High Temperature Corrosion on Biodust Firing

PhD Thesis

Sunday Chukwudi Okoro
June 2016
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By

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June 2016
Cover photo: Plan view SEM image of Fe-rich oxides formed on TP 347H FG after exposure to conditions mimicking biomass firing.
Colour enhancement courtesy of Art of Akin
To my beloved parents, for your selfless efforts

To the girls in my life, Miriam & Chiamaka
Preface

This PhD thesis is submitted in partial fulfilment of the requirements for the award of a PhD degree at the Technical University of Denmark (DTU). The work presented in the thesis was conducted within the period, March 2013 to June 2016, collaboratively at, the Department of Mechanical Engineering – Section of Materials and Surface Engineering, and the Department of Chemical and Biochemical Engineering – The Centre for Combustion and Harmful Emission Control. The work was carried out under the supervision of Associate Professor Karen Pantleon, Associate Professor Flemming J. Frandsen and Senior Researcher Melanie Montgomery.

This work was part of the strategic research centre for Power Generation from Renewable Energy (GREEN), under work package 5, tasked with the development and testing of advanced corrosion resistant superheater materials. The centre was financed by the Danish Council for Strategic Research.

Kongens Lyngby, June 2016

Sunday Chukwudi Okoro
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First, I wish to express my profound gratitude to my supervisor, Associate Professor Karen Pantleon. Her support, mentorship and dogged passion for scientific excellence were priceless in the course of this project. It has been a privilege to benefit from these.

It has also been a privilege to be co-supervised by Associate Professor Flemming J. Frandsen and Dr. Melanie Montgomery, who both granted me access to their encyclopaedic knowledge on biomass-related operational challenges in power plants. I am deeply thankful for the fruitful discussions and constructive criticisms in the course of this project.

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The vast amount of work presented in this thesis would also not have been possible if not for the support and encouragement from my family. Heartfelt thanks to my parents and siblings for their words of encouragement and support. To my loving wife, Miriam, words will fail me if I attempt to express my appreciation for your support, love and understanding over these years. I will forever remain indebted to you. To my darling daughter, Chiamaka, thank you for the wonderful and energetic relaxation moments you provided after work.

Lastly, and above all, I am grateful to God for His grace which has sustained me during this project.
Abstract

The high content of alkali metals and chlorine in biomass gives rise to fouling/slagging and corrosion of heat exchange components, such as superheaters, in biomass fired power plants. Increasing the lifetime of these components, and in addition, preventing unwarranted plant shutdowns due to their failure, requires understanding of the complex corrosion mechanisms, as well as development of materials that are resistant to corrosion under biomass firing conditions, thereby motivating the current work.

To understand the mechanisms of corrosion attack, comprehensive analysis of corrosion products was necessary. In the present work, two complementary methodologies based on analysis of cross sections and plan views were applied to achieve comprehensive characterization of corrosion products. The suitability of these methods for both laboratory scale and full scale corrosion investigations was demonstrated by the combined use of complementary information from microscopy, energy dispersive X-ray spectroscopy and various X-ray diffraction characterization techniques.

In light of the wide variation in operating conditions in biomass fired power plants, systematic and well-controlled, but realistic laboratory scale exposures were carried out to understand the effect of process parameters such as gas phase chemistry, time and temperature variations, on the corrosion process. By conducting corrosion exposures under: oxidizing, oxidizing-chlorinating, oxidizing-sulphidizing and oxidizing-chlorinating-sulphidizing gas mixtures, it was possible to observe the contributions of chlorination, sulphation and sulphidation on the complex corrosion mechanisms. Comparative exposure of KCl-coated and KCl-free samples under each of the gas atmospheres revealed that the corrosion attack due to the presence of a deposit overrules the effect of the gas phase chemistry. Further, using the oxidizing-chlorinating-sulphidizing gas mixture corresponding to straw-firing conditions, the evolution of corrosion with time and temperature variation was studied. Corrosion attack does not decrease with time after longer exposures under isothermal conditions and is accelerated once the material encounters a higher temperature.

For the investigated austenitic stainless steels, FeCrAl alloys and Ni-based superalloy, the formation of a protective oxide layer that suppressed corrosion attack was not observed. However, it was established that among the alloying elements present in these alloys, Ni exhibits a relatively greater resistance to corrosion attack. Surface modification approaches with the aim to form resistant oxides or coatings on superheater surfaces were evaluated. This included preoxidation to obtain Al₂O₃ and Ti-Cr-rich oxides, as well as formation of SiOₓ coating, Ni electroplating and NiAl coatings on commercial alloys. For most of the modified surfaces, in particular α-Al₂O₃ obtained by preoxidation, poor mechanical integrity of the oxide layer nullifies its otherwise excellent chemical integrity towards corrosion attack. Nonetheless, corrosion attack on most of the modified surfaces was substantially lower than attack on the virgin alloys. Thus, with further optimization, these approaches may provide alternative corrosion resistant materials for application in biomass fired power plants.
Resumé


For at forstå mekanismerne i korrosion, har en omfattende og detaljeret analyse af korrosionsprodukter været nødvendig. I dette arbejde, er to komplementære metoder, baseret på analyser af hhv. gennemskärne og plane flader blev anvendt, for at opnå en så omfattende karakterisering af korrosionsproduktene som muligt. Egnet heden af disse metoder til både laboratorie- og fuldskala korrosionsundersøgelser er blevet grundigt testet og dokumenteret, gennem en kombineret anvendelse af supplerende oplysninger fra mikroskopi, energi dispersiv røntgen spektroskopi, og forskellige røntgendiffraction karakteriseringsteknikker.


