Figure 67 shows the oxide growth morphology for the samples oxidised at 750°C for (a) 1,000 and (b) 3,000 hours respectively. The oxide scales formed were compact but occasionally exhibited cracks from the outer into the inner oxide layers. The cracks also occurred across the oxide scales but these were primarily within the outer oxide layers as shown in Figure 67(b) and for samples exposed for longer exposure times. After 1,000 hours of oxidation, Figure 67(a), the oxide scale formed had a multilayered growth profile consisting of an outer layer with a double layered structure, with the inner oxide layer showing oxide phase with comparatively smaller microvoids than those observed for samples oxidised at 650°C. The double layered structure observed on the outer oxide layer consisted of a thin outer phase (1) and a thick inner phase (2).

Within the inner oxide layer, bands were observed, which for short exposure times, occurred parallel to the substrate/oxide interface. However, with increasing exposure times, as shown Figure 67(b), these bands also occurred in a perpendicular direction to the substrate/oxide interface.
interface. The presence of internal oxidation was observed along the substrate grain boundaries for long exposure times, whose profile was similar to the substrate prior austenite and martensite lath boundaries. Microvoids were observed within the inner oxide layer but these occurred between the banded regions and the density of the microvoids appeared to increase towards the substrate/oxide interface.

Figure 67 shows SEM micrographs of the scales formed on P92 steel substrate at 750°C after (a) 1,000 and (b) 3,000 hours of oxidation in air.

The EDS oxide phase composition analysis, Figure 68(a), identified the outer oxide layer as Fe rich oxide phase whereas the inner oxide layer exhibited the presence of Fe-Cr and Cr rich oxide phases. From the Cr and Fe EDS maps, the Cr rich oxide phases occurred as bands within the inner oxide layer and were correlated with the banded effect shown in Figure 67(a). The bands also exhibited interconnectivity that was associated with the formation of the Cr rich oxide phases on prior substrate grain boundaries.

After 2,000 hours of oxidation, Figure 68(b), the Cr rich banding that initially occurred parallel to the substrate/oxide interface was less pronounced but primarily occurred in a perpendicular direction relative to the substrate/oxide interface. For the outer oxide layer, there was no change in oxide chemistry as it was identified as the Fe rich oxide. The perpendicular Cr rich banding effect observed in Figure 68(b) is better illustrated in Figure 69 showing its strong...
relation to the internal oxidation occurrence on former substrate grain boundaries. The microvoids observed within the inner oxide layer occurred in the Fe rich regions whereas the Cr rich bands exhibited fewer voids. At 750°C, the second phase particles were absent but traces of the constituent elements, such as W, were observed around the substrate/oxide interface and within the internal oxidised regions, Figure 69.

Figure 68 shows SEM micrographs and the corresponding EDS maps of the oxide scales formed on P92 steel substrate oxidised at 750°C after (a) 1,000 and (b) 2,000 hours of oxidation

Figure 69 shows SEM micrographs of the scales formed on P92 steel substrate at 750°C after 3,000 hours of oxidation in air
6.4 DISCUSSION – P91/P92

6.4.1 Oxide scale thickness

Comparing the oxide scale thickness analysis between the P91 and P92 steel substrates suggests that faster steam oxidation rates occurred on the P92 steel substrate compared to the P91 steel. This difference in oxidation rates between the two steels could be related to the alloying composition, substrate microstructure or the changes in alloy microstructure as a function of long-term aging.

For the alloy composition, the main difference between the P91 and P92 steel substrate was the addition of W in P92 by replacing Mo, mainly for its desirable impact on the creep strength of the alloy. However, its effect on high temperature oxidation is not well understood, but from mass gain and oxide scale thickness measurements, several authors have reported the detrimental effect of W on high temperature oxidation. Itagaki et al. [127] reported that an increase of 1.3 times in mass gain occurred when W replaced Mo in 9Cr steels. Lepingle et al. [82] also reported that W containing T92 steel substrates exhibited faster oxidation rates than the T91 steel (or steels with ~ 1% wt in Mo). This was similar to Osgerby and Fry’s [83] work, which showed that W had a detrimental effect on the oxidation behaviour of ferritic steels. Similar results have been shown in this study with thick oxide scale formation on the P92 steel compared to P91 steel. However, in this study, a hypothesis accounting for the observed difference in the oxide scale kinetics was related to the stability of the martensitic microstructure during long term aging. For the P91 and P92 steel substrates, these were shown in Section 4.3.1 and 4.3.2 to contain M23C6 and MX particles with the P92 steel substrate exhibiting an additional laves phase, which as reported in the literature [118], aids in stabilising the martensite matrix, whereas a localised ferrite formation occurred in the P91 steel substrate. The apparent localised phase transformation in P91 steel substrate reduced the high density of diffusion paths adjacent to the substrate/scale interface and hence affected the effective diffusion coefficient for the outward and inward ionic species transport. The net effect is the reduction in the effective diffusion rate of the migrating species from the P91 steel substrate compared to the P92 steel substrate resulting in thin oxide scale formation.

The comparison of air and steam oxidised T/P92 samples oxidised at 650°C showed the effect of water vapour containing environments on the high temperature oxidation behaviour of the 9Cr steels. The results showed that thick oxide scales, ~ 160µm to 260µm thick, occurred on steam oxidised samples compared to the static air oxidised samples, ~ 35µm to 70µm thick, for 1,000 to 3,000 hours of oxidation. Several authors [68-70, 128] have shown that water vapour containing environments are detrimental to the protective oxide scale formation in a number of ways, first, for alloys with low Cr concentration below the critical level required for protective oxide scale formation, the development of thick non protective Fe rich oxides.
occurs. Secondly, the undesired formation of volatile Cr species in steam environments that are readily lost instead of forming the preferred protective Cr rich oxide scales further exacerbates the effect. Finally, the negative effect of hydrogen from the dissociation of steam aids the inward transport of oxidant species through the hydrogen proton effect enhancing oxide scale formation [74, 75, 129].

The oxide scale formation at 750°C in air exhibited considerably thicker oxide scales compared to the steam oxidised samples at 650°C for similar exposure times. Although the oxidising environments were different, the thicker oxide scales observed at 750°C could be attributed to the rise in temperature, which has an effect on the diffusion coefficient of migrating species, and as also shown thermodynamically using Thermocalc, a shift to the right or to high oxygen partial pressures occurs in the phase diagrams of both ferritic and austenitic steel alloys with increasing temperature. This suggests increased activity of migrating species responsible for accelerated oxide scale formation.

6.4.2 Scale morphology and chemistry

The multilayered scale structure formed on the P91 and P92 steels has been shown to consist of an outer thick Fe-O rich layer and an inner spinel mix of Fe-Cr-O and Cr rich Cr-Fe-O rich phases as shown in Figure 51 and Figure 52. Similar oxide profiles have been reported by Ennis et al. [118] and Ren et al. [130] working on the 9Cr steels where they showed that a multilayered scale was formed consisting of a thick outer magnetite layer and an inner spinel mix of Fe-Cr-Mn-O phases. The multilayered scale exhibited voids which were attributed to cationic diffusion across the scale resulting in vacancy formation. The vacancies formed coalesced to form microvoids and as oxidation progressed, the microvoids coalesced into larger voids observed on the outer oxide layer. Within the inner oxide layers, microvoids were also observed for both the P91 and P92 steel substrate, Figure 48 and Figure 49. For P91 scale, the microvoids observed were larger at low exposure times but their size decreased after 3,000 hours of oxidation. For P92, the microvoids observed were significantly smaller and had similar size for all the exposure times. The presence of larger microvoids has been proposed by Ennis and Quadakkers [124] to slow the oxidation rates by lowering the density of diffusion paths for cations and anions, and this could provide one explanation for the slower oxidation rates observed on the oxide scale formed on P91 steel. For the P92 air oxidised samples, the samples oxidised at 650°C had an inner oxide layer that exhibited voids with needle-like Cr rich oxide phases. The formation of the larger voids at 650°C could be attributed to the formation of protective Cr rich oxides at the substrate/oxide interface that impede the outward cation diffusion. This results in the Fe rich oxide phases adjacent to the Cr rich oxide phase undergoing oxide dissociation to support the outward Fe rich oxide growth, with the associated development of larger voids. At 750°C, the observed microvoids
within the inner oxide layer were smaller compared to those formed at 650°C and this was attributed to the faster diffusion rates of the inward and outward migrating species at elevated temperatures, such that the Cr rich oxide formation was preceded by the Fe rich oxide formation without the protective nature of the Cr rich oxide impeding the outward cationic transport.

The inner oxide layer of P91 steel also exhibited microcracks which occurred within the Cr-Mn rich oxide phase but these were absent on the inner layer of the P92 steel substrate. These cracks were attributed to Mo, which has been reported to form volatile hydroxyl species known to cause scale cracking [37]. This was supported by Mo distribution in the inner oxide layer of P91 steel, Figure 53(b), which occurred within the Cr-Mn rich phases and proposed to interact with OH ions to form the undesirable volatile Mo species. Macro-cracks were also observed running across the scale. These were attributed to the growth stresses set up during oxide scale growth, and were easily propagated in areas where large voids occurred. Thermal stresses have also been reported to cause cracking due to the variability in the coefficient of thermal expansion between the substrate and scale as well as within the different oxide phases observed in a multilayered oxide scale [46]. Furthermore, the scale adherence to the substrate also causes additional stress development in the scale resulting in the oxide scale cracking. This occurs due to the oxide scale’s inability to plastically deform as it continuously grows with time resulting in the formation of the observed cracks. For example, high Cr containing steels are known to form a protective Cr-rich oxide phase at the initial stages of growth that strongly adheres to the substrate. However, the subsequent oxide scale growth by increasing exposure time results in the crack formation in the protective Cr rich oxide phase, which exposes the underlying substrate to further inward anion attack and outward cation diffusion [131].

The inner oxide layer exhibited faint but dense bands, which were more pronounced with increasing oxidation time for the P91 steel but were present in the P92 samples for all the exposure times forming a lamella like banding effect, illustrated in Figure 49. For the EDS line profiles and the combined EBSD/EDS maps, Figure 51 to Figure 54, the bands were identified as Cr-O rich phases with appreciable Mn content alternating with Fe rich Fe-Cr-O oxide regions. Wright and Doley’s [10] review concluded that the formation of the lamella like banding observed on the inner oxide layers of 9Cr steels is not well understood due to insufficient interest in this phenomena. However, Cory et al. [132] observed a similar effect in ferrous alloys and suggested that the lamella-like banding effect was due to the Cr-rich oxide bands undergoing mechanical plastic settlement, as iron cations diffuse from the Fe-Cr spinel grains resulting in the observed wavy appearance. Their results indicated that an initial Cr rich spinel phase (Cr-Mn-O) was formed which protected the substrate leaving behind a Cr depleted zone. With further oxidation, Fe diffusion continued to occur across the scale to form
the outer Fe rich oxide as well as the inner Fe-Cr-Mn and Fe-Cr spinel phases. A similar effect was observed by Schutze et al. [37, 133] looking at the role of alloy composition on oxidation resistance of 9Cr steel. Therefore, the consumption of Fe and Cr exposed the inner un-oxidised Cr rich substrate grains, which in addition to the preferential diffusion of Cr and Mn along grain boundaries, were oxidised to form the Cr rich Cr-Mn-O spinel bands. This resulted in the formation of the observed lamellar effect with several authors reporting similar results [46, 68, 134]. Literature reports [10, 37, 82] that Mn together with Cr form Cr-Mn-rich spinels in steam oxidising conditions, these inhibit the loss of volatile Cr species as well as outward Fe ion diffusion promoting the development of the Cr rich scales. The resultant effect of diffusion and consumption of the cations resulted in the alternating effect of Fe and Cr peaks observed on the EDS line maps, which were concentrated closer to the substrate/inner layer interface, and related to the oxide bands. This effect was also observed on air oxidised samples, but was primarily on the samples exposed over longer oxidation times at 650°C, and was highly pronounced at 750°C. For the latter, increasing the oxidation time resulted in the preferential formation of the Cr rich bands in a perpendicular manner, related to internal oxidation on prior austenite and lath boundaries, in relation to the substrate / oxide interface. This illustrated the effect of significantly increasing the oxidation temperature on the outward diffusion of cationic species.

The formation of the inner oxide layer below the substrate surface has been reported to occur due to the anion diffusion in the substrate. However, its thickness depends on the depth at which the concentration of dissolved oxygen is sufficient to form an oxide. Since oxidation tests were carried out in a 100% steam conditions, presence of water vapour is known to significantly affect the oxides formed [68-70, 134]. Presence of water vapour has been shown to accelerate anion diffusion into the substrate along the micro-channels, voids and cracks formed during oxide growth. Essuman et al. [68, 135] also proposed that water vapour increased the oxygen solubility in the alloy. This was attributed to hydrogen, which is known to rapidly diffuse in steels, causing a shift of H-O-H₂O equilibrium such that a high concentration of oxygen exists at the sample surface resulting in an increased inward flux of the oxidant species. This inward oxidant flux causes subsequent oxide growth at the oxide/substrate interface. The results shown in Figure 50 support the suggestion that the inward anion transport along cracks and oxide grain boundaries results in subsequent inner oxide growth as observed by the formation of hematite within magnetite matrix. Thus, the presence of micro-channels and cracks within the inner oxide layer would also provide easier diffusion paths for the anion species to permeate the scale, which at high temperature causes internal oxidation to occur [70].
For the features observed in the outer oxide layer, Figure 50, hematite formed within the outer magnetite matrix where pores/voids occurred on the P91 steel and had a sharp pointed growth profile. Hematite layer was also observed to occur inwards as a thin surface oxide layer on top of magnetite layer. Literature reports [132, 136] that when hematite is formed on a substrate, it forms short-circuit diffusion paths for anion or oxidant species to occur at the center of hematite blades or platelets, which results in hematite growth at its tip. Therefore, the observed needle like growth profile could be attributed to the short circuit paths on hematite, which allow the inward transport of oxidant species present within the voids and cracks, to diffuse through and cause subsequent growth at the tips into the bulk of magnetite layer. However, the extent of this growth is low indicating that as much as anion diffusion occurs, the transformation of magnetite to hematite must be occurring at relatively short exposure times, probably during the periods of cooling or in service conditions during power plant shutdown.

The re-oxidation of magnetite to hematite has also been shown to occur due to magnetite being thermodynamically unstable at the magnetite/steam interface [14, 40, 134]. For the scale formed on P92, the re-oxidation of magnetite to hematite did not occur within the voids but was observed where cracks had developed and as a thin surface oxide.