På ingen af de undersøgte austenitisk ståltyper, FeCrAl-legeringer og Ni-superlegeringen, blev der observeret et beskyttende oxidlag, som normalt undertrykker korrosion. Det blev imidlertid konstateret, at blandt de legeringselementer, som er tilstede i disse legeringer, udviser Ni en relativt større modstandsdygtighed, overfor korrosion. Overflademodifikation med henblik på at danne resisterent oxide eller belægninger på overfladen af overheder, er også blevet evalueret. Dette omfattede foroxidering, mhp. dannelse af Al2O3 og Ti-Cr-rique oxider, samt dannelsen af en SiOx coating, Ni-galvaniserings og Nial belægninger, på kommercielle legeringer. For de fleste af de modificerede overflader, især α-Al2O3 opnået ved preoxidation, ophæver en dårlig mekanisk integritet af oxidlaget en ellers udmærket kemiske integritet, i relation til korrosionsangreb. Ikke desto mindre, var korrosionsangreb på de fleste af de modificerede overflader, væsentligt lavere end angreb på ikke foroxiderede legeringer. Således må det forventes at disse teknikker, med yderligere modificering, kan give alternative korrosionsbestandige materialer til anvendelse i biomassefyrede kraftværker.
List of Publications

Peer reviewed publications included in the thesis


Peer reviewed publications not included in the thesis


Non-peer reviewed publications not included in the thesis


# List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AD XRD</td>
<td>Angular dispersive X-ray diffraction</td>
</tr>
<tr>
<td>AMV 1</td>
<td>Amager power station, unit 1</td>
</tr>
<tr>
<td>BESSY</td>
<td>Berlin synchrotron radiation facility (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung)</td>
</tr>
<tr>
<td>BSE</td>
<td>Backscatter electron</td>
</tr>
<tr>
<td>CG</td>
<td>Coarse grain</td>
</tr>
<tr>
<td>cs</td>
<td>Cross section</td>
</tr>
<tr>
<td>ED XRD</td>
<td>Energy dispersive X-ray diffraction</td>
</tr>
<tr>
<td>EDDI</td>
<td>Energy dispersive diffraction beamline at BESSY</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>ESEM FEG</td>
<td>Environmental scanning electron microscope with a Field emission gun</td>
</tr>
<tr>
<td>FG</td>
<td>Fine grain</td>
</tr>
<tr>
<td>LOM</td>
<td>Light optical microscopy</td>
</tr>
<tr>
<td>pv</td>
<td>Plan view</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electrons</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
<tr>
<td>ZAF</td>
<td>Matrix corrections based on atomic number (Z), X-ray absorption (A) and X-ray fluorescence (F)</td>
</tr>
<tr>
<td>$\Delta G^0$</td>
<td>Standard Gibbs free energy change for a reaction</td>
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</table>
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Chapter 1 – Introduction

1.1 Motivation for energy production from biomass

Global warming is a universally recognized threat to the earth’s climatic system. It affects geological, ecological and biological systems, consequently leading to harsh weather conditions, rising sea levels, glacier retreat, spread of infectious diseases, food insecurity, to name a few [1,2]. According to the fifth assessment report by the Intergovernmental Panel on Climatic Change, the rising emission of greenhouse gases (CO$_2$, CH$_4$, N$_2$O, F-gases, etc.) from anthropogenic activities is probably responsible for the global warming experienced since the mid-20th century [3] (although other reports suggest that this dates back to the 16th century [4]). As shown in Figure 1, anthropogenic activities such as burning of fossil fuel, cement production and flaring largely accounts for the increase in CO$_2$ emission recorded over the years. In particular, the combined CO$_2$ emission flux from combustion of gaseous (natural gas), liquid (gasoline, liquid oil) and solid (coal) fossil fuels accounts for about 90% of the total global CO$_2$ emission from fossil fuels and industrial processes [5].

![Figure 1. Global CO$_2$ emissions from anthropogenic activities [3].](image)

In line with international energy treaties that have advocated the use of renewable energy sources [6], the Danish government in recent years, has increased the share of biomass in its energy production (Figure 2a). Biomass utilized for energy production in Denmark is mainly straw (herbaceous biomass), waste wood (contaminated biomass) and woody biomass (Figure 2b).

The combustion of biomass for energy production is particularly encouraging from a CO$_2$ emission standpoint because the emitted CO$_2$ can be sequestered via photosynthesis in a shorter period of time ($\sim$10$^2$-10$^3$ years), relative to fossil fuels ($\sim$10$^6$-10$^7$ years), such as coal [7,8]. Furthermore, the combined production of heat and power (CHP) from biomass in small and industrial CHP plants can compensate the fluctuating energy production from wind. Other factors such as, the sustainability of fossil fuels in
the long term and the need for liberalization of the energy market also motivate and drive the use of biomass for energy production.

Figure 2. Trends in Danish energy production from renewable sources. Data sourced from the Danish Energy Agency [9].

1.2 Biomass composition and challenges resulting from its combustion in power plants

In solid fuels such as biomass, inorganic elements are typically associated either as minerals, organically bound or as water soluble simple inorganic salts [8]. Na, K, Cl and S are usually associated as water soluble salts while organically associated elements include Ca, Mg, K, S, P and Na. The elements Si, Al, Fe, Ca, Mg, Na, K and S can be associated as minerals [8].

The composition (Table 1) and combustion properties of biomass differ essentially from that of coal. Consequently, operational challenges such as slagging/fouling, corrosion of heat exchange components, and poisoning of catalysts in flue gas cleaning systems are to be expected when biomass is used as fuel in power plants. This is mainly due to the high fraction of alkali/alkaline earth metals and Cl in biomass, relative to coal [10–12]. During combustion, ash forming elements such as K, Cl and S in biomass are released into the vapour phase [13–19]. Subsequent complex physical and chemical processes result in aerosol formation, adhesion of ash species and build-up of slagging/fouling and corrosive deposits on heat transfer surfaces [8,20–26].

The gas phase K-S-Cl chemistry occurring during biomass combustion often gives rise to the formation of slagging/fouling deposits which are enriched in KCl and K2SO4 (Figure 3). In addition, such chemistry generates a flue gas rich in corrosive species such as HCl and SO2 [8,23,24,27,28]. These (solid and gaseous) species incite fast corrosion of superheaters through a temperature dependent mechanism, and consequently, limit the maximum steam temperature at which biomass fired power plants can be operated, compared to power plants fired with fossil fuels [29–31]. The dependence of plant efficiencies on steam temperatures therefore implies that biomass fired plants operate at low electrical efficiencies to
avoid catastrophic corrosion problems. Mechanisms causing high corrosion rates during biomass firing are discussed in chapter 2.

**Table 1.** Comparison of typical composition of coal with biomass (wood and straw) [11].

<table>
<thead>
<tr>
<th>Moisture content and chemical compositiona (wt %)</th>
<th>Coal</th>
<th>Wood</th>
<th>Straw</th>
</tr>
</thead>
<tbody>
<tr>
<td>Moisture content</td>
<td>6-10</td>
<td>5-60</td>
<td>17-25</td>
</tr>
<tr>
<td>Carbon, C</td>
<td>50-87</td>
<td>48-52</td>
<td>45-47</td>
</tr>
<tr>
<td>Hydrogen, H</td>
<td>3.5-5</td>
<td>6.2-6.4</td>
<td>5.4-6</td>
</tr>
<tr>
<td>Nitrogen, N</td>
<td>0.8-1.5</td>
<td>0.1-0.5</td>
<td>0.4-0.6</td>
</tr>
<tr>
<td>Oxygen, O</td>
<td>2.8-11.3</td>
<td>38-42</td>
<td>40-46</td>
</tr>
<tr>
<td>Sulphur, S</td>
<td>0.5-3.1</td>
<td>&lt;0.05</td>
<td>0.05-0.20</td>
</tr>
<tr>
<td>Chlorine, Cl</td>
<td>&lt;0.1</td>
<td>0.01-0.03</td>
<td>0.14-1.05</td>
</tr>
<tr>
<td>Potassium, K</td>
<td>0.003</td>
<td>0.02-0.05</td>
<td>0.69-1.30</td>
</tr>
<tr>
<td>Calcium, Ca</td>
<td>4-12</td>
<td>0.1-1.5</td>
<td>0.1-0.6</td>
</tr>
</tbody>
</table>

*a chemical composition given on a dry basis.

**Figure 3.** Summary of the K-S-Cl chemistry occurring during combustion of biomass (straw) in power plants [8,28].
1.3 Thesis objectives and outline

The present work was part of a larger strategic research centre “Power Generation from Renewable Energy” GREEN (founded by the Danish Council for Strategic Research) with the general objective of developing a scientific and technical basis for converting coal and gas-fired power plants to 100% biomass fired power plants.

Specifically, the project aimed at giving a greater understanding into high temperature corrosion of superheaters during firing of biomass, as well as assessing candidate corrosion resistant materials or dedicated surface treatments. The three core objectives of the project cover:

a. development of a comprehensive method using microscopic, spectroscopic and diffraction based techniques, for the characterization of complex corrosion products formed under biomass firing conditions.

b. improved understanding of the influence of parameters, such as flue gas composition, metal temperature and exposure time, on biomass induced corrosion under controlled laboratory conditions.

c. assessing the corrosion performance of alternative materials/coatings and the effect of surface modification, under controlled laboratory conditions simulating biomass firing.

The thesis continues with a literature survey covering the basics of high temperature corrosion, and subsequently reviews relevant literature on biomass induced high temperature corrosion; both are collated in chapter 2. In chapter 3, details of the experimental set-up, characterization techniques and methodologies employed to achieve the objectives of the project are presented.

The results of the project begin in chapter 4, with focus on the use of complementary techniques for characterization of corrosion products from both laboratory and full scale exposures. Chapter 5 addresses the effect of process parameters such as gas chemistry, temperature variation and time on biomass induced high temperature corrosion. In chapter 6, the corrosion performance of modified alloy surfaces, coatings and alternative materials under controlled laboratory conditions mimicking biomass firing are reported. The results in chapters 4, 5 and 6 are presented and discussed in the form of scientific journal articles, which has either been published or submitted, or added as manuscripts yet to be submitted.

An overall discussion of these results as well as important conclusions is contained in chapter 7. This is followed by chapter 8 which summarizes the findings from this study. In chapter 9, an outlook with proposed future investigations is given.
Chapter 2 – High temperature corrosion

High temperature corrosion experienced by superheaters in biomass fired power plants is a complex phenomenon due to the complex deposit and gas composition involved. This chapter first begins with a basic and concise overview of the thermodynamic and kinetic principles of the underlying gas-metal interactions at high temperatures before reviewing the relevant literature on high temperature corrosion under more complex conditions related to biomass firing.