For the air oxidised P92 steel substrates, the oxide scale formed exhibited cracks within the outer oxide layers particularly for the samples oxidised at 750°C. The formation of such cracks was related to the rapid outer Fe rich oxide layer growth with the associated void formation from vacancies attributed to migrating species transports. The developed vacancies undergo coalescence and at high temperatures and due to the increased activity of the migrating cations, rapid void formation and growth occurs. And since these voids had a profile parallel to the oxidant/ gas interface, the void laden region provided an easier path for crack development and propagation in the outer oxide layer.

### 6.4.3 The role of alloying elements

The main alloying element added in P91 and P92 steel substrates for oxidation resistance is chromium. Cr is known to preferentially form protective Cr-rich oxide layers on steels, but this is dependent on the bulk concentration, which subsequently influences the stoichiometry of the inner oxides formed [10, 70, 82]. These range from the protective Cr$_2$O$_3$ to the Fe-Cr-O rich oxide spinels. As previously discussed in Section 6.4.1, the main difference between P91 and P92 steel substrate is the replacement of Mo in P91 with W in P92 steel. These alloying elements have different effects on the oxidation behaviour of these steels. It was shown in Section 6.4.1 that W was detrimental by accelerating the oxidation kinetics, whereas Mo in concentrations of ~ 1%wt had a positive effect to oxidation kinetics. From the thermodynamic phase predictions in Section 4.3, Cr, Mo and Fe form various second phase particles, such as $M_{23}C_6$ particles in P91 whereas W replaces Mo in the $M_{23}C_6$ particles of the P92 steel. These
particles were observed on the former austenite grain boundaries and martensite lath boundaries such that during high temperature oxidation processes, provided a source of Cr for the formation of the protective Cr-rich oxide phases. W was also shown to form the Laves phase in P92, which played a key role in stabilising the martensitic microstructure, with its associated effect on the oxidation behaviour of P92. The effects of Mo, W and Mn have been discussed in Section 6.4.2 on how they affect the oxide phases formed and the associated oxide growth morphology.

Si additions in chromia forming alloys have often been related to the development of protective oxide scales [37]. Its influence during high temperature oxidation is its segregation beneath the Cr rich oxide at the substrate/oxide interface where it impedes the outward diffusion of Cr by reducing the direct contact between the external scale and the substrate [89]. The presence of Si rich oxide phase was thermodynamically predicted as shown in Figure 24 approximately at the substrate/oxide interface on the 9Cr steels as was observed in the results of this study in Figure 60. The Si rich phase was present and occurred adjacent to the Cr rich oxide phase and as proposed, provides a thin layer that impedes the cationic diffusion across it. Several authors [85, 91, 132] have also reported that Si additions to ferritic steels with Cr levels below 12% wt were more effective in reducing the overall oxidation rates.

6.5 OXIDE GROWTH MECHANISMS

6.5.1 Steam oxidised

From the observed oxide morphology and chemistry, the oxide growth mechanisms on 9Cr steels involve the outward cationic and inward oxidant species transport across the scales formed as schematically illustrated in Figure 70.

During the initial oxide growth, the Fe and Cr ions diffuse outwards reacting with the adsorbed and dissociated water molecules to form the Fe-O nuclei as nodular features, whereas the Cr ions form the Cr rich oxide phase bordering the substrate/oxide interface. The Fe rich and Cr rich oxide phases uniformly cover the substrate surface, Figure 70 (a) and (d), however, these phases are not fully protective. Increasing the exposure time, further oxide scale growth occurs by the outward Fe ions reacting with the oxidant species to form the Fe rich oxide phase identified as magnetite, \(\text{(Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{OH}^- \leftrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}^+)\), whereas the subsurface oxide phases are also formed by the Cr and Fe rich ions reacting with inwardly moving oxidant species \(\text{(xCr}^{3+} + \text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{OH}^- \leftrightarrow \text{FeFe}_{2-x}\text{Cr}_x\text{O}_4 + 4\text{H}^+)\), Figure 70 (b) and (e). Since the subsurface oxide scale grows inwardly by oxidant species transport into the substrate, the substrate grain boundaries play a significant role on the resultant oxide morphology. This results in the formation of Cr rich oxide phases along prior austenite and martensite lath substrate grain boundaries.
Results and Discussion – Ferritic Steels

Figure 70 schematic illustrations of oxide growth models of P91 (a) to (c) and P92 (d) to (f) steel substrates oxidised at 650°C in a 100% flowing steam with increasing exposure time. For P91 steel substrate, Figure 70(b), this was attributed to the localised martensite (M) to ferrite (F) grain boundaries bordering the substrate/scale interface as shown in Figure 70(c). The interconnecting Cr rich phase between the Cr rich bands had a similar profile to the ferrite (F) grain boundaries, which the model proposes as the preferred sites for internal oxidation within the substrate. For P92 steel substrate, Figure 70(e), the interconnectivity was less pronounced and random but the Cr rich oxide bands occurred with a higher periodicity, Figure 70(f). The higher periodicity of formation of the bands is proposed to occur due to the rapid Cr transport towards the substrate/oxide interface where it forms the Cr rich oxides leaving a depleted zone underneath it. This is further oxidised to form the Fe rich Fe-Cr-O rich phase as there is still supply of Cr cations in the substrate to the Cr depleted zone. With continued oxidation, the inner Cr rich zone within the substrate is now available for Cr rich Fe-Cr-O rich oxide phase formation. The process is continuously repeated resulting in the formation of the bands predominantly observed on the P92 oxide scale.

Void formation occurs during high temperature oxidation, and these are observed with the inner oxide layer on the Fe rich Fe-Cr-O rich oxide phase. The formation of the voids was attributed to the migrating species transport occurring within the inner oxide layer as well as the in-scale oxide dissociation of Fe rich oxide phases ($\text{Fe}_3\text{O}_4 \leftrightarrow 2\text{Fe}^{3+} + \text{Fe}^{2+} + 4\text{O}^{2-}$). The latter effect could account for the apparent increase in the void area fraction starting at the
original substrate surface towards the substrate/oxide interface. The formation of these voids also enhances the tendency of the scales to crack through scale stress relief, which could also aid in the relaxation of the Cr rich bands providing an explanation for the wavy appearance of the Cr rich bands in a profile parallel to the substrate/oxide interface [10, 137].

For the outer oxide scale layer of both P91 and P92 steels, voids and cracks were also observed within the magnetite phase, Figure 70(c) and (f). These have been proposed to occur due to the cationic transport processes and the associated vacancy and void formations. For hematite phase formation within the voids in a matrix of magnetite, this has been proposed to occur by two mechanisms. First, the oxidant species transport into the voids via cracks and along grain boundaries causes a higher oxygen partial pressure within the voids for magnetite transformation into hematite \(2\text{Fe}_3\text{O}_4 + \text{OH}^- \rightarrow 3\text{Fe}_2\text{O}_3 + \text{H}^+\). Secondly, hematite formation could also be related to the dissociation of magnetite, (x) in Figure 70(c), into Fe ions and O\(^{2-}\) ions, with the outward Fe diffusion for the growing magnetite grains and O\(^{2-}\) ions for the oxidation of magnetite to hematite \(2\text{Fe}^{3+} + 3\text{O}_2 \leftrightarrow \text{Fe}_2\text{O}_3\). The hematite layer also occurred as a thin outer phase from the reaction of Fe ions with the oxidants species, which are at a higher oxygen partial pressure.

### 6.5.2 Air oxidised

For air oxidised samples, there were similarities between the steam and air oxidised samples for the P92 steel substrate. The main observable difference on the growth model was in the inner oxide layer, such that air oxidised samples exhibited more Cr rich oxide phases adjacent to the substrate as well as presence of larger voids. This was attributed to the presence of oxygen gas as the only oxidant species, whose inward transport to the metal/oxide interface caused void creation. For the samples oxidised at 750°C, the oxide growth morphology had similarities with the steam oxidised samples with the occurrence of Cr rich oxide bands extensively within the inner oxide layer as well as the interconnectivity between the bands.
7 OXIDE SCALE FORMATION ON AUSTENITIC STAINLESS STEEL

7.1 AUSTENITIC STAINLESS STEEL E1250

7.1.1 Introduction

This chapter addresses the oxide growth and the microstructural changes occurring in E1250 austenitic stainless steel substrate exposed to air and steam oxidising environments. During early stages of this study, the oxidation experiments were carried out in steam simulating the expected conditions in supercritical or advanced supercritical boilers ~ 650 – 700°C. The main drivers for investigating these conditions are the beneficial thermal efficiency improvements with the associated CO₂ emissions reduction per kWh of electricity generated. Oxidation experiments were also carried out in air in the same temperature range for comparisons with steam oxidised samples with the intent of fully understanding the oxide growth phenomena. Further investigations were also carried out on the effects of cold working on the oxidation behaviour of these alloys, which will be addressed in this chapter.

The discussion will highlight the role of the substrate microstructure, the alloying elements, the oxidation conditions and the effect of surface preparation on oxide scale development of austenitic steels. Oxide growth models have also been developed and will be presented to explain the oxide growth behaviour of E1250 stainless steels.

7.2 STEAM OXIDATION

7.2.1 Oxide scale thickness analysis

Figure 71, shows the oxide scale thickness measurements as a function of time on the scales formed on E1250 steel substrate. It is worth noting that in certain areas of the oxide scale, it exhibited oxide spallation effects, which occurred on the interface of the inner and outer oxide layers leaving an intact inner oxide. Where spallation did not occur, the scale thickness ratio of the inner to the outer oxide layers was ~ 1:1 and this was taken into consideration for the scale thickness measurements carried out as also reported by Viswanathan et al. [45] and Wright et al.[10]. The results of this study showed that the oxide scale growth on E1250 steel substrate had a characteristic parabolic growth profile, with the oxide scale thickness variation from 1,000 to 2,000 hours being ~ 10 µm, whereas from 2,000 – 3,000 hours of oxidation was ~ 4 µm, a decreasing trend. The total oxide scale thickness measurements averaged between 50-85 µm for up to 3,000 hours of oxidation.

Viswanathan et al. [45] review of plant trials carried out in the USA for E1250 steel substrate showed that for exposure times of up to 12,000 hours at 600°C in Wilhemshaven plant and 13,000 hours at 660°C in North Wiford plant, the oxide scale thickness measurements recorded were ~ 40-80 µm and ~ 100-148 µm respectively. The plant trials results are
comparable to the results of this study although the high temperature condition employed in this study was much aggressive. This is a good indication of the oxidation resistance of E1250 steel substrate despite the somewhat lower Cr concentration than the majority of the corrosion resistance austenitic stainless steels with a minimum Cr concentration of ~ 18 wt.%.

![Graph showing average oxide scale thickness analysis](image)

**Figure 71** Average oxide scale thickness analysis of the scales formed on E1250 steel substrate oxidised at 700°C in argon - 50% H₂O steam

### 7.2.2 Surface oxide morphology and chemistry

The surface oxide morphologies observed on E1250 substrate oxidised for 1,000 to 3,000 hours are illustrated in Figure 72(a-c). The scale exhibited two differing oxide crystal profiles; namely octahedral type oxide grains, which formed the bulk of the oxide and the thick plate-like oxide grains. The octahedral oxide grain region after 1,000 hours of oxidation exhibited a sharp faceted surface profile. These were also observed on the oxide nodules that had formed on top of the plate-like oxide regions. The sharp faceted profile was not observed for exposures above 2,000 hours, as the grains exhibited a smoother grain surface profile. The change of the surface oxide grain profile from sharp and smooth on the octahedral shaped crystals, suggests a slow grain growth with increasing temperature. This indicates that the cationic diffusion that occurs during oxide growth results in grain enlargement as opposed to faster outward grain growth. These octahedral crystals were identified as Fe rich oxides with an appreciable Mn concentration as shown in Figure 73. The plate-like oxide crystals were surrounded by the octahedral grains and/or in areas where oxide nodules had formed. These plate-like crystals were identified as Cr-Mn rich oxide phase from the EDS maps. Several authors [10, 59, 63] have also reported the formation of these Cr-Mn rich oxide phases, which
act as the protective oxides during high temperature oxidation of austenitic stainless steels. The octahedral Fe rich oxides formed on E1250 steel substrate also exhibited cracks, which have been proposed to provide additional pathways for the oxidant species ingress into the oxide [10].

Figure 72 Oxide crystal growth morphology of the scales formed on E1250 steel substrates oxidised at 700°C in steam for (a) 1,000 (b) 2,000 and (c) 3,000 hours respectively.
These Fe rich and Cr-Mn rich oxides observed on E1250 steel were also identified using XRD analysis as illustrated in Figure 74. The oxide phases present were identified as Fe$_2$O$_3$ (JCPDS 33-0664), Fe$_3$O$_4$ (JCPDS 85-1436) and Cr$_{1.5}$Mn$_{1.5}$O$_4$ (JCPDS 33-0892), from peak search and comparisons with the JCPDS-ICDD database.
7.2.3 Cross-sectional oxide morphology and chemistry

The cross-section oxide morphology exhibited a double layered structure consisting of an outer layer and an internal oxidised region as shown in Figure 75. The outer layers exhibited pores and voids for all the exposure times and showed areas where cracks, which were also observed on the surface oxide, had developed in regions with a high area fraction of voids. The outer oxide was shown from EDS line analysis to consist of an Fe-Mn rich oxide phase. The inner oxide layer exhibited an interconnected network of an oxide phase, whose growth profile mimicked that of the former austenite substrate grain boundaries as well as occurring at the inner oxide/metal interface. The phase was identified as the Cr-Mn rich oxide phase from EDS line analysis, as was also predicted by Thermocalc calculations, Figure 25(a), adjacent to the substrate/oxide interface. The Cr-Mn rich oxide phase was observed to have also encircled substrate grains adjacent to the former substrate/gas interface. The encircled grains appeared to have subsequently been oxidised with the remaining Cr and Mn cations in the grains forming discrete Cr-Mn rich phase with Fe-Ni rich matrix. Figure 76, shows a detailed morphology and chemistry at the substrate/oxide interface, the results show the Cr-Mn rich oxide phase formation adjacent to the substrate, and the formation of isolated Si rich oxides. The Fe-Ni rich matrix was also observed and within it the presence of the discrete Cr-Mn rich oxide phase. Similar results were also reported by Hansson and Montgomery [138] working on the oxidation of TP347HFG austenitic stainless steel.