2.1 Concise overview of high temperature corrosion

2.1.1 Basics of gas-metal interactions at high temperatures

The basic interaction between a metal (M) and oxygen (O) at high temperature is given by reaction (2.1) and results in formation of an oxide (M\textsubscript{x}O\textsubscript{y}).

\[
2xM(s) + yO\textsubscript{2}(g) \rightarrow 2M_xO_y(s) \quad (2.1)
\]

The various stages (which may overlap) involved in the development of an oxide on a metal are illustrated in Figure 2.1 and in simple terms include [32,33]:

a. the impingement of oxygen molecules, physical adsorption facilitated by van der Waals forces followed by subsequent dissociation on the metal surface,

b. place exchange of surface oxygen and metal atoms leading to nucleation and formation of an oxide monolayer, which then exhibits a three-dimensional growth,

c. transport of metal or oxidant species through the oxide to facilitate reaction between oxidant and metal thereby propagating growth of the oxide,

d. oxide breakdown by development of porosities, cracks or spallation and possible healing to regain protection.

In principle, the growth of a given oxide is governed by both thermodynamics and kinetics. For the oxidation of most transition metals present in alloys employed for high temperature applications, the forward reaction in reaction (2.1) is accompanied by a negative change in Gibbs free energy (\(\Delta G\)). As a result, such reactions are spontaneous [34].

Under isobaric conditions, \(\Delta G\) can be written as:

\[
\Delta G = \Delta G^0 + RT \ln(k) \quad (2.2)
\]

\(\Delta G^0\) is the Gibbs free energy at standard state while, \(R\) and \(T\) are the universal gas constant and reaction temperature, respectively; \(k\) is the reaction equilibrium constant. However, under isobaric and isothermal
conditions, $\Delta G^o$ is related to the change in reaction enthalpy ($\Delta H^o$) and entropy ($\Delta S^o$) according to equation (2.3).

$$\Delta G^o = \Delta H^o - T \Delta S^o$$  \hspace{1cm} (2.3)

For reaction (2.1), the equilibrium constant ($k_e$) can be defined as:

$$k_e = \frac{a_{M_xO_y}^2}{a_M^{2x} \times p_{O_2}^y}$$  \hspace{1cm} (2.4)

The activities (a) of the metal and oxide can be approximated to unity assuming these phases are present in their pure states. The partial pressure of oxygen ($p_{O_2}$) can then be related to $k_e$ as
Under equilibrium conditions, substitution of equation (2.5) into (2.2) results in the relationship shown in equation (2.6) from which a direct relation between $\Delta G^\circ$, $p_{O_2}$ and $T$ is obtained through further relationship to equation (2.3).

$$\Delta G^\circ = RT \ln(p_{O_2}) = \Delta H^\circ - T \Delta S^\circ$$  \hspace{1cm} (2.6)

Equation (2.6) reveals the dependence of a given oxidation reaction on temperature and the oxidant partial pressure. The corresponding plot, referred to as the Ellingham diagram, is shown in Figure 2.2 for oxides of common alloying elements of high temperature alloys.

The growth rate of an oxide resulting from gas-metal interactions at high temperatures is often limited by one of the previously outlined stages (a-d). Although formation of an oxide may be favoured by thermodynamic predictions, kinetics of the oxide growth is also an important factor. In Figure 2.3a, the various kinetics of oxide growth encountered in high temperature oxidation are schematically illustrated [33]. By following the development of the oxide or monitoring the consumption of the metal or oxidant as a function of time ($t$), the kinetics of high temperature oxidation can be ascertained [35]. The general rate of oxide formation follows equation 2.7.

$$\frac{dX}{dt} = f(t)$$  \hspace{1cm} (2.7)

$X$ is the thickness of the oxide or depth of metal recession which is often directly related to the volume of the oxide or mass gain per unit area of the metal.

In the case of linear growth rate of an oxide (i.e. a non-protective oxide), the growth process is often not limited by transport through the scale thickness ($X$), but rather depends either on interfacial reactions or transport through cracks in the oxide [33–36]. The rate equation for linear oxide growth then reduces to

$$\frac{dX}{dt} = k_i$$  \hspace{1cm} (2.8)
Figure 2.2. Ellingham diagram showing the relationship between temperature, oxygen partial pressure and the standard Gibbs free energy for formation of typical oxides [34,37].
where $k_l$ denotes the linear rate constant. However, if the growth process is limited by transport through a compact oxide (i.e., a protective oxide) of thickness $X$ oxidation then follows a parabolic kinetics and the rate equation becomes

$$\frac{dX}{dt} = \frac{k_p}{X}$$

(2.9)

with $k_p$ being the parabolic rate constant. Most high temperature alloys exhibit parabolic oxidation kinetics in pure oxygen. Since transport through the oxide occurs by diffusion, which is thermally activated, the growth rate of these oxides follows the Arrhenius equation as shown in Figure 2.3b.

In cases where evaporation of the oxide affects the oxidation kinetics, an evaporation term ($k_v$) is introduced into the parabolic rate law (equation 2.9) according to the Tedmon equation to accommodate for this [35,38,39]. Oxidation in this case usually follows paralinear kinetics.

$$\frac{dX}{dt} = \frac{k_p}{X} - k_v$$

(2.10)

Other rate laws such as the logarithmic and inverse-logarithmic laws may apply at low temperatures or for thin oxide films. Also, the oxidation kinetics in some real applications may be controlled by both diffusion and interfacial reactions. The rate laws under such situations can be found in high temperature oxidation textbooks [33,34,40]. Further details on the fundamental theories of high temperature oxidation are contained in the extensive literature summarized in references [32–34,38,40].
2.1.2 Overview of gas-metal interactions in atmospheres other than oxygen

Apart from O₂, other oxidants such as CO₂, CO, SO₂, H₂O, HCl, Cl₂, N₂, etc. may interact with metals during high temperatures processes. In addition to the outlined interactions between metal and oxygen in section 2.1.1, such gases may induce formation of liquids, evaporation of reaction products, increased transport through defects in corrosion products, etc. which in some cases will provoke high metal consumption rates [36,38,41–58].

Metal-sulphur interactions result in formation of sulphides and often occur in a manner similar to oxidation. Sulphide formation also has high Gibbs free energy and hence is thermodynamically favoured [59]. Sulphidation of most metals has been reported to also display parabolic kinetics [38,59]. However, the high defect nature of sulphides [38,49,59] often leads to higher corrosion rates relative to oxides (Figure 2.4).

Figure 2.4. Comparison of the parabolic constants of sulphidation and oxidation of common metals as a function of temperature [38].

In carbon containing atmospheres, carburization of metals is likely to occur under carbon activities less than 1. However if the carbon activity in an atmosphere is greater than 1, metal-carbon interactions leading to formation of metastable carbides at low oxygen partial pressure conditions result in metal dusting, which is a severe degradation mechanism for alloys [38,42,60].
Atmospheres containing H$_2$O may induce evaporation of protective oxides by increasing their vapour pressures [53], or they may promote internal oxidation of alloys [61,62]. Most of the processes outlined for metal-oxygen interactions, are modified by the presence of water vapour in similar atmospheres. The review in reference [63] contains further details on the interactions between metal and water vapour.

Interactions between metals and halogens (e.g. Br, Cl, F, etc.) in principle follow similar rules as outlined for the interaction between metals and oxygen (section 2.1.1). However, the high electronegativity of halogens results in their high reactivity with most metals. Reactions between halogens and metals have been often employed in positive aspects for extraction of such metals [57]. With respect to corrosion, interactions between metals and halogens (or halides) provoke high corrosion rates and in some cases have even caused ignition of samples [64]. Metal-halogen interactions are complicated by the fact that the limiting step varies with respect to metal type, temperature, concentration (partial pressure) of the halogen/halide specie, interfacial reactions as well as the kinetics of gas boundary reactions [56,57,65–76].

### 2.1.3 High temperature corrosion under deposits

During operation at high temperatures in certain process atmospheres, different types of deposits form and cover the metal surface. The composition of such deposits may vary from Si/Al oxides and sulphates for materials employed in coal fired power plants to K/Na sulphate mixtures, chlorides and carbonates in black liquor plants [77]. Superheater deposits in biomass fired power plants are often rich in K-chloride/sulphate with inclusions of Si, Ca, Al, etc. [22,24,27,78]. The term ‘hot corrosion’ is generally used to describe the accelerated oxidation of metals in the presence of deposits [38].

The presence of deposits may alter the interactions between metal and gases [79]. For instance, a deposit may alter the oxygen partial pressure at the metal/deposit interface to the extent that formation of a protective oxide becomes impossible [79]. The interaction between deposits and metals under gaseous atmospheres at high temperatures is a complex phenomenon. However, a general trend reported in most textbooks on deposit induced high temperature corrosion is that the presence of a deposit often increases the degree of corrosion attack on the metal (Figure 2.5a) [38,79,80]. Factors such as metal type/alloy composition, reactivity between the deposit and metal, temperature, gas composition and concentration, etc., affect high temperature corrosion induced by deposits [38,77,79].

Most deposits in combustion atmospheres are salts (often in the form of chlorides or sulphates) which possess the capability to react with protective oxides at high temperatures [79]. In addition, melting of such deposits may occur leading to acceleration of corrosion attack because such melts are able to dissolve protective oxides formed on the metal surface [38,79,80]. In this respect, the terms, ‘Type I’ and ‘Type II’ hot corrosion are used to distinguish between hot corrosion occurring above and below the melting point of the salt, respectively [80].
Figure 2.5. (a) Increase in reaction kinetics of pure Ni at 900 °C due to the presence of Na₂SO₄ deposits in an atmosphere comprising of O₂-4% SO₂. (b) Morphology of melt induced corrosion attack on a superheater tube at ~550 °C in a waste fired power plant [80].

For sulphate melts, the thermodynamics and different electrochemical stages involved in the corrosion process have been studied in detail [38,59,79–88]. The mostly accepted condition for continuous fluxing of an oxide of a pure metal by a sulphate melt is that the oxide exhibits a negative solubility gradient in the melt from the oxide/melt interface towards the melt/gas interface [38,80,84]. If such a criterion is fulfilled, the dissolved oxide at the oxide/melt interface is precipitated at the melt/gas interface.

In the case of chloride deposits, the resulting metal chlorides from reaction of the deposit with the metal are able to induce formation of low temperature melts (eutectics) [80]. In addition, metal chlorides exhibit high vapour pressures and may provoke gas phase transport which often leads to formation of porous oxides and high metal wastage. The micrograph in Figure 2.5b shows the morphology of a typical corrosion product resulting from chloride melt induced corrosion of superheaters in a waste fired power plant [80]. Investigations on chloride deposit induced corrosion in biomass fired power plants will be addressed in the next section.