Nb rich areas were observed discretely within the substrate and the inner oxide. These Nb rich areas relate to the second phase particles observed within the substrate and in the oxides formed adjacent to the substrate/oxide interface as illustrated by the Nb ‘kinks’ in the EDS line scans, Figure 75 (b) and (c). These particles, as shown in Figure 77, are consumed to form the Fe-Nb-Cr rich oxide phases within the inner oxide region, whereas on the outer layer, they formed Fe-Nb rich oxide phase. Both the Nb rich oxides exhibited significant microporosity that could influence the inward transport of oxidant species within the vicinity of the Nb rich oxides. The presence of the NbC particles within the innermost oxides as discrete particles related to their stability at low oxygen partial pressures as observed from Thermocalc phase predictions, Figure 25(a), before consumption to form the stable Fe-Nb rich oxide phase.

The inner oxide layer also exhibited voids that occurred at the substrate/inner oxide interface and/or adjacent to the Cr-Mn rich oxide phase, Figure 76. These voids are attributed to the transport processes occurring within the inner oxide layer such that vacancies, which form due outward cation transport from the substrate, coalesce into voids at the oxide/metal front. Other proposed mechanisms suggest that Fe rich or Fe-Cr rich oxides do form within the Cr and Mn depleted grains and that these phases tend to dissociate due to the in-scale oxidation resulting in the formation of voids [10]. The voids were also observed ~ 1 – 2µm into the
substrate and these were attributed to the vacancies created during cationic transport and/or where the second phase particles had been consumed on the substrate grain boundaries. Cracks were also observed within the Cr-Mn rich oxide phase throughout the inner oxide zone in a profile mimicking former substrate grain boundaries.

Figure 75 EDS line analysis across the oxide scale into the substrate on E1250 steel oxidised at 700°C in steam for (a) 1,000, (b) 2,000 and (c) 3,000 hours.
Figure 76 (a) SEM micrograph and EDS maps of a TEM thinfoil illustrating the Fe-Ni rich matrix with the discrete Cr-Mn oxide phase adjacent to a Cr-Mn rich oxide taken from the inner oxide scale formed on E1250 steel.

Figure 77 SEM micrograph showing Nb rich particles within the substrate and at the interface of the inner and outer scale layers on E1250 steel substrate oxidised at 700°C in steam for 1,000 hours.

These cracks are proposed to enhance inward transport of oxidant species resulting in further attack along the substrate grain boundaries. The resultant effect is the formation of the Cr-Mn rich oxide phase deep into the substrate along the substrate grain boundaries, Figure 78. It is evident from the EDS map profiles that Cr and Mn depletion occurred along grain boundaries, with the depleted elements forming a thin protective Cr-Mn rich phase observed at the initial substrate/steam interface. With increasing exposure times, the internal oxidised zone occurred...
by further reaction of the diffusing cations with the inward diffusing oxidant species along the cracks and pores created. This results in the formation of more Cr-Mn rich oxide phase along the grain boundaries, Figure 75, as well as the oxidation of inner substrate grains. These internal oxidised grains, Figure 78, were encircled with the protective Cr-Mn rich oxide phase whereas the bulk of the grain exhibited discrete Cr-Mn rich oxide phase formation in Fe-Ni rich matrix, similar to the results observed in Figure 76.

Figure 78 Micrograph showing internal oxidation and the corresponding EDS component distribution of the scale formed on E1250 showing Cr, Mn depletion profiles on substrate grain boundaries and the preferential Cr-Mn rich oxide formation
7.3 AIR OXIDATION

7.3.1 Oxide scale thickness analysis

Figure 79 shows the oxide scale thickness measurements as a function of time of the oxide scales formed on E1250 steel substrate under static air conditions on the as-received surface. As observed in section 5.3.4, oxide spallation was prevalent on the as-received surface resulting in the large variation of the oxide scale thickness measurements. The scale thickness measurements were carried out on the assumption that the ratio of the inner to outer scale layers was approximately 1:1. The results showed that the samples oxidised at 750°C resulted in thick oxide scales ~ 30µm compared to the scales formed on the samples oxidised at 650°C ~ 15µm. However, there was minimal oxide scale growth from 2,000 to 3,000 hours of oxidation for both exposure temperatures indicating that the Cr-Mn rich oxide scales were impeding faster outward or inward transport of migrating species.

For the ground surface, the oxide scales formed were considerably thinner with the average oxide scale thickness values for the samples oxidised at 650°C and 750°C respectively below 8µm thick, Figure 80. The large errors observed in the graph were attributed to the nodular oxide growths observed on the ground surface. Whenever these oxide nodular features occurred, the scale thickness measurements were greater to about 10 times the average oxide scale thickness of the adjoining thin oxide scales on either side of the nodule. The results showed that surface modification through cold work of E1250 steel substrate had a positive effect on reducing the rates of oxide scale growth.

![Figure 79 Average oxide scale thickness analysis of the scales formed on E1250 steel substrate oxidised at 650°C and 750°C in static air on the as-received surfaces](image-url)
Figure 80 Average oxide scale thickness analysis of the scales formed on E1250 steel substrate oxidised at 650°C and 750°C in static air on the ground surface.

7.3.2 Oxide morphology and chemistry on the as-received surface

For the samples oxidised at 650°C, the oxides scales formed on the as-received surface exhibited a uniform cover of thick oxide scales, Figure 81(a) to (d), with the oxidised surfaces showing areas with ‘waffle-like’ features (X) shown in Figure 81(a). The surface oxide scales also exhibited porosity as well as showing discrete ‘plate-like’ crystal growths. These ‘plate-like’ crystal growths were more pronounced and appeared thicker for the samples exposed above 2,000 hours, Figure 81 (c) and (d). Oxide scale spallation was observed on all the oxidised samples but this was more pronounced on the samples oxidised above 1,000 hours, Figure 81(b). Where spallation had occurred and for longer exposure times, oxide scale regrowth was observed forming a uniform cover of new surface oxide.

The ‘waffle-like’ surface growth features were identified as the Fe-Nb-O rich oxide, whereas the bulk of the surface oxides mainly consisted of Fe-O rich phases with appreciable Mn concentration as shown in Figure 82. For the ‘plate-like’ surface growth features, these were identified as Fe-Mn-O rich oxide phase occurring above the Fe rich oxides. The resultant effect of the observed oxide spallation was the exposure of the inner Fe-Ni rich areas and the Cr-Mn-O rich areas. Oxide spallation appeared to have occurred within the outer Fe-rich oxide layer and at the inner/outer oxide layer interface. Si-O rich phases were also observed but these occurred discretely as surface oxides.
Figure 81 SEM micrographs of surface oxide growth profiles for the samples oxidised at 650°C for exposure times in hours of (a) 500 (b) 1,000 (c) 3,000 and (d) 5,000 on the as-received surface of E1250 steel substrate

Figure 82 SEM micrographs and EDS maps illustrating the surface oxides features formed on E1250 steel substrate oxidised at 650°C for 1,000 hours on the as-received surface

For the samples oxidised at 750°C, Figure 83(a) to (d), the oxides scales formed exhibited a thick cover of surface oxides as observed in areas where oxide spallation had occurred. For all the exposure times studied, oxide scale spallation was more pronounced for the samples oxidised at 750°C compared to the samples oxidised at 650°C. Oxide spallation was also observed to occur within the outer oxide layer, Figure 83(a) and (c) or at the interface between the inner and outer oxide layers, Figure 83(c) and (d). The resultant effect of oxide scale
spallation was the exposure of the inner oxide layer as observed by the discernible former substrate grain boundaries in Figure 83(b) and (d). The remaining inner oxide layer exhibited microporosity, which was observed within the exposed former substrate grain boundaries, as well within the oxidised grains.

The surface oxide chemistry was similar to that observed at 650°C, but due to the pronounced oxide spallation, it consisted of the Fe-Ni rich areas and re-grown Cr-Mn rich surface oxides, Figure 84. For the Fe-Ni rich areas, these occurred within the former substrate grains with the Cr-Mn rich oxide phase occurring on the former substrate grain boundaries. Within the Fe-Ni rich areas, they exhibited microporosity and voids which were attributed to the transport processes occurring within the oxidised former substrate grain. Where oxide spallation had not occurred, the surface oxides mainly consisted of the Fe rich oxide phase with appreciable Mn concentration. There were also discrete Si-O rich areas for all the exposure times studied. The presence of the isolated Si-O rich phase can be related to the Thermocalc calculations, Figure 25, which predicted the formation of SiO₂ phase with a lower mass fraction as well as being thermodynamically stable at low and high oxygen partial pressures.

Figure 83 SEM micrographs of surface oxide growth profiles for the samples oxidised at 750°C for exposure times in hours of (a) 500 (b) 1,000 (c) 3,000 and (d) 5,000 on the as-received surface of E1250 steel substrate.
7.3.3 Oxide morphology and chemistry on the as-ground surface

For the samples oxidised at 650°C, Figure 85(a) to (d) the oxide scales formed exhibited a uniform cover of faceted crystal shaped surface growths, which appeared to be thin as the prior surface roughness attributed to the 600 grit finish was easily discernible even after 5,000 hours of oxidation. With increasing exposure times, nodular features were observed on the ground surface with some exhibiting ‘plate-like’ crystal growths similar to those observed on the as-received surface, Figure 85(d). Oxide spallation was less pronounced on the oxidised ground surface with the oxide scales formed exhibiting good adherence to the substrate. The surface oxides formed were identified as Cr-Mn-O rich phase, with the observed nodular features being Fe-O rich phase, Figure 86. Ni was also detected on the surface; this was attributed to its concentration within the substrate which is detected by EDS due to the technique having a large sampling volume and the fact that the oxide scales formed on the ground surface were thinner. In certain areas of the surface, the Fe-Ni rich matrix was also detected accounting for the high Ni detection in the EDS maps. With increasing oxidation times, there were more Fe rich nodular growths detected as surface oxides indicating that a break occurred in the outer protective Cr-Mn rich oxide phase allowing the outward diffusion of Fe and Mn cations as well as the inward ingress of oxidant species.

For the samples oxidised at 750°C, Figure 87(a) to (d), the oxide scales formed on the ground surface also exhibited a uniform cover of faceted surface crystal growths, as well as nodular growth features along the observed surface roughness. The oxides formed were thicker compared to those formed at 650°C and exhibited more porosity. There were also large gem-shaped crystal growths (Y), which for exposure times below 1,000 hours exhibited a multifaceted crystal shape, Figure 87(a) and (b). With increasing oxidation times, the large gem-like crystals exhibited a ‘melt-like’ appearance, which was more pronounced after 5,000 hours of oxidation, Figure 87(d). These faceted oxide crystals were identified as being V-Mn-O rich crystals from the EDS map profiles, whereas the surrounding oxide phases were identified
as the Cr-Mn rich oxide phase, Figure 88. The observed nodular growth features were identified as Fe rich oxides with an appreciable Mn concentration.

Figure 85 SEM micrographs of surface oxide growth profiles for the samples oxidised at 650°C for exposure times in hours of (a) 500 (b) 1,000 (c) 3,000 and (d) 5,000 on the ground surface of E1250 steel substrate.

Figure 86 SEM micrographs and EDS maps showing the surface oxides features formed on E1250 steel substrate oxidised at 650°C for 1,000 hours on the ground surface.
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Figure 87 SEM micrographs of surface oxide growth profiles for the samples oxidised at 750°C for exposure times in hours of (a) 500 (b) 1,000 (c) 3,000 and (d) 5,000 on the ground surface of E1250 steel substrate

Oxide spallation on the ground surface was less pronounced, however, where it occurred, the inner Fe-Ni matrix was exposed and appeared not to have undergone further oxidation for short oxidation times. For longer exposure times, the spalled surface appeared to have been oxidised with subsequent formation of Fe rich oxide nodules in a matrix of Cr-Mn rich oxide phase.

Figure 88 SEM micrographs and EDS maps illustrating the surface oxides features formed on E1250 steel substrate oxidised at 750°C for 1,000 hours on the ground surface
7.3.4 Cross-sectional oxide morphology and chemistry

On the as-received surface, the oxide cross-section morphology exhibited a double layered structure consisting of an outer oxide layer and an internal oxidised region as illustrated in Figure 89 and Figure 90. The outer layers exhibited microporosity for all the exposure times studied. In certain areas, such as the interface between the inner and outer oxide layers, a high density of voids were observed providing a favourable condition for microcrack development, as shown in Figure 89(c) and Figure 90(a) and (b). This could provide an explanation for the observed outer oxide layer spallation. The outer oxide was identified from EDS line analysis as an Fe rich oxide phase with the outermost oxide grains exhibiting appreciable Mn concentration. The inner oxide layer exhibited a multiphase region consisting of Fe-Ni-Cr-Mn-O rich phase. Within the inner oxide layer and closer to the metal oxide interface, NbC particles were observed as shown in Figure 89 (b) and (c), these appeared to have been consumed to form Nb rich oxides, Figure 89 (c). NbC second phase particles incorporation in the inner oxide layer was similar to the Thermocalc phase predictions where this phase was predicted to be stable at low oxygen partial pressures with the Cr-Mn rich spinels. At 750°C, there was a clear enrichment of Mn in the outer oxide occurring as Fe-Mn rich oxide phase. The inner oxide layers exhibited multiphase regions similar to those observed at 650°C, however at 750°C, the Cr-Mn rich oxide phase was more pronounced and occurred at the metal/oxide interface, Figure 90. Adjacent to the Cr-Mn rich oxide phase was the Fe-Ni-Cr-Mn rich oxide phase, which occurred up to the interface between the inner and the outer oxide layers. The microporosity observed within the inner oxide was more pronounced at 750°C compared to 650°C and this is attributed to the increased activity of the migrating species due to increased temperature.

On the ground surface, the oxide cross-section morphology mainly exhibited a single layered structure for all the oxidation times studied as shown in Figure 91(a). There were areas that showed a double layered structure as represented in Figure 91(b), however, this double layered structure occurred where pronounced nodular growths had formed coalescing into a continuous outer oxide. The outer layer did not exhibit pores or voids but where nodular growths had occurred, voids were observed at the interface between the inner and outer oxides layer with the occasional crack development. For both oxidation temperatures, there were similarities in the outer oxide chemistry, with the bulk of the outer oxide scale consisting of a Cr-Mn rich oxide phase, Figure 91. At 750°C, the oxide nodular features were more pronounced, which indicates increased activity of outward Fe and Mn species diffusion, and these were identified as Fe-Mn rich oxide phase. The oxide scale cross section also showed areas with Fe-Nb rich oxide phase formation, which was attributed to the NbC second phase particles found in E1250 steel substrate, Figure 92. The NbC second phase particles during
early stages of oxidation formed oxides, which were characteristically porous in nature as shown in Figure 81. These Nb rich porous oxides are proposed to provide the additional pathways for easy transport of the oxidant species into the substrate as well as aiding the outward cationic transport of Fe, Mn and to a lesser extent Cr.

Figure 89 EDS line analysis across the oxide scale formed on E1250 steel oxidised at 650°C in static air for (a) 1,000, (b) 2,000 and (c) 3,000 hours on the as-received surface
Figure 90 EDS line analysis across the oxide scale formed on E1250 steel oxidised at 750°C in static air for (a) 1,000, (b) 2,000 and (c) 3,000 hours on the as-received surface.
Figure 91 EDS line analysis across the oxide scale formed on E1250 steel oxidised at (a) 650°C and (b) 750°C in static air for 3,000 hours on the ground surface.

A further investigation of these Nb rich oxides exhibited a strong correlation with the formation of the Fe-Mn rich nodular features as shown in Figure 93. A considerable number of the Fe-Mn rich nodular features were observed to contain the Nb rich oxide phase, which emanated from the substrate into the nodular growth, Figure 92.

Figure 92 SEM micrographs of a nodular feature formed on E1250 steel substrate oxidised at (a) 650°C for 3,000 hours and (b) 750°C for 1,000 hours.
This supports the proposition that the porous nature of the observed Nb rich oxides affected the outward transport of Fe and Mn cations for the outer oxide nodular growth, and this allowed the inward ingress of gaseous oxidant species to form internal oxides.

Figure 93 SEM micrograph and EDS maps of Fe rich oxide nodule formed in the vicinity of Nb rich particle. On either side of the nodule, Cr-Mn-O rich phase was observed on E1250 steel substrate oxidised at 750°C for 500 hours.
7.4 DISCUSSION – E1250

7.4.1 Effect of the oxidising environment

The results showed that steam containing environments had a marked effect on the growth kinetics of the scales formed on E1250 steel substrate. From the scale thickness measurements, the samples oxidised in steam at 700°C, Figure 72, had oxide thickness averaging between 50-85µm thick whereas the samples oxidised in air at 650°C and 750°C averaged about 15µm and 30µm thick in Figure 79 and Figure 80 respectively. Several authors [66-69, 128, 139, 140] have reported that water vapour containing environments significantly accelerates the oxide scale growth rates on ferritic, austenitic and nickel alloys, as well as influencing the types of oxides formed, the growth morphology and the adhesion of the resultant oxide scales. For the oxide growth morphology, the main observable differences were on the subsurface oxides, with the steam oxidised samples exhibiting pronounced Cr-Mn rich oxide phase formation of former substrate grain boundaries and encircling grains close to the original substrate surface. The bulk of the internal oxidised zone showed encircled oxide grains that had microporosity with discrete Cr-Mn rich oxide phase in Fe-Ni rich matrix. For the static air oxidised samples, the subsurface oxides exhibited a layered profile with the Cr-Mn rich oxide phase occurring at the interface between the substrate and the bulk of the inner oxide which was Fe-Cr-Mn-Ni rich oxide phase.

The observed growth morphology could be attributed to the transport processes occurring across the scale towards the substrate/oxide interface. The process is such that in steam environments, the oxidant species are reported to exist as gaseous of H₂, 1/2O₂, and OH from the dissociation of H₂O [10]. The determinant factor as to which oxides are likely to form is the oxygen partial pressure in steam, which is considerably lower in steam than oxygen rich environments [21]. These species rapidly transport through the oxide scales formed, resulting in pronounced internal oxidation. The transported oxidant species react with the outward diffusing Cr and Mn cations along grain boundaries to preferentially form the Cr-Mn rich oxide phase. For static air, the oxidant O reacts with the outward diffusing cations to form the Cr-Mn rich oxide at the substrate/oxide front at lower oxygen partial pressure, and with increasing P(O)₂, more Fe-Cr rich and Fe- rich oxides are formed towards the oxide/gas interface.

In both steam and air, voids were observed within the inner and outer zones, with steam oxidised samples showing pronounced void formation on former substrate grain boundaries and within the Fe-Ni rich encircled grains. For the air oxidised samples, at 650°C and 750°C, the microvoids uniformly covered the inner oxide zone, however, at 750°C, the microvoids were more pronounced with an apparent large area fractions. The presence of microporosity is associated with the transport phenomena occurring across the scale. The apparent pronounced voidage is related to the increased activity cations with increasing temperature,
which results in the pronounced vacancies generation that are responsible for the void’s creation. Furthermore, the in-scale oxide diffusion and the oxide dissociation for Fe rich oxides might account for the generation of microvoids in the inner oxide zone of the air oxidised samples. The in-scale oxide diffusion could be attributed to the presence of the Cr-Mn rich oxide phase found at the substrate/oxide interface ~ 10µm thick, that also exhibited increased Cr content with increasing oxidation times. This aids in the formation of the protective Cr rich oxides that impede the outward cation transport. The resultant effect is the increased in-scale diffusion and oxide dissociation resulting in the formation of the observed voids.

7.4.2 Effect of surface grinding

The results have shown that surface modification through cold work has an effect on the oxide scales formed, such that different oxide morphologies, chemistry and scale thicknesses were observed on the as-received and the ground surfaces. Surface modification is thus proposed to change the surface substrate grains, such that localised regions with a high density of dislocations are created. Naraparaju et al. [102] work on the effect of shot peening on an austenitic 18wt.% Cr steel showed that rapid diffusion paths were produced due to shot peening resulting in the formation of protective chromia layers. They attributed this to the increase in surface dislocation density that enhanced the diffusion of chromium responsible for chromia formation. Grabke et al. [141] also showed that a surface ground to 600grit finish exhibited fine grained surface microstructure resulting in a higher fraction of grain boundaries. Their TEM results showed that the surface grains had a high density of dislocations, which were suggested to enhance diffusion of Cr and Mn cations to the surface to form the protective Cr-Mn rich oxide phase. Thus, the increase in surface dislocation density due to grinding provides a high density of diffusion paths for faster outward Cr and Mn species diffusion. These species react with the oxygen at the metal/gas interface, forming the protective Cr rich oxide scales. The Cr-Mn rich oxide scales impede further outward diffusion of the cationic or inward diffusion of the anionic species and thus slowing down the oxidation rate. Similar observations were also reported by Evans [142] who showed that surface roughness had an effect on the oxidation behaviour of a Ni-based superalloy. The oxidised surfaces were ground using SiC paper from 220, 600 and 1,200 grit with the results showing that the corresponding mass gains after oxidation decreased with decreasing surface roughness. However, he also reported that no significant difference was observed for the samples ground to 600 and 1,200 grit respectively for the exposure times studied.

7.4.3 Effect of surface roughness

The good adherence of the oxide scales formed on the ground surface was associated with the observed surface roughness attributed to grinding. During oxide growth, growth stresses
are known to develop and these are generally dissipated into the oxide resulting in oxide deformation, with a wavy appearance, and subsequent oxide detachment causing oxide scale spallation. The observed surface roughness, which is evident even after 5,000 hours, is proposed to have a positive effect on the dissipation of the developing growth stresses into the peaks and troughs on the surface. This allows good adherence of the oxide scales formed in the substrate, it should also be noted that other effects such as internal oxidation along substrate grain boundaries, the rates of cation diffusion, and the concentration of the key alloying elements such as Cr have been reported to play a significant role on oxide scale adherence [137].

7.4.4 Formation of the V-Mn-O rich crystals

The V-Mn-O crystals reported in Section 7.3.3, also shown in Figure 94, were observed to occur above the Cr-Mn-O rich surface oxides as multifaceted crystals at 750°C. These V-Mn-O crystals have also been reported by Higginson et al. [143] on E1250 steel substrate oxidised at 750°C for exposure times of up to 720 hours. To investigate their formation focussed ion beam serial cross-sections of the crystals were carried out, Figure 95. The V-Mn-O crystals appeared not to show any correlation, as regards to their nucleation and growth, with the adjacent Cr-Mn or Fe-Mn rich outer surface oxides or with the underlying substrate matrix as shown in Figure 95. Further work using the TEM was carried out to fully characterise these crystals, Figure 96(a), and these were found to exhibit no grain boundaries but occurred as as single crystals. The results also confirmed the non-existence of a relation with the adjoining Cr-Mn oxide grains. The V-Mn-O crystals were characterised as monoclinic, whereas the adjoining Cr-Mn-O grains had a cubic structure as exhibited by the diffraction spot analysis, Figure 96(b). From the elemental compositions, the V-Mn-O rich crystals were empirically calculated as being Mn$_2$V$_2$O$_7$. Chung et al. [144] work on the stable phases formed in Mn-V-O system under ambient atmosphere showed that the equilibrium stable phases were Mn$_2$V$_2$O$_7$ and Mn$_2$O$_3$ for exposures below 900°C. However, this was dependent on the concentration of the reactants used, V$_2$O$_5$ and MnO. They also found that for concentrations ranging from 0-50% of V$_2$O$_5$ the stable phases observed were Mn$_2$V$_2$O$_7$ and Mn$_2$O$_3$. Liao et al. [145] work on the synthesis and properties of Mn$_2$V$_2$O$_7$ reported that its structure was monoclinic agreeing with the TEM results observed in this study. EDS analysis was also carried along an arbitrary line starting from the V-Mn-O crystal towards the substrate, Figure 97, to show the elemental chemistry distribution. The results showed the crystal to be V-Mn-O rich with the ratio of V to Mn concentration in weight % approximately 1:1. The V content dropped to nearly zero whereas the Mn concentration gradually drops towards the substrate concentration levels. V is clearly absent or in considerably low concentration in the adjoining oxide grains as well as within the substrate. The results suggested that the V-Mn-O
crystals must have formed during early stages of oxidation attributed to the presence of V rich second phase particles.

From the equilibrium thermodynamic phase calculations, Figure 25, vanadium containing second phase particles were identified as the MX and Z phase. However, these second phase particles contained low vanadium concentration to account for the formation of the V-Mn-O crystals. Analysis of un-oxidised E1250 steel substrate was carried out to confirm which second phase particles were present, Figure 98. The results showed the presence of V-Mn-Si rich particles, which were not predicted to occur under equilibrium conditions using Thermocalc. The presence of these V-Mn rich second phase particles are thus proposed to provide a reservoir for V and Mn responsible for V-Mn-O crystal formation. This proposition was further supported by the good correlation between the V-Mn-O rich second phase particles observed on oxidised E1250 steel substrate, as shown in Figure 94 and the V-Mn-Si rich second phase particles observed in virgin material of E1250 steel as shown in Figure 98. The melt like appearance observed for exposures above 2,000 hours of oxidation was attributed to the incongruent decomposition of Mn$_2$V$_2$O$_7$ at higher temperatures or for longer exposures times[145].

Chung et al. [144] work also showed that vanadium oxides, were not stable at temperatures above 690°C, where at equilibrium conditions occurred as liquid oxides. However, decreasing the equivalent composition (%) of V$_2$O$_5$ and increasing the equivalent composition (%) of MnO$_2$, the reactants used to study the V-Mn-O system, the most stable phase formed was the Mn$_2$V$_2$O$_7$. This would provide an explanation for the formation of the V-Mn-O phase at 750°C and not at 650°C.

![SEM micrograph and EDS elemental composition maps of V-Mn-O rich crystals in a Cr-Mn-O rich oxide phase on the ground surface of E1250 steel substrate oxidised at 750°C for 500 hours](image)
Figure 95 Showing focussed ion beam serial cross-sections of the V-Mn-O rich crystal and the corresponding EDS maps for the sample oxidised for 1000 hours at 750°C.

Figure 96 (a) TEM micrographs of the V-Mn-O crystal above the Cr-Mn oxide grains after 1,000 hours of oxidation at 750°C, with (b) showing the corresponding diffraction patterns for (A) the V-Mn-O (monoclinic) crystal and (B) the Cr-Mn-O (cubic).
Figure 97 Showing EDS point analysis along an arbitrary line starting from the V-Mn-O rich crystal (1) to the substrate (8) for E1250 steel substrate exposed for 1,000 hours at 750°C.

Figure 98 SEM micrograph and EDS elemental composition maps of the substrate illustrating the presence of V rich second phase particles, Nb carbonitrides and Mn-S rich particles of un-oxidised E1250 steel substrate.
A further investigation was carried out to confirm whether the formation of these V-Mn-O crystals occurred on the as-received surface. This involved preparing rectangular coupons such that the surface originally considered as the as-received surface was ground to a 600 grit finish and oxidised for 250 and 500 hours respectively. The oxidation results on the rectangular coupons also exhibited the V-Mn-O crystals confirming that grinding any surface of the tube section would expose the underlying second phase particles, Figure 98, which are responsible for the observed V-Mn rich oxide features.

7.4.5 The role of key alloying elements Cr, Mn, Mo and Nb in E1250

The Cr, Mn, Mo and Nb have been reported to have a direct and/or indirect effect on the oxidation behaviour of austenitic stainless steels. Cr is well known to preferentially form protective Cr rich oxide layers but this depends on the oxidising environment and the bulk Cr concentration of the alloy [10, 70, 82, 146]. In dry atmospheres, austenitic stainless steels form protective Cr$_2$O$_3$ layer, whereas in water vapour containing environments and dependent on the alloying elements present, Fe-Cr, Fe-Mn, Cr-Mn or even Cr$_2$O$_3$ have been reported to occur. Mn is a common alloying element in austenitic stainless steel, which in E1250 stainless steel has been added at a considerable higher concentration as an alternative to nickel as an austenite stabilizer. The addition of Mn, in appreciable concentration, has been shown to affect oxidation characteristics, with Stott et al. [97] reporting that together with Cr, it formed the less protective MnCr$_2$O$_4$ spinels as opposed to Cr$_2$O$_3$ formation in air. Similar results were observed from Thermocalc phase predictions which showed the Cr-Mn rich spinels as the stable oxide phase at low oxygen partial pressure and with a higher mass fraction compared to the chromia. From the surface and cross sectional oxides observed in this study, Mn was shown to form spinels with Cr, as well as forming the outer Fe-Mn rich oxides with Fe whether in air or in steam oxidising environments [37, 147].