2.2 High temperature corrosion in biomass fired power plants

Superheater tubes in biomass fired power plants are prone to deposit and gas-induced corrosion (on their outer surfaces) as well as gas-induced corrosion (on their inner surfaces). The high temperature degradation suffered by these surfaces is referred to as fireside corrosion and steam side oxidation, respectively, and are schematically shown in Figure 2.6. The present project focused on fireside corrosion. Hence, subsequent sections will emphasize previous investigations on fireside corrosion of superheaters in biomass fired power plants and under laboratory conditions related to biomass firing.
2.2.1 Full-scale corrosion investigations

Full-scale investigations in waste fired incinerators were among the first studies to highlight the potentials of Cl- and S-containing melts to provoke severe corrosion in the convective heat transfer tubes [89–91]. Investigation of exposed probes by X-ray diffraction revealed that a continuous layer of FeCl₂ was present at the corrosion front (corrosion product-metal interface) on the fireside. Fe₂O₃ and Fe₃O₄ were observed between the layer of FeCl₂ and the bulk deposit. Between the FeCl₂ and Fe₂O₃ layer, FeS was also identified. These studies suggested that severe corrosion was initiated by the reaction between SO₂ in the gas, with alkali (Na/K) chlorides releasing HCl (reaction 2.11) which then reacted with Fe in the alloy to form the identified FeCl₂ [90,91]. Oxidation of the formed FeCl₂, accounted for the observation of Fe-oxides. Alkali pyrosulphates, trisulphates and bisulphates were postulated to react with Fe resulting in the formation of FeS and Fe₂O₃ (reaction 2.12 and 2.13) [91].

\[
\begin{align*}
2\text{KCl}(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}(g) & \rightleftharpoons \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g) \quad (2.11) \\
2\text{KHSO}_4(l) + 3\text{Fe}(s) & \rightleftharpoons \text{Fe}_2\text{O}_3(s) + \text{FeS}(s) + \text{K}_2\text{SO}_4(s) + \text{H}_2\text{O}(g) \quad (2.12) \\
\text{K}_2\text{S}_2\text{O}_7(l) + 3\text{Fe}(s) & \rightleftharpoons \text{Fe}_2\text{O}_3(s) + \text{FeS}(s) + \text{K}_2\text{SO}_4(s) \quad (2.13)
\end{align*}
\]

With respect to biomass fired power plants, most of the full-scale corrosion/deposition investigation have been carried out in Scandinavia, probably because of indigenous supply of biomass in these countries [92].

In Sweden, full scale investigations using air and water cooled probes have been undertaken at the Nässjö combined heat and power (CHP) plant and at the Jordbro district heating plant, with metal temperatures ranging from 640-670 °C. These investigations lasted for a maximum duration of 3000 h [93] during
which, Nässjo (a circulating fluidized bed, CFB power plant) was co-fired with 70 % biomass and 30 % coal (thermal basis) while Jordbro (a hot water boiler plant) was fired with 100 % biomass. The corrosion performance of various austenitic stainless steels and a high Cr martensitic steel in these plants revealed that corrosion increased with metal temperature, and that high Cr and Mn content in the alloys were beneficial for improved corrosion resistance. Preferential sulphidation of Mn in high Mn containing steels permitted the formation of a protective chromia scale which reduced corrosion [93].

In a pulverized-fuel (PF) fired Vattenfall AB boiler (also located in Sweden) combusting 100 % pulverized wood, the corrosion performance of austenitic stainless steels TP 347H FG and HR3C has been investigated [94,95]. These investigations exposed probes of the alloys for 3770 h, at metal temperatures of 600 °C and 650 °C. Variation in corrosion attack along the circumference of the tubes suggested that the deposit (which comprised mainly of KCl and K_2SO_4) imposes greater influence on the corrosion process, than the gas phase chemistry. On the alloy TP 347H FG, three general layers of corrosion products were observed [94] (Figure 2.7). Layer I was the outermost layer which formed parallel to the metal surface and was also observed to contain sintered deposits. In Layer II, completely or partly attacked grains were identified while intergranular attack occurred in Layer III.

Alloy HR3C, on the other hand, exhibited three different types of internal corrosion attack (Figure 2.8) [95]. Type I internal attack contained a thicker chromia layer. A thinner chromia layer on regions with Type II internal attack resulted in large voids which were inhibited at higher metal temperatures (650 °C) due to sintering of the deposits. Regions with Type III internal attack contained a denser and thicker chromia layer.

Full-scale corrosion investigations have also been carried out in two wood fired CFB boilers located in Sweden, namely, a 105 MW_{tot} boiler in Nyköping, and a 98 MW_{tot} boiler in Munksund [96]. These investigations demonstrated the potential of ammonium sulphate, (NH_4)_2SO_4 (in generic terms, ‘ChlorOut’) to minimize the corrosion rate of a range of ferritic and austenitic stainless steels which were employed as probes. Remarkably, ‘ChlorOut’ injection in the Munksund boiler was reported to decrease the 2 μm thick corrosion layer on the alloy, 13CrMo44, to only 0.5 μm after 3h of exposure.

In the Chalmers University CFB research boiler, full-scale investigations on the initial stages of corrosion of the austenitic stainless steel, 304L at a metal temperature of 500 °C, during combustion of woody biomass was carried out [97]. The reaction between the protective (Cr,Fe)_2O_3 and KCl in the deposit was concluded to have occurred according to reaction 2.14, resulting in corrosion products with high K content. This reaction depleted the oxide in chromium and consequently triggered rapid oxidation of the alloy.

\[
(Cr_xFe_{1-x})_2O_3(s) + 4xKCl(s) + 1.5xO_2(g) + 2xH_2O(g) \\
\Rightarrow (1-x)Fe_2O_3(s) + 2xK_2CrO_4(s) + 4xHCl(g) \tag{2.14}
\]
Figure 2.7. The different morphologies of internal attack along the tube circumference of alloy TP 347H FG after exposure for 3770 h at 600 °C, in a wood fired PF boiler. The micrographs (a-f) show the variation of corrosion products along the corresponding positions on the tube circumference [94].
Figure 2.8. The different morphologies of internal attack observed on alloy HR3C after exposure for 3770 h at 600 °C in a wood fired PF boiler. (a) Type I, (b) Type II and (c) Type III internal corrosion attack [95].