Despite there being an appreciable Mo concentration within the substrate matrix, it was not detected in the EDS maps. From the thermodynamic phase calculations, Mo was predicted to participate in the formation of sigma particles, which were observed along the substrate grain boundaries. Mo has been proposed to form volatile species (MoO$_3$ in air or MoO$_2$(OH)$_2$ in steam) even at moderate temperatures [37, 147, 148]. These species are lost during high temperature oxidation and could provide an explanation for the lack of Mo detection within the oxide scales formed on E1250 steel substrate. Furthermore, the volatile Mo species have been proposed to cause cracks within the inner oxide layers and therefore impede crack healing when they occur. Given that the results showed cracks within the Cr-Mn rich oxide phase in a profile similar to that of the former substrate grain boundaries, their formation could be attributed to the Mo volatile species.
Nb has also been reported to affect the oxidation kinetics of stainless steels, work by Ramanathan et al. [149] on the effect of Nb (0.44-1.88 wt.%) on the oxidation of 15 wt.% Cr and 15 wt.% Ni austenitic steels between 800-900°C, showed that slower kinetics occurred with increasing Nb content. They detected Nb at the metal/oxide interface and proposed that a high Nb containing austenitic stainless steel facilitated the formation of Cr₂O₃. The works of Brady et al. [92] on alumina forming austenitic stainless steels also concluded that increasing the Nb content resulted in improved oxidation resistance for steels oxidised from 650-850°C in air - 10% H₂O. They proposed that the Nb addition had an effect on increasing Al reservoirs for the alumina layer formation, which offers a high oxidation resistance to the underlying substrate. For the steam oxidised samples, the results of this study suggests that at 700°C, Nb may have an effect on the oxide scale formed if a higher volume fraction of NbC particles occurred. However, these particles were found distributed within the inner oxide layer as discrete particles in a profile similar to that observed of the NbC in the substrate. Some of the particles appeared to have been consumed to form Fe-Nb-Cr rich oxides with those found at the interface between the inner and outer oxide zone forming Fe-Nb rich oxide phase. For the air oxidised samples, similar results were observed for the inner and outer oxide zones, however, during the early stages of oxidation, the NbC were oxidised to form porous oxides. These porous Nb rich surface oxides acted as the preferred sites for the Fe-Mn rich nodular growths resulting in the formation of unprotective oxides.
7.5 AUSTENITIC STAINLESS STEEL 347HFG

7.5.1 Introduction

This chapter addresses the oxide growth and the microstructural changes occurring on 347HFG austenitic stainless steel substrate exposed to air and steam oxidising environments. The oxidation experiments were also carried out in air in the same temperature range for comparisons with steam oxidised samples with the intent of fully understanding the oxide growth phenomena. Further investigations were also carried out on the effects of cold working on the oxidation behaviour of 347HFG, which will be addressed in this chapter. The discussion section will highlight the role of the substrate microstructure, the alloying elements and the oxidation conditions on the oxide scale development of 347HFG austenitic steels. Oxide growth models have also been developed and will be presented to explain the oxide growth behaviour.

7.6 STEAM OXIDATION

7.6.1 Oxide scale thickness analysis

The results of oxide scale growth on the 347HFG steel substrate oxidised at 650°C and 700°C for 1,000 to 3,000 hours are shown Figure 99. At 650°C, the results showed a decreasing oxide scale growth, which was attributed to oxide scale spallation, formation of thin outer oxide layers and the uneven formation of subsurface internal oxides. For exposures below 2,000 hours of oxidation, the oxide scale formed was intact and had an inner oxide scale exhibiting uneven formation. After 3,000 hours of oxidation, the loss of the outer oxide layer occurred due to oxide scale spallation resulting in the scale thickness measurements exhibiting a decreasing trend. It is worth noting that due to the uneven formation of the inner oxide on the scale formed on the 347HFG steel substrate, the general assumption that the ratio of the inner to outer oxide layers is approximately 1:1 could not be applied here and hence the thickness measurements carried out were based on the existing intact oxide [10]. Montgomery and Karlsson [150] work on 347HFG had similar observations for the oxide scales formed and on their thickness measurements, they only reported the inner oxide layer thickness. They attributed this to the formation of thinner outer oxide layers, which readily spalled off leaving the inner oxide layer as the protective oxide scale. For the samples oxidised at 700°C, the analysis exhibited random scale thickness measurements, which were affected by the scale spallation effects and the formation of uneven inner oxides. The large error values observed in Figure 99 for 700°C oxidised samples were related to the pronounced oxide scale spallation observed at higher oxidation temperatures and with increasing exposure time.
7.6.2 Surface oxide morphology and chemistry

The surface oxide morphologies observed on 347HFG substrate oxidised for 1,000 to 3,000 hours are illustrated in Figure 100 and Figure 101. For the samples oxidised at 650°C, Figure 100, the scale exhibited a varying surface oxide crystal profile with increasing exposure time. After 1,000 hours of oxidation, the surface oxides had lath shaped oxide crystals, which after 2,000 hours of oxidation exhibited less lath like surface crystals but also exhibited polyhedral crystal shapes. After 3,000 hours of oxidation, the surface oxides were characterised by octahedral crystal shaped oxides, which were associated with the regrowth of surface oxides after oxide scale spallation had occurred, and had a whisker-like growth morphology.

The observed oxide crystal change from sharp to smoothened lath shapes in a matrix of faceted oxide crystals from 1,000 to 2,000 hours oxidation was an indication of slower oxide grain growth. Pores (X) were also observed within the oxide grains as shown in Figure 100(d) and (e), and these are proposed to allow the inward ingress of oxidant species for further internal oxide scale growth. Due to the pronounced oxide scale spallation after 3,000 hours of oxidation, the inner oxide and the substrate rich areas were exposed to steam and the resultant effect was the rapid regrowth of the surface oxides, which were observed with a whisker like growth profile. The whiskers also exhibited polyhedral crystal shapes as shown in Figure 100(c) and (f).
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Figure 100 Surface oxide morphology of the oxide scales formed on 347HFG steel substrates oxidised at 650°C for (a) 1,000 (b) 2,000 and (c) 3,000 hours respectively with (d), (e) and (f) showing higher magnifications of the surfaces.

For the samples oxidised at 700°C, Figure 101, the surface oxides were characterised by plate-like and whisker-like oxide growths. After 1,000 hours of oxidation, Figure 101 (a), the surface oxides exhibited plate-like and globular oxide growths. The surface oxides had a rough profile and exhibited porosity that allowed the inward ingress of oxidising species. The oxide scale observed was less dense compared to the oxide scale formed at 650°C. After 2,000 hours of oxidation, the observed surface oxides had similar growth profiles to those formed at 650°C and for longer exposure times. The surface oxides formed exhibited pronounced whisker-like oxide growth that also showed polyhedral crystal shaped growth morphology. Where whisker-like growth profile were not observed, the surface oxides exhibited closely packed polyhedral crystal growths with sharp faceted edges.
Results and Discussion – Austenitic Stainless Steels

Figure 101 Surface oxide morphology of the scales formed on 347HFG substrates oxidised at 700°C for (a) 1,000 (b) 2,000 hours respectively with (c) and (d) showing higher magnifications of the surfaces.

Figure 102 Oxide phase identification using XRD analysis of the surface oxides formed on the 347HFG substrate oxidised at 650°C and 700°C from 1,000 to 3,000 hours.

- a: Fe₂O₃
- b: Cr₂O₃
- c: FeCr₂O₄
- d: M₃O₄, M = Fe,(FeCr) or (FeMn)
- e: Austenite (γ)
Oxide phase identification using XRD analysis showed the presence of cubic and trigonal oxides phases. There were identified as mainly Fe$_3$O$_4$ (JCPDS 85-1436), (FeCr)$_3$O$_4$, FeCr$_2$O$_4$ (JCPDS 34-0140) Fe-Si-O (JCPDS 34-0178) rich phase, Fe$_2$O$_3$ (JCPDS 33-0664) occurring as the outer most surface oxides and Cr$_2$O$_3$ (JCPDS 38-1479). From Figure 102, the Fe-Si-O rich phase was presented by the peak marked (x), which from the observed XRD pattern showed that this phase was pronounced with increasing exposure time for the samples oxidised at 650°C, whereas for the samples oxidised at 750°C the phase was present even after 1,000 hours of oxidation. For the 2θ values between 60° and 70°, the samples oxidised at 700°C exhibited additional peaks attributed to cubic and trigonal oxide phases when compared to 650°C. This correlates well with the observed surface oxides, such that at 700°C there were more polyhedral crystal shaped phases relating to the cubic oxide phases as well as the plate-like oxide growths relating to the trigonal oxide phases. For both oxidation temperatures, strong peaks at 2θ values between 42°, 53° and 71° were attributed to the substrate matrix which further suggests that the oxide phases formed were thinner on austenitic stainless steels.

7.6.3 Cross-sectional oxide morphology and chemistry

From the oxide cross-sectional morphology at 650°C, and where the outer oxide layer was intact, this was identified as predominantly two phase Fe-O rich oxide phase consisting of a thick magnetite and a thin uneven hematite layer, Figure 103(a). Where the outer oxide layer had spalled off, Figure 103(b), only the inner oxide layer was observed with discrete areas where the Fe-Ni rich zone (ψ) were observed to occur up to the original substrate surface. Starting from the substrate, and taking into consideration the main alloying elements, the substrate was identified as Fe-Cr-Ni rich adjacent to a thin Fe-Ni rich zone due to the depletion of Cr. The Cr depletion is due to its participation in the formation of the Cr rich oxides adjacent to the Fe-Ni rich zone. The bulk of the inner oxide was an Fe-Cr-Ni rich oxide that also exhibited discrete Cr-Fe rich oxide phases. With increasing exposure time, Figure 103(b), there were regions with isolated internal oxidised grains with similar composition to the bulk of the inner oxide. The depletion profiles observed from the consumption of Fe and Cr cations are represented by X, Y and Z regions, such that region X showed Fe-Ni enrichment with Cr depletion. Region Y exhibited the formation of Cr rich oxide with an appreciable concentration of Fe and there were no traces of Ni, whereas region Z exhibited an Fe-Cr-Ni rich region associate with the bulk of the inner oxide. The observed EDS compositional profiles have a good correlation with the predicted oxide phases from thermodynamics calculations, which showed the presence of Cr-Mn-O rich phases and Fe-O rich oxide phases.
Results and Discussion – Austenitic Stainless Steels

Figure 103 EDS line scans of the oxide scale formed at 650°C for (a) 1,000 hours and (b) 3,000 hours of oxidation respectively.

Figure 104 EDS line scans of the oxide scale formed at 700°C for (a) 1,000 hours and (b) 3,000 hours of oxidation respectively.

For the samples oxidised at 700°C as shown in Figure 104, after 1,000 hours of oxidation (a) and starting from the substrate, internal oxides were observed and occurred as Cr-O rich oxide phases marked by (Z). The bulk of the inner oxide was a Cr-Fe-O rich oxide phase that
also exhibited a high Ni enrichment. Where the outer oxide was intact, this was identified as an Fe-O rich oxide phase as shown in Figure 104(a). With increasing exposure time, oxide spallation was more pronounced at 700°C resulting in the loss of the outer oxide layer as shown in Figure 104(b), leaving Cr-Fe rich oxide as the protective oxide. The inner oxide layer exhibited a varying oxide morphology consisting of Fe-Ni rich, Cr-Fe rich, and Fe-Ni-Cr rich zones as shown in Figure 104(b) by the distribution profiles of Fe, Cr and Ni components. Starting from the substrate, the oxide phase adjacent to the substrate was a Cr-O rich oxide phase followed by oxidised substrate grains, which exhibited increasing Fe and Ni content and a decrease in Cr content. However, the Cr content increased towards the former substrate grain boundaries where Cr rich oxide phases were observed. There was a trace of Nb at the substrate oxide interface, which was related to the Nb carbonitrides, these Nb rich areas occur as second phase particles in the substrate. For the oxidised grains immediately below the original substrate surface, the Ni enrichment was significantly higher, up to ~ 45wt.% from the low levels of ~ 10wt.%. This related to the formation of the Fe-Ni rich matrix attributed to the consumption of Cr and Fe contents for the formation of outer Fe rich oxides and the Cr-Fe rich oxides observed at this interface. It is clear that spallation preferentially occurred at the original substrate surface, as shown by the crack in Figure 104(a), where the Fe-Cr-O rich oxide phase occurred. Once spallation had occurred, the oxide phase left behind as the protective layer was an Fe-Cr-O rich oxide phase, Figure 104(b).

Figure 105 shows the distribution profiles of the constituent elements found on the outer layer and the inner oxide regions. Similar to the results observed in Figure 103 and Figure 104, the EDS maps showed that the outer oxide layer was an Fe-O rich oxide phase whereas the inner oxide region exhibited oxide phases of different stoichiometry, and mainly consisted of Fe, Cr and O elements. The Cr and O EDS maps show that a Cr rich oxide phase preferentially occurs adjacent to the substrate, and it was observed as internal oxide along substrate grain boundaries. The Cr depletion profile was observed near the substrate grain boundaries leaving a Fe-Ni rich zone. From the image quality map, the inner oxide as shown by the oxidised substrate grains (a), (b) and (c) occurs through the inward transport of the oxidant species as internal oxides. The oxidised grain shown in Figure 105 denoted by (b) exhibited the characteristic twin boundary associated with the former austenite substrate grain, which affirms that internal oxidation of austenitic 347HFG is through the inward transport of oxidant species. Where smaller substrate grains existed, these were rapidly depleted of Cr leaving a Ni rich Fe-Ni matrix observed on the Fe and Ni EDS maps. The Ni rich Fe-Ni matrix was observed to occur up to the original substrate surface and this was mainly close to the substrate grain boundaries. The presence of the Nb rich phases was also confirmed from the Nb EDS map and these occurred discretely within the inner oxide regions and observed in the bulk of the substrate grains and were related to the Nb carbonitrides second phase particles.
Figure 105 Image quality and SEM micrograph showing the inner and outer oxide layers of the oxide scale formed on the 347HFG substrate with its corresponding EDS maps after 2,000 hours of oxidation, with regions marked by (a), (b) and (c) show oxidised grains on previous austenite substrate grains.
7.7 AIR OXIDATION

7.7.1 Oxide scale thickness analysis

Figure 106, shows the thickness measurements of the oxide scales formed on the 347HFG steel substrate oxidised in air on the as-ground surface. The oxide scale formed on the ground surface were thinner and showed good adherence to the substrate for exposures at 650°C. At 750°C, the samples exhibited pronounced scale spallation, which preferentially occurred at the original substrate surface, however, the outer layer loss was not uniform across the surface. From the thickness measurements, the oxide scale formed was thinner having a maximum thickness of ~ 6µm, and for exposure times below 2,000 hours, the scale thickness measurement were below ~ 3µm. Figure 106 also shows that there was an increase in scale thickness with increasing time, however, long time exposures are required to ascertain whether the oxidation kinetics are parabolic or linear in nature. On the other hand, literature reports [10, 51, 63, 146] that parabolic growth kinetics are commonly observed on austenitic stainless steels, such as 347HFG steel, when oxidised in air or steam environments. The scale thickness analysis for both exposure temperatures showed thin oxide scales were formed for up to 3,000 hours of oxidation, and this was attributed to the effect of surface modification through mechanical grinding. The effect of mechanical grinding was demonstrated in Section 7.3.1 and discussed in Section 7.4.2 for E1250 austenitic stainless steel substrates, with the results strongly showing a direct influence on the oxide scale growth rate and/or associated mass gains during high temperature oxidation. The effect was attributed to the rapid formation of protective Cr rich oxide phases that impede the inward and outward transport of the cation and oxidant species responsible for the growth of inner and outer oxide layers.

![Figure 106 Oxide scale thickness analysis of the scales formed on the 347HFG steel substrate oxidised in air at 650°C and 750°C for 1,000 to 3,000 hours of oxidation](image-url)
7.7.2 Surface oxide morphology and chemistry

For the samples oxidised at 650°C, Figure 107, nodular features were observed with platelet profiles on an underlying matrix of multifaceted crystals. The grinding marks attributed to the mechanical working were observed on the surface for exposures of up to 2,000 hours of oxidation indicating that thin oxide scales were formed. The platelet nodular features (X) were also present for long exposure times and after 3,000 hours of oxidation, no grinding marks were observed indicating a complete coverage with surface oxides. The surface also exhibited nodular features (Y) which did not exhibit the platelet features suggesting that the nodular feature was a different phase.

Figure 107 SEM micrographs of the surface oxide morphology of the samples oxidised at 650°C for (a) 1,000 (b) and (c) 2,000 and (d) 3,000 hours of oxidation on the ground surface of 347HFG substrate.

The EDS maps in Figure 108 show the surface oxide chemistry after 1,000 hours as consisting of Cr rich oxide phases with traces of Mn. The nodular features observed after (a) 1,000 and (b) 2,000 hours respectively with platelet crystal profiles were identified as Cr-O rich oxide phase related to chromia phase from the Cr and O EDS maps. Nb-rich oxides were also detected on the surface, however, these occurred distinctly where the nodular growths were observed and within the bulk of the surface oxides. The formation and distribution of the Nb-rich phases on the surface suggested a strong relation with the presence of the Nb second phase particles observed in the substrate. The Fe and Ni EDS maps also showed appreciable surface concentration, and were significantly higher where thin surface oxides were observed.
Traces of discrete Si rich areas were also observed on the surface, but these occurred to a lesser extent and at sub-micron levels compared to the Nb rich areas. For the samples exposed for 3,000 hours of oxidation (c), the observed nodular features without platelet profiles were identified as being Fe-O rich with the bulk of the outer oxide identified as the Cr-O rich with an appreciable concentration of Mn.

Figure 108 SEM micrographs and EDS map profiles of the surface oxide morphology of the samples oxidised at 650°C for (a) 1,000 (b) 2,000 and (c) 3,000 hours of oxidation on the ground surface of 347HFG substrate.

Figure 109 (a) and (b) show the surface oxide morphology of the as-received surface of 347HFG steel oxidised at 650°C for 1,000 and 3,000 hours respectively. The surface morphology is characterised by pronounced oxide scale spallation with the exposure of the
underlying substrate rich areas (S). Where the regrowth of the surface oxides occurred, these had polyhedral (P) shaped oxide crystals relating to Fe-rich cubic oxides. There were occasional platelets observed on the surface where the outer oxide layer, an Fe-O rich oxide phase, was still intact and these were related to the hematite phase.

Figure 109 SEM micrographs of the surface oxide morphology of the samples oxidised at 650°C for (a) 1,000 and (b) 3,000 hours of oxidation on the as-received surface of 347HFG substrate.

For samples oxidised at 750°C, Figure 110, after 1,000 hours of oxidation the surface was covered with oxides exhibiting nodular growth some of which have plate-like profiles and others without plate-like crystal growths. Surface grinding marks were still discernible with the formed oxide fully covering the surface. There were additional surface features observed with rod-like crystal growths (Z) with lengths extending from submicron to approximately 100 microns. These were mainly observed within the nodular growths and on the bulk of the underlying oxide where they occurred in a non-uniform manner. Oxide scale spallation was also observed with increasing exposure time as shown in Figure 110 (c), which exposed the underlying substrate rich areas such that the substrate grain boundaries were easily discernible. For the samples oxidised for 3,000 hours, there was pronounced oxide spallation with the subsequent regrowth of the surface oxides which uniformly covered the surface as well as exhibiting the presence of the plate-like nodular growths observed after 1,000 hours of oxidation.

The oxide chemistry for low exposure times, Figure 111 (a), exhibited the presence of Cr rich surface oxides with a considerable Mn content. Traces of Nb rich areas were also observed on the surface which occurred discretely and randomly on the surface. The Nb rich phase however, occurred where nodular growths were observed. The rod like crystal growths were identified as the Si-O rich phase. The EDS Mn map also exhibited strong concentrations around the nodular growths suggesting preferential transport and the formation of Cr-Mn rich oxide phase. Figure 111(b) shows the effect of oxide spallation observed in Figure 110(c), such that the substrate rich grains were observed from the Fe, Ni and Si rich maps, whereas the bulk of the outer oxide layer was a Cr-Mn rich oxide phase. After 3,000 hours of oxidation, Figure 111 (c), the outer oxide layer was identified as an Fe-O rich phase with considerable
amount of Mn. Where spallation occurred, the underlying Fe-Ni rich areas relating to the substrate were observed from their EDS maps, whereas certain areas exhibited the presence of Cr-O rich oxide phase. Nb rich areas occurred discretely across the surface as shown on the Nb EDS maps.

Figure 110 SEM micrographs of the surface oxide morphology of the samples oxidised at 750°C for (a) and (b) 1,000 (c) 2,000 and (d) 3,000 hours of oxidation on the ground surface of 347HFG substrate.

Figure 112 shows the surface oxide morphology of the as-received surface of 347HFG steel oxidised at 750°C for 1,000 and 3,000 hours respectively. The surface oxide morphology was also characterised by pronounced oxide scale spallation however, due to the oxide regrowth, the surface was completely covered with oxides. The regrown surface oxides had polyhedral (P) shaped oxide crystals relating to the Fe-rich cubic oxides. The occasional platelets observed at 650°C were not observed, however, the surface oxides exhibited additional porous oxides that formed on top of the polyhedral crystals shaped layer. These were identified from EDS maps as Fe-O rich oxide phases.
Results and Discussion – Austenitic Stainless Steels

Figure 111 SEM micrographs and EDS map profiles of the surface oxide morphology of the samples oxidised at 750°C for (a) 1,000 (b) 2,000 and (c) 3,000 hours of oxidation on the ground surface of 347HFG substrate.

Figure 112 SEM micrographs of the surface oxide morphology of the samples oxidised at 750°C for (a) 1,000 and (b) 3,000 hours of oxidation on the ground surface of 347HFG substrate.
7.7.3 Cross-sectional oxide morphology and chemistry

From the oxide cross-sectional morphology of the substrate oxidised at 650°C, thin surface oxides were observed, which were identified as Cr-Mn rich oxide phase with occasional nodular growths identified as Fe-O rich phase with an appreciable concentration of Cr and Mn, Figure 113(a). The earlier observed discrete Nb rich surface features were also observed from the Nb EDS maps and had a correlation with the observed Nb carbonitrides that occurred within the substrate supporting the observed surface distribution of the Nb rich oxides in Section 7.7.2. During low exposure times, below 1,000 hours, the formation of the Fe-rich and Cr-rich nodular features appeared to have occurred where the former Nb rich second phase particles were discretely observed on the substrate surface and were exposed to the oxidant species.

The formation of the thin outer Cr-Mn rich oxide resulted in the formation of a depletion zone adjacent to which was rich in Fe and Ni from their corresponding EDS maps. With increasing exposure time, Figure 113(b), thicker oxides were formed that exhibited an outer layer...
identified as Fe-O rich oxide phase with an appreciable concentration of Mn, whereas the inner oxide was a Cr-Mn rich oxide phase. The depth of the Cr-Mn depletion zone was approximately three times that of the sample oxidised for 1,000 hours, indicating increased outward Cr and Mn diffusion with increasing exposure time.

For the samples oxidised at 750°C, Figure 114, after (a) 1,000 hours of oxidation the cross-sectional oxide morphology exhibited a thin Cr-Mn rich oxide phase as the outermost protective oxide layer. There was also the presence of the Fe-rich nodular growths similar to those observed at 650°C, which occurred in the vicinity of the Nb rich second phase particles within the substrate. There was also an additional thin oxide phase observed between the Cr-Mn rich phase and the substrate and this was identified as a Si rich oxide phase from the Si EDS maps. With increasing exposure time, after 3,000 hours of oxidation (b), similar cross-sectional oxide chemistry was observed, whereas in this case, the nodular feature observed was identified as a Cr-Mn rich oxide phase.

Figure 114 SEM micrographs and EDS map profiles of the cross-sectional oxide morphology of the samples oxidised at 750°C for (a) 1,000 (b) 3,000 hours of oxidation on the ground surface of 347HFG substrate
The earlier preposition relating the Nb second phase particles with the formation of the Fe rich nodular growths was further confirmed from the Nb EDS map. The Nb particles observed in the substrate and adjacent to the original substrate surface, were oxidised to form porous Nb rich oxides allowing inward and outward transport of oxidant species.

7.8 DISCUSSION – 347HFG

7.8.1 Effect of the oxidising environment

From the scale thickness measurements, the samples oxidised in steam at 650°C and 700°C, Figure 99, exhibited oxide thickness above 20µm thick, whereas the samples oxidised in air at 650°C and 750°C averaged below 6µm thick in Figure 106. The observed oxide scale spallation resulted in the loss of the outer oxide layer, which together with the formation of the Fe and Cr rich oxide nodular growths, resulted in the scale thickness measurements exhibiting the large thickness variations with increasing exposure time and/or temperature. However, it was evident that steam oxidised samples exhibited thicker oxide scales compared to air oxidised samples, and as discussed in Section 7.4.1, several authors [66-69, 75, 128, 139] pointed out the effect of water vapour containing environments in accelerating the growth rate of various stainless steel alloys. Asteman et al. [75] showed how steam oxidising atmospheres affected the type of oxide scales formed, the growth morphology and the oxide compositional chemistry similar to the results of this study. From the observed oxide growth morphology of steam oxidised samples, the surface oxides were characterised by polyhedral shaped crystal growths were identified as the Fe rich and Cr rich oxide spinels, whereas the surface platelets were identified as Fe$_2$O$_3$ growth and the whisker-like growth profiles with the serrated faces observed at 700°C, Figure 101, was identified as Fe$_3$O$_4$. For the air oxidised samples, the surface oxides were characterised by the nodular growths and the nodular features that exhibited platelets were related to Cr$_2$O$_3$ formation in a matrix of multifaceted Cr-Mn rich spinel oxides, whereas those without the platelets were identified as Fe$_3$O$_4$ nodules. There were also additional whisker-like crystal growth with a rod-like profile for the samples oxidised at 750°C, these were identified as Si-O rich oxide phase.

For the steam oxidised samples exposed for shorter times, the surface oxides exhibited a uniform cover of Fe rich oxides. And with increasing exposure time, the development of growth stresses due to the differences in CTE between the oxide and the substrate as well as the stresses generated from the growth of different oxide phases [151] resulted in the observed oxide scale spallation. This exposes the underlying Cr rich oxides phases that act as the protective oxide scales from further oxidant species attack. For air oxidised samples at 650°C and 750°C, the surface oxides were primarily Cr rich phases and were significantly thinner compared to the steam oxidised samples. Given that the Fe and Ni EDS maps of the static air oxidised samples exhibited appreciably high concentrations on the surface confirms
the presence of thin surface oxides. The differences observed in the outer oxide layer composition and thickness agree with literature reports [22, 99] that austenitic stainless steels form protective outer Cr-O rich scales in air, whereas in water vapour containing environments, the formation of Fe rich oxide phases and less protective Cr rich spinels were reported.

For the inner oxide morphologies, these were significantly different for steam oxidised samples, Figure 103 and Figure 104, and air oxidised samples, Figure 113 and Figure 114. For the steam oxidised samples, they exhibited pronounced internal oxidation, such that Cr-Mn rich oxides phases were observed on the former austenite substrate grain boundaries, where they encircled the substrate grains. The Cr-Mn rich encircled grains were subsequently oxidised to form discrete Cr-Mn rich phases with the remainder of the grain forming an Fe-Ni rich matrix. Similar results were observed for E1250 steel as shown in Section 7.2.3 as was also reported by Hansson et al. [63, 64, 138, 146] with their studies on austenitic steel TP347HFG. For the air oxidised samples, the internal oxide morphology observed on steam oxidised samples was not observed, however, where the Fe and Cr rich nodular growths occurred, the internal oxides exhibited a closer resemblance to the internal oxides observed on steam oxidised samples. These nodular growths occurred in the vicinity of the Nb rich second phase particles in the substrate suggesting that the second phase particles had a significant influence on the formation of the oxide nodular growths during the initial oxide growth. The observed results were similar to those reported in Section 7.4.5 for E1250 austenitic stainless steel, which showed that Nb rich second phase particles underwent oxidation to form porous structures consisting of Fe-Nb rich oxide phases at the oxidant / substrate interface. The formation of the porous structures aided the inward ingress of oxidation species resulting in the formation of internal oxides within the substrate. For air oxidised samples, the surface oxides exhibited the presence of Nb rich phases within the nodular growths, and from the cross-sectional morphology, the Nb rich phases were also observed extending into the substrate where they also occurred as second phase particles. Thus, the internal oxides within the Cr and Fe rich nodular growths of air oxidised samples, and aided by the inward transport of oxidant species through the Nb rich porous phases, exhibited Cr rich oxide phase formation. For the steam oxidised samples, the presence of the Nb rich second phase particles within the substrate appeared to aid the formation of the Cr-Mn rich phase around them and wherever they occurred, these were observed as distinct particles in the inner oxides.

From the thermodynamic phase calculations, Figure 25, the phase prediction indicated that under equilibrium conditions, the oxide phase thermodynamically favoured to occur at the substrate/oxide interface was the Cr rich corundum phase. Furthermore, at this oxygen partial
pressure, the Nb rich second phase particles were also predicted to be stable with the additional Fe-Cr-O rich spinel phase. The prediction was similar to the experimentally observed steam oxidised samples, where discrete Nb rich second phase particles were observed within the internal oxides encircled in Cr rich oxide phases. Furthermore, the Cr rich corundum, Fe-Cr rich spinel phase, and Nb carbonitrides coexisted together at low oxygen partial pressures similar to conditions expected in steam oxidising environments. For air oxidised samples, the formation of the Cr rich phases as a surface oxide was attributed to the high concentration of Cr in the bulk alloy that preferentially diffuses to the surface as was shown in the Cr depletion profiles observed in the EDS maps, Figure 113.