The study in reference [98] further reports on the full-scale investigation of alloy 304L at 600 °C during co-combustion of biomass and waste in the Chalmers University CFB research boiler. In reference [99] other related full-scale investigations in Swedish power plants are reported.

A series of full-scale investigations addressing deposition and corrosion in biomass fired plants have also been carried out in Denmark [24,29–31,100–104]. Most of these investigations were carried out in straw-fired boilers where it was observed that the deposit composition close to the metal surface could change from being KCl rich during short exposure times, to K₂SO₄ rich after exposures lasting up to a year (Figure 2.9) [24,100,101,104].

Figure 2.9. Microstructure of innermost deposit layers on probes inserted in straw-fired boilers in Denmark. (a) The Rudkøbing CHP after maximum exposure times of 16h. (b) The Masnedø CHP after exposures for approximately 1 year. Adapted from references [24,100].
The presence of KCl in the deposits caused high corrosion rates of the investigated ferritic and austenitic stainless steel probes in these plants. The KCl induced corrosion was initiated either by direct reaction with the protective oxide or by reaction with gaseous components according to a mechanism similar to that represented in reaction 2.11 [101]. The selective nature of such corrosion attack resulted in preferential attack of Fe and Cr. For investigated ferritic steels, the increased Cr content in X20 (11.6 wt%) compared with T22 (2.2 wt%) reduced the corrosion rate. However due to reaction of Cr with Cl to give volatile chromium chloride, an increased selective attack was observed with increasing Cr content in the investigated austenitic stainless steels [101]. Generally, it was observed that the total material loss was minimized in alloys with Cr content between 15-18 wt% [29,30,101].

Full-scale investigations in Danish straw-fired boilers showed that the corrosion rate of both ferritic and austenitic stainless steel grades increases with metal temperature and exhibits an Arrhenius type of relationship as shown in Figure 2.10 for the example of TP 347H [101,104].

![Figure 2.10. Arrhenius plot showing metal temperature relationship with the corrosion rate of austenitic stainless steel, TP 347H probes inserted in different Danish straw fired boilers [104].](image)

Danish full-scale corrosion investigations have also revealed that KCl induced corrosion is reduced when co-firing biomass with other fossil fuels like coal. However, the KCl corrosion mechanism is replaced by sulphidation and hot corrosion [103,105]. During biomass co-firing with coal, KCl reacts with SO₂ or
aluminosilicates before its deposition on superheaters. This generates less corrosive species as outlined in reactions 2.11 and 2.15. The extent of corrosion reduction when co-firing depends on the share of straw co-fired with coal.

\[
2\text{KCl}(s) + \text{Al}_2\text{O}_3(s) + 6\text{SiO}_2(s) + \text{H}_2\text{O}(g) \rightleftharpoons \text{K}_2\text{OAl}_2\text{O}_3 6\text{SiO}_2(s) + 2\text{HCl}(g) \tag{2.15}
\]

Full-scale investigations addressing the performance of thermal spray coatings [106] as well as the possibility of online measurement of corrosion [107–110] in biomass fired power plants have also been reported.

### 2.2.2 Lab-scale investigation of corrosion under biomass firing conditions

Due to the wide variations in operating conditions such as temperature, fuel type, deposit composition, etc. often encountered in full-scale investigations, controlled lab-scale investigations have been meaningful for detailed mechanistic understanding of high temperature corrosion in biomass fired boilers. The focus of most lab-scale studies has often been either on the influence of deposit composition [111–122], gas phase chemistry [112,118,123–133], temperature [113,118,134–137], or on the performance of different materials (pure metals, alloys, coatings) under specific conditions [67,122,130,134,138–156].

#### 2.2.2.1 The influence of deposit composition

Extensive studies have generally shown that reaction between protective oxides and deposits such as KCl, NaCl, and K$_2$CO$_3$ disrupt the formation of protective oxides on superheater materials [116,118,119,122]. The reaction between the alkali metal in these deposits and the oxide leads to consumption of oxide forming elements according to reaction 2.14 (for the example of KCl and (Cr,Fe)$_2$O$_3$). However, studies reported in [118,122] suggest that the presence of Cl in the deposit will exercise a greater influence on catastrophic corrosion leading to development of porous and multi-layered non-adherent corrosion products. Figure 2.11 illustrates the difference in terms of the nature of corrosion attack initiated by KCl and K$_2$CO$_3$ on a Ni based superalloy (Nimonic 80A) after exposures at 600 °C for 168 h in a gas mixture comprising of N$_2$(g) + 5% O$_2$(g) + 15% H$_2$O(g) [122]. It is clear from Figure 2.10a that Cl is capable of initiating the formation of a porous corrosion product, as reported in [118].