The phase prediction also exhibited the presence of Si-O rich phase formation at low oxygen partial pressures. From the surface oxide, Si-O rich phase was observed as rod-like growths occurring where nodular growths were observed, Figure 110(b). The phase also occurred as a thin layer at the substrate/oxide interface, Figure 114(a), reinforcing the protective nature of the Cr rich oxide phases formed in air. The formation of the rod like Si-O rich phase could be attributed to the preferential diffusion of Si to the surface where it oxidises to form the Si rich oxide. Si concentration ~ 1wt.% in the bulk alloy of 347HFG was sufficiently high under low oxygen partial pressures to form the Si-O rich oxide phase. The formation of the nodular features allowed access to the inner Si rich phases existing as second phase particles and through their consumption and preferential diffusion to the substrate oxide interface resulted in the formation of the observed Si-O rich rod-like phases. For the steam oxidised samples, XRD analysis in Figure 102 showed that there was presence of Si rich oxide phase, whose peak was observed to increase with exposure time at 650°C and was present for all exposure times at 700°C. The Si rich areas were observed to occur discretely at the substrate/oxide interface for 347HFG and as illustrated from the analysis of the TEM thinfoil for E1250 steel substrate in Figure 76, where the Si-O rich phase occurred in a discontinuous manner at the interface of Cr-Mn rich oxide phase and the substrate.

### 7.8.2 Effect of surface grinding

Section 7.4.2 discussed the effect of surface modification through mechanical grinding on E1250 austenitic stainless steel substrate, where thin oxide scales were formed with the formation of Cr-Mn rich surface oxides as the protective oxides. The mechanism by which the surface affects the formation of the protective Cr-Mn rich oxide is through surface grain modification, which affects the dislocation density as well as causing the formation of a surface characterised by a fine grained profile. Several authors [10, 102, 108, 141, 152] have reported the effects of cold working and grain size on the oxidation resistance of various high Cr containing steels, all agreeing on improved oxidation resistance and this was attributed to the increase in the dislocation density, as well as the resultant outer fine grained morphology.
Nishikawa et al. [153] and Matsuo et al. [154] separately showed that fine grained 347HFG and 304H austenitic steels had far superior oxidation resistance compared to their coarse grained grades and that shot peening the steels further improved their oxidation resistance even when overheating of the tubes occurred. For austenitic stainless steels, the increase in short circuit diffusion paths had an effect on the diffusion coefficient of migrating species, which results in the rapid diffusion of Cr and Mn species to the surface for the formation of Cr-Mn rich oxide phases. For the 347HFG substrate with its high Cr concentration compared to E1250 resulted in the formation of predominantly Cr rich surface oxides. These oxides were also marginally thinner compared to those formed on E1250 steel substrate with increasing exposure conditions and this is associated with the formation of protective Cr rich oxide that impedes the outward diffusion of cations.

7.8.3 The role of key alloying elements Cr, Mn, Nb and Si in 347HFG

As discussed in Section 7.4.5, the main alloying elements found in austenitic stainless steels are Cr, Ni, Mo, Mn, Si and Nb all of which have either a direct and/or indirect effect on the oxidation behaviour of austenitic stainless steels. For the 347HFG steel substrate, the alloying elements observed to affect the oxide scale growth and chemistry were Cr, Mn, Si, and Nb. Cr has been shown to form Cr rich oxide layers that provide protection to the underlying substrate matrix from consumption by the oxidant species. In dry atmospheres, Cr has been reported to preferentially form Cr$_2$O$_3$ as the protective oxide layer. The presence of 2wt.% Mn in the bulk alloy of 347HFG also had an influence on the oxide scales formed, which as reported by Stott et al. [97] jointly with Cr formed Cr-Mn rich spinels in air.

The presence of Nb in the bulk alloy had an influence on the oxidation kinetics of austenitic stainless steel. The work of Ramanathan et al. [149] showed the effect of Nb increase on the oxidation of an austenitic steels oxidised between 800-900°C, where they showed that there was a decreasing trend for mass gain measurement with increasing Nb content. They also proposed that Nb presence in the alloy facilitated the formation of Cr$_2$O$_3$ oxide phases. Brady et al. [92] also concluded that increasing the Nb content resulted in improved oxidation resistance for steels oxidised from 650-850°C in air - 10% H$_2$O. They proposed that the Nb addition had an effect on increasing Al reservoirs for the alumina layer formation, which offered a high oxidation resistance to the underlying substrate. The above mentioned literature agreed with the results of this study, which suggested Nb had an effect on the oxide scales formed such that within the subsurface oxide, the regions adjacent to the Nb rich carbonitrides exhibited Cr rich oxide formation. The Cr rich phase completely encircled and protected the particles from further oxidation. For air oxidised samples and particularly on the 600 grit ground surface, the observed discrete Nb rich areas underwent oxidation to form Nb rich oxide.
phases, which from their porous structures, acted as a starting points for internal oxidation and the subsequent growth of the observed Fe and Cr rich oxide nodular growths.

The presence of Si within the bulk alloy of up to 1wt.% was also observed to have an effect on the oxide scale formed. For steam oxidised samples, Si rich phases were observed at the substrate/inner oxide interface but these occurred as discontinuous layers. For air oxidised samples and particularly for the samples oxidised at 750°C, continuous and thin Si rich oxide phase was observed at the oxide/substrate interface, with the outer layer being Cr rich oxide phase. Si rich oxides were also observed in the vicinity of the Fe and Cr rich nodular growths where they occurred as rod-like growth features. Bamba et al. [155] in their work on the effect of Si content (0, 0.5 and 1wt.%) on a 15Cr ferritic stainless steel oxidised at 850°C and 950°C argued that the formation of a discontinuous Si-O rich phase at, and beneath, the metal/chromia scale interface resulted in slower oxidation kinetics as opposed to the presence of a continuous Si-O rich layer. They proposed that the discontinuous Si rich oxide phase observed in the 0.5wt.% Si containing steel, inhibited the counter flow of the Cr vacancies to the bulk of the alloy by acting as sinks, and thus reducing the outward diffusion of Cr cations for the continued growth of the Cr rich oxides. On the other hand, Mikelsen et al. [89] work on the effect of small additions of Si on an Fe-Cr rich alloy proposed that where discontinuous Si-O rich phase occurred at the substrate/oxide interface, it reduced the overall cross-sectional area for the outward Cr diffusion, and this had the effect of slowing the oxidation kinetics of Si containing steels. They also concluded that the formation of a continuous Si-O rich phase was desirable in slowing the kinetics of oxidation, contrary to the work of Bamba et al. [155], however this effect depended on the Si concentration in the alloy. Furthermore, Wright and Doley’s [10] review reinforced Mikelsen et al. [89] observation on the positive effect of Si addition to steels high temperature oxidation. Therefore, from the observed oxidation results, the presence of Si in 347HFG resulted in the formation of Si rich oxide phases at the substrate/oxide interface, which acted as a barrier for the outward and inward diffusion of the oxidant species.

In summary, the austenitic stainless steel 347HFG exhibited good oxidation resistance compared to E1250 steel from their respective oxide scale thickness measurements. This has been attributed to its fine grained microstructure in addition to the high Cr concentration in the bulk of the alloy. The high concentration of Si in 347HFG also had a positive effect through the formation of Si-rich oxides at the scale/substrate interface, which impeded the outwardly diffusion cations for further oxide growth. There was also a good correlation between breakaway oxidation and the subsequent formation of the Fe-rich oxide nodules and the presence of Nb carbonitrides in the substrate.
7.9 PROPOSED OXIDE GROWTH MECHANISMS ON AUSTENITIC STAINLESS STEEL

7.9.1 Oxidation in Steam

From the substrate and microstructural analysis of the oxide scales formed on E1250 and 347HFG steel substrates and their corresponding compositional analysis, the oxide growth behaviour suggests the main transport processes occurring across the scale were the outward cationic and the inward oxidant species transport [10]. The proposed growth mechanisms of the oxide scale observed in steam conditions are described as follows, Figure 115:

1) The adsorption and subsequent dissociation of steam (H$_2$O) into H$_2$, 1/2O$_2$, OH$^-$ and H$^+$ species occurs at the metal/steam interface, in addition to the presence of molecular (H$_2$O) available for oxide nucleation, Figure 115 (a). The available hydrogen is desorbed but some will be dissolved into the oxide and has been reported to diffuse through the substrate.

2) Nucleation and growth of the outer oxide occurs at the metal/steam interface by OH$^-$ and H$_2$O ions reacting with fast diffusing Cr and Mn ions along substrate grain boundaries to form a thin protective (Cr-Mn-O) phase.

3) For breakaway oxidation and the subsequent nodular growths, two mechanisms are proposed as follows:
   a. Though a protective (Cr-Mn-O) phase was formed, the presence of growth stresses attributed to the mismatch in coefficient of thermal expansion between the substrate and the oxides, resulted in crack development in the (Cr-Mn-O) phase providing additional pathways for steam ingress. The presence of permeating hydrogen from the dissociation of steam is dissolved as protons in the metal oxide, which further aids the inward transport of OH$^-$ species where the scale is intact enabling the attack of the underlying substrate matrix. Where cracks occurred, breakaway oxidation would be observed with the resultant formation of nodular growths, as shown Figure 115 (b).
   b. For both steels, the presence of the Nb rich carbonitrides observed on the substrate surface and extending approximately 1-2µm into the substrate were responsible for breakaway oxidation occurrence. These Nb carbonitrides were oxidised to form porous Nb rich oxides that allowed the inward ingress of steam for the outward nodular and internal oxide formation.

4) The oxide nodular features had an outer scale layer identified as Fe-Mn-O rich for E1250 whereas for 347HFG had Cr rich Fe-O phase with traces Mn. For E1250 steel, the Fe-Mn-O phase formed by the outward diffusion of Fe and Mn ions reacting with OH species as

$$\text{(Fe}^{2+} 2\text{Fe}^{3+}) + (\text{Mn}^{2+} 2\text{Mn}^{3+}) + 4\text{OH}^- \leftrightarrow (\text{Fe, Mn})_3\text{O}_4 + 4\text{H}^+.$$
5) Due to the formation of the thin outer Cr-Mn-O rich spinel phase, substrate matrix depletion occurs along prior substrate grain boundaries, and on the outermost substrate grains. However, these outermost substrate grains are still rich in Cr, Mn, Fe and Ni in solid solution, and with the depleted grain boundaries providing easy pathways for the oxidant species. The remaining Cr and Mn diffuses towards the substrate’s outermost grain peripheries, which are adjacent to the already depleted grain boundaries with a high concentration of oxidant species. This results in internal oxide formation encircling grains as well as the formation of the discrete Cr-Mn-O rich phase within the grains as shown in Figure 115 (c) and schematically illustrated in Figure 116.

6) For E1250 steel substrate, the presence of Mo along grain boundaries, which is attributed to the consumption of the Mo rich second phase particles, results in the formation of the Mo volatile species with steam. These volatile species cause the formation of the observed microcracks within the Cr-Mn-O rich phase along grain boundaries, which also provides additional pathways for the inward transport of oxidant species, Figure 115 (d). For 347HFG, no cracks were observed in the Cr-Mn-O phase.

Figure 115 schematic illustrations of the proposed oxide growth mechanisms of the scales formed on austenitic stainless steel substrates in water vapour containing environments (E1250 and 347HFG)
7) These microcracks observed on E1250 steel substrate are also proposed to occur due to the cationic grain depletion profiles occurring in the vicinity of substrate grain boundaries. The proposed mechanism is such that with increasing exposure time, the grains adjacent to the depleted boundaries are further oxidised by the outward diffusion of Cr and Mn ions to the grain peripheries where they form protective shells of Cr-Mn-O rich phase as shown in Figure 116. Since the grain boundaries were already depleted in Cr and Mn during the initial oxide formation as well as acting as sinks for vacancies and microvoids formation, the defect laden depleted grain boundaries provide easier paths for the microcrack development.

8) With increasing exposure time, the outwardly growing oxide nodules coalesce and grow to form outer Fe rich oxide layers, Figure 115 (d). A thin hematite layer also occurs as the outermost surface oxide and this is proposed to occur during cooling, as evidenced by its uneven formation on the surface. This occurs by the conversion of magnetite to hematite as $2\text{Fe}_3\text{O}_4 + \text{OH}^- \rightarrow 3\text{Fe}_2\text{O}_3 + \text{H}^+$. 

9) Voids/pores observed within the inner and outer oxide layers were attributed to vacancies created during the outward cationic transport. For the outer layer, larger voids were concentrated closer to the interface of the inner and outer oxide layers. Within the internal oxidised zone, the voids were observed on oxidised grains consisting of Fe-Ni rich matrix and the discrete Cr-Mn rich oxide phase and at the inner oxide/substrate interface. An additional cause of void formation and enlargement is the dissociation of Fe rich oxides as $\text{Fe}_3\text{O}_4 \leftrightarrow 2\text{Fe}^{3+} + \text{Fe}^{2+} + 4\text{O}^2-$, which further supplies the Fe cations for the outward oxide growth.

10) The mismatch in coefficient of thermal expansion of the oxide scales formed on E1250 and 347HFG substrates aids the preferential development of cracks at the interface of the inner to outer oxide layers. This results in oxide scale spallation and hence the loss of the outer Fe-rich oxide leaving Cr-Mn-O rich oxide phase as the outermost phase and an underlying Fe-Ni rich matrix with discrete Cr-Mn-O rich phases as the rate controlling oxide scale, Figure 115 (e).
7.9.2 Oxidation in air

The proposed growth mechanism of the scale formed in air is as follows, Figure 117:

1) The adsorption and subsequent dissociation of (O$_2$) into ionic species (O$^{2-}$) occurs at the metal/gas interface, in addition to the presence of molecular (O$_2$) available for oxide nucleation ($\frac{1}{2}$O$_2$ + 2(e) $\leftrightarrow$ (O$^{2-}$).

2) Nucleation and growth of the outer oxide occurs at the metal/gas interface by the adsorbed oxidant reacting with Cr ions along substrate grain boundaries to form (Cr-O) rich phase for 347HFG. For E1250 steel substrate, the high concentration of Mn in the substrate and its apparent lower crystal field packing energy in comparison to either Fe or Cr, results in its rapid diffusion to the surface to preferentially form the Cr-Mn rich spinel. (Cr$^{3+}$) + (Mn$^{2+}$) +4O$^{2-}$ $\leftrightarrow$ (Cr,Mn)$_3$O$_4$.

3) Due to the oxide growth stresses, cracks develop in the (Cr-Mn-O) or in (Cr-O) rich phases providing additional pathways for O$_2$ ingress. This exposes the underlying substrate matrix to further attack resulting in the breakaway oxidation, as evidenced by the oxide nodular growths.

4) The oxide nodular features have an outer scale layer identified as Fe-Mn-O rich, which forms by the outward diffusion of Fe and Mn ions reacting with O$^{2-}$ ions (Fe$^{2+}$ 2Fe$^{3+}$) + (Mn$^{2+}$ 2Mn$^{3+}$) +4O$^{2-}$ $\leftrightarrow$ (Fe, Mn)$_3$O$_4$.

Figure 117 schematic illustrations of the proposed oxide growth mechanisms of the scale formed on austenitic stainless steel E1250 and 347HFG substrate in dry air environment
5) Due to the formation of the outer Cr-Mn-O rich spinel phase, substrate matrix depletion occurs on prior substrate grain boundaries as well as within the outermost substrate grains. This creates a vacancy laden region that results in the formation of microvoids. The voids provide additional pathways for the inward transport of oxygen and thus create a high PO$_2$ condition within the inner oxide. However, the partial pressure is not sufficient for the rapid growth of oxides and will therefore favour the formation of the thermodynamically favoured Cr rich oxides.

6) The Cr-Mn depleted zone becomes a zone with a high concentration of Fe and Ni in addition to microvoids.

7) With increasing exposure time, the oxide nodules coalesce and grow to form a uniform cover Fe rich oxide layer. A thin and even hematite layer also occurs as the outer most oxide but exhibits a high concentration of Mn (Fe$_3$O$_4$ + Mn$^{2+}$ + O$^{2-}$ → 3(Fe,Mn)$_2$O$_3$).
8 CONCLUSIONS

An in-depth study into the oxidation behaviour of ferritic (T22, T23, P91 and P92) and austenitic stainless steels (347HFG and E1250) has been carried out. The alloy materials were oxidised in steam and air conditions at temperatures ranging between 510°C to 750°C and exposure times ranging between 500 to 5,000 hours.

8.1 STEAM OXIDISED MATERIALS

- Oxidation of the ferritic steels (T22, T23, T/P91 and T/P92) in steam environments produced multilayered oxide scales with the outer layer exhibiting a duplex structure identified as Fe rich consisting of hematite and magnetite layers. The inner oxide layers consisted of spinel type Fe-Cr rich oxide phase whose composition depended on the Cr concentration levels in the bulk alloy. The scales formed also exhibited internal oxides, which occurred as discrete oxide particles within the substrate outermost regions adjacent to the substrate/oxide interface. The internal oxides also occurred on substrate grain boundaries.

- The inner oxide morphology for the 2.25Cr steels exhibited a lamellar layer formation, which was attributed to the transport mechanisms and microstructural stability. The periodicity or frequency of formation of the lamella layers was related to the substrate microstructural stability. The T23 steel with a more stable microstructure at elevated temperature exhibited more microlayers compared to the T22 steel substrate. Similarly, the oxide scales formed on 9Cr steels exhibited the laminate effect, however, this was more pronounced on the P92 steel substrate compared to the P91 steel substrate which exhibited faint microlayers. The T/P91 steel substrate was less stable exhibiting martensitic transformation to a ferrite microstructure with fewer short-circuit diffusion paths. These observations reaffirmed the importance of substrate microstructural stability in the formation of the laminate layer.

- The oxide scale thickness of ferritic steels showed that for the 2.25Cr steels, there was no significant difference in the scale thickness measurement for the T22 and T23 steels. However, for the martensitic 9Cr steels, the T/P91 steel substrate exhibited thinner scales compared to T/P92 steel substrate, which was attributed to the microstructural stability of the martensitic microstructure of the T/P92 substrate with increasing time and/or temperature. The substrate matrix stability had a direct effect on the effective diffusion coefficient of the substrate, with T/P91 steel exhibiting an apparent decrease in the density of short circuit diffusion paths due to the microstructural changes and hence inhibiting faster transport of oxidant species from and into the substrate.
Conclusions

- Oxidation of the austenitic stainless (347HFG and E1250) steels produced oxide scales with duplex layered structures, with the outer scale layers identified as Fe rich oxide, however, the presence of high Mn concentrations in these steels resulted in Fe-Mn rich phases with varying stoichiometries. For the inner oxide layer, they exhibited a mixed oxide profile consisting of Cr-Mn rich oxide phases, which preferentially occurred on former substrate grain boundaries and was also observed discretely for short exposure times as a protective surface oxide. With prolonged exposure times, the surface was mainly characterised by the Fe rich oxide phases with appreciable Mn content.

- Furthermore, the inner oxide layers formed on the austenitic stainless steels exhibited the presence of Fe-Ni rich matrix, which occurred as a result of the Cr-Mn depletion from the substrate grains to form the protective Cr-Mn rich oxide phase along substrate grain boundaries. The internal formation of the Cr-Mn oxide phase along grain boundaries resulted in the encircling of the Cr-Mn depleted substrate grains leaving them rich in Fe and Ni. The protective nature of the Cr-Mn rich oxide phase subsequently affected the transport phenomena into the depleted grains by inhibiting the inward diffusion of oxidant species. However, discrete particles of Cr-Mn rich oxide phase was formed within the Fe-Ni rich grains suggesting that diffusion through the Cr-Mn rich occurred although this was to a lesser extent. For 347HFG, the Fe-Ni rich matrix was more pronounced and this was attributed to the high Cr content in the bulk of the alloy which preferentially formed protective Cr rich oxides (with high Cr concentration) around grains in comparison to the E1250 steel substrate.

- For both ferritic and austenitic stainless steels, voids and pores were observed at both the outer and inner oxide layers and these were proposed to occur due to the outward cationic species transport with its associated vacancy creation. The created vacancies coalesce with increasing exposure time and temperature into microvoids and also grew to form larger voids observed in the oxides. There are also additional effects, such as oxide dissociation where lower state oxides are readily dissociated to provide anionic species for internal oxide phase formation or the inward ingress of oxidant species into the existing voids creating a high oxygen partial pressure for subsequent oxide growth. The latter effect was more pronounced on ferritic steels resulting in magnetite conversion to hematite within voids and cracks in the outer oxide layers.

- The oxide scale thickness of austenitic stainless steels exhibited a parabolic like growth profile for E1250 steel as shown by a diminishing oxide growth from 1,000 to 3,000 hours, however, for the 347HFG steel, under the same conditions, showed pronounced oxide spallation with the subsequent loss of the outer scale layers. The results did not provide a clear growth profile though literature reports that parabolic growth profiles are to be expected for this steel. The main differences between the two
steels was the uniformity of the internal oxide layer, whereas E1250 steel substrate exhibited a more uniform inner oxide layer with a distinct substrate/oxide interface, the 347HFG steel, exhibited a non-uniform inner layer with internal oxides ranging a few microns to ~ 80µm into the substrate.

- The study also showed a relation between the observed oxide scales from the outer to inner oxide scale layers and the thermodynamically predicted oxide phases using Thermocalc for both ferritic and austenitic stainless steels. Furthermore, the observed substrate microstructural changes and the presence of second phase particles within the substrate and inner oxide layers, all of which had an effect on the observed morphology, related to the predicted phases as a function of oxygen partial pressure.

- The study has also proposed oxide growth mechanisms for the growth of the scales formed on ferritic and austenitic stainless steels, which is consistent with the results of this study.

### 8.2 AIR OXIDISED MATERIALS

For the air oxidised samples, these were carried out in static laboratory air at 650°C and 750°C for times ranging from 500 to 5,000 hours of oxidation. The samples investigated were ferritic steels (T23 and T/P92) and austenitic stainless steels (E1250 and 347HFG). For the austenitic stainless steels the samples were also categorized based on whether they were oxidised on the as received surfaces or on the mechanically ground surfaces.

- The surface oxides formed on the T23 and P92 exhibited porous surface oxides that were intact and exhibited no spallation despite the outer oxide layers exhibiting cracks. The surface oxides were mainly Fe-O rich for the studied ferritic steels. For the austenitic steels, the surface oxides were characterised by nodular features identified as either Fe-rich, Nb-rich, Cr-rich and Si rich oxide phases. Oxide spallation effects were prevalent on the austenitic stainless steels was also com

- Oxidation of the ferritic steels (T23 and P92) in air also produced multilayered oxide scales with the outer layer exhibiting a duplex structure similar to that observed in steam environments. The outer oxide layers were Fe rich oxide phases whereas the inner oxide layers consisted of spinel type Fe-Cr rich oxide phases.

- The inner oxide morphology for the ferritic steels also exhibited a laminate layer but this was less pronounced compared to that observed in steam environments over the same exposure time. This was attributed to the accelerated growth in water vapour containing environments.

- The oxide scale thickness analysis of ferritic steels exhibit thin oxide scale formation in comparison to steam oxidised samples. For both the T23 and T/P92 steels oxidised at 650°C for exposure of up to 3,000 hours, they exhibited parabolic like growth profiles,
Conclusions

whereas oxidation at 750°C exhibited an approximately linear profile and thick oxide scale formation.

- Austenitic stainless steels exhibited varying oxide scale thickness depending on whether the substrate surface oxidised was on the as received surface or on the mechanically ground surface. The results showed that the as received surface exhibited thicker oxide scales compared to the oxide scales formed on the mechanically ground surface.

- The oxide scale thickness of austenitic stainless steels E1250 exhibited minimal change with increasing exposure time on the as received surfaces whereas, on the ground surfaces for the exposure times studied, these showed an increase. However, the overall scale thickness measurements observed on the as received surfaces were significantly higher than on the ground surfaces. For the 347HFG steel substrate, under the same conditions of oxidation, showed thinner scales, which was attributed to the high Cr concentration levels in the bulk of the alloy promoting the formation of Cr rich protective oxide scales. The results did not provide a clear growth profile though literature reports that parabolic growth profiles are to be expected for austenitic stainless steels.

- Furthermore, cold working through the mechanical grinding of the substrate surfaces was shown to affect the surface oxide morphology and the oxide chemistry. The results showed that thin Cr-Mn-O rich oxide phases were formed on the ground surface compared to the thick Fe-Mn-O rich oxide phases observed on the as-received surface. There was no oxide scale spallation on the ground surface and where it occurred, it was to a lesser extent compared to that observed on the as-received surface. The formation of thin Cr-Mn-O rich oxide scales on the ground surface was attributed to the high density of diffusion paths in the outermost substrate grains as a result of mechanical grinding that is also reported to form a fine grained morphology. A finer grained morphology presents a substrate with a higher density of grain boundaries which results in higher diffusion rates of cations (Cr,Mn) responsible for the formation of protective oxide phases.

- Oxidation of the austenitic stainless steels (347HFG and E1250) produced oxide scales that exhibited a single to duplex layered structure. For E1250, the oxide grown on the as received surfaces exhibited a duplex structure consisting of an outer Fe-Mn rich oxide layer and inner Cr-Mn rich oxide layer. On the ground surface, the substrate exhibited a single outer layer consisting of Cr-Mn rich oxide phase, which acted as the outermost protective oxide layer. Furthermore, there were nodular features which were identified as Fe rich oxide nodules with considerable Mn and Nb concentrations. The presence of Nb on the surface was related to the Nb carbonitrides observed and
predicted as second phase particles in the bulk of the substrate. Where these particles occurred on the surface, they were oxidised to form porous Nb rich oxide phases, which this study showed contributed to the breakaway oxidation occurrence and hence the formation of the nodular growths on the surface.

- For the internal oxides of austenitic stainless steels, these were not prevalent on air oxidised samples for both E1250 and 347HFG. However, these occurred discretely and predominantly in the vicinity of oxidised Nb rich second phase particles whose porosity this study showed aided the inward transport of oxidant species into the substrate.

- The study also showed the behaviour of alloying elements added in small concentrations on the observed oxide features such as the formation of V-Mn rich crystals in E1250, Si rich oxide formation at the substrate/scale interface, whereas further work need to be carried out on Si rich whiskers observed on 347HFG.
9 FURTHER WORK

This thesis presented the effect of temperature, time, oxidising environments and alloying elements on the growth, kinetics and microstructural development of the oxide scales formed on ferritic (T22, T23, T/P91 and T/P92) and austenitic stainless steels (E1250 and 347HFG). However, there were areas of this research where further work would support the already presented work. The main suggestions are outlined as follows:

- Further work on cyclic or non-isothermal oxidation experiments of the alloys investigated to simulate scenarios expected in power plants, such as the daily start / stop (DSS) attributed to the electricity load demands, as these conditions do affect the mechanical properties of the resultant oxide scale layers.
- Further work on the effect of cold working / mechanical grinding by using different roughness levels as determined by the SiC grinding paper at 400, 600 and 1200 grit levels, in addition to polishing the substrate surfaces to 6µm and 1µm levels.
- Further work to be carried out under steam oxidising environments to evaluate the role of surface grinding on the resultant oxide scale morphology and chemistry to corroborate the air oxidised results.
- Transmission electron microscopy (TEM) work of the outermost substrate grains of the alloys investigated, to demonstrate the changes in the dislocation density and grain size and its effect on the observed surface oxides and chemistry distribution from the substrate into the oxide.
- Further work on quantifying the effect of mechanical grinding by the measurements of surface roughness and its relation to the mechanical properties of the scales formed, particularly scale adhesion and spallation.
- Electron backscatter diffraction (EBSD) work on the microtexture of the grown oxide scales since initial studies showed a good correlation between textural changes and the cross-sectional oxide growth morphology.
- The study showed a good correlation between the thermodynamically predicted substrate and oxide phase with the experimentally observed oxide phases. Further work should be carried out to relate the calculated oxygen partial pressures with the actual depths at which different oxide phases are formed from the original substrate surface / oxidant gas interface for both inward and outward growing oxide scales.
- Further work on thermodynamic modelling plotted elemental compositional profiles starting from the substrate into the predicted oxide phases with increasing oxygen partial pressure. Quantification work using energy dispersive spectroscopy (EDS) could be carried out to corroborate the thermodynamics predictions.
• A further study on the behaviour of alloying elements present in small concentrations on the resultant surface oxide features during the early stages of high temperature oxidation, such as Si rich whisker formation on 347HFG steel.

• For oxide growth kinetics studies, further work on weight gain measurements would provide a clear picture for the austenitic stainless steels considering the effect of oxide scale spallation and the associated loss of outer scale layers.
10 REFERENCES


[115] N. Komai, F. Masuyama, M. Igarashi, 10-year experience with T23(2.25Cr-1.6W) and T122(12Cr-0.4Mo-2W) in a power boiler, J Press Vess-T Asme, 127 (2005) 190-196.