Studies reported in [111,119] demonstrated that K$_2$SO$_4$ deposits are relatively less corrosive than KCl containing deposits. This is because the reaction of K$_2$SO$_4$ with the protective oxide (according to reaction 2.16) is not thermodynamically favoured ($\Delta G^\circ = 135$ kJ/mol at 600 °C) and as a result, protective oxide formation under K$_2$SO$_4$ deposits is possible [119].

\[
\frac{1}{2}\text{Cr}_2\text{O}_3(s) + \text{K}_2\text{SO}_4(s) + \frac{3}{4}\text{O}_2(g) \rightleftharpoons \text{K}_2\text{CrO}_4(s) + \text{SO}_3(g) \tag{2.16}
\]
At 600 °C in 5% O₂(g) + 40% H₂O(g), CaCl₂ was reported to be less corrosive than KCl and NaCl on an austenitic stainless steel (304L) [116]. In more complex gas mixtures containing sulphidizing and chlorinating species (mimicking straw-firing conditions), SiO₂ addition to a KCl deposit exercised no influence on corrosion. However, CaO addition influenced the degree of corrosion attack under such gas phase chemistry. This is because CaO reacts with HCl to give CaCl₂ which, relative to the influence of SiO₂, enhance the corrosion attack on the austenitic stainless steel (TP 347H FG) [112].

Figure 2.11. Different corrosion product morphologies observed after exposure of (a) KCl coated and (b) K₂CO₃ coated Nimonic 80A samples at 600 °C for 168 h in N₂(g) + 5% O₂(g) + 15% H₂O(g) [122].

2.2.2.2 Investigations on the influence of flue gas chemistry

Lab-scale investigations have been fundamental in clarifying the influence of flue gas components on the mechanisms of corrosion under biomass firing conditions. The major focus of these studies is on the influence of SO₂, H₂O and HCl. In chapter 5, a detailed review of the literature on the influence of gas phase chemistry is presented.
2.2.2.3 The influence of temperature

Corrosion under biomass firing conditions is accelerated with increase in temperature. This is also in agreement with observations from full-scale investigations in straw-fired power plants (see Figure 2.10). From results observed after corrosion exposure of austenitic stainless steel 304L within the temperature range of 400-600 °C, the temperature dependence of the reaction between KCl and the protective oxide (reaction 2.14) accounted for an increase in corrosion with temperature [137]. The lower extent of corrosion at 400 °C was attributed to the possibility of the Cr-depleted oxide to render protection at such temperatures. However, other reports [134] suggest that the increased volatility of metal chlorides (Figure 2.12) with temperature leads to high material corrosion. This was based on a Cl-catalyzed mechanism, the so-called active oxidation, which will be addressed in section 2.3.

![Figure 2.12. The influence of temperature on the equilibrium vapour pressure of different metal chlorides [134].](image)

2.2.2.4 Studies on the corrosion performance of different materials

The Gibbs free energy of the reaction between metals and chlorides (resulting in the formation of metal chlorides) plays a critical role with respect to the corrosion performance of a given metal under biomass firing conditions [76,134,156,157]. The thermodynamics of the reactivity between the deposit and the protective oxide formed by alloys also plays a role for the corrosion performance of such alloys under biomass firing conditions.
Among the three common alloying elements Fe, Cr and Ni used in high temperature materials, Ni exhibits greater resistance to Cl-induced corrosion attack due to the lower Gibbs free energy for NiCl₂ formation [134,156]. In agreement with this, evaluation of commercial ferritic and austenitic stainless steels, and the Ni based alloy 625, under laboratory conditions that mimicked biomass firing have shown comparatively best corrosion resistance for alloy 625 [142].

Al and Si are other alloying elements that may promote good resistance to biomass induced corrosion. Additions of Al and Si to Fe-Cr based model alloys have been reported to yield reduction in corrosion rates [151–153]. The effect of alloying with Al is however not as encouraging as that of Si because a positive effect of Al is only observed at very high Al concentration (45 at%) in model Fe-Cr based alloys [151]. Moreover, investigations with commercial Al-containing alloys have shown that alloying with Al may not necessarily result in formation of a protective Al₂O₃ that renders protection against KCl induced corrosion [122,124,158]. Further details on the role of Al are considered in chapter 6.

Carbides are often preferentially attacked, or induce attack of the surrounding metal matrix, in chlorine containing atmospheres. The type of metal carbide determines which effect occurs. The Cr-carbides, Cr₂₃C₆ and Cr₃C₃, are preferentially attacked relative to the surrounding alloy matrix [156,159]. However, Cr₂C₂ shows good resistance to gas phase chloride attack, but this is lost in the presence of a solid Cl-containing deposit [160]. Molybdenum rich carbides (Mo₆C) are stable in chloride atmospheres while the surrounding alloy matrix is attacked [156]. The corrosion of Ti rich carbides (TiC) is not clear with respect to their susceptibility to preferential attack, or ability to provoke attack of the surrounding alloy matrix [156,159].

For TiAlN and enamel coatings, lab-scale testing has shown that these coatings do not suffer corrosion attack under NaCl deposits at 450 °C [161]. Also, Fe-Al coatings on P91 and HCM12A steels have been non-uniformly attacked after exposures at both 560 and 610 °C for 336 h under KCl deposits [162].

Cr-containing coatings applied by high-velocity oxy-fuel spraying (HVOF), laser cladding and plasma spraying have also been evaluated for protection of superheaters in biomass fired power plants [145,155]. The porosity of coatings resulting from these processes is vital with respect to penetration of corrosive species through the coatings. Plasma sprayed coatings exposed to biomass co-firing conditions were better than those obtained by HVOF spraying, due to the high porosity of the latter coatings [145]. Splat boundaries in HVOF sprayed coatings may present transport pathways for corrosive species [155]. The porosity of HVOF sprayed coatings becomes more important than the coatings composition for deposit compositions which may form molten salts [163].

### 2.3 Mechanisms of high temperature corrosion under biomass firing conditions

Corrosion product composition and morphologies observed from both full-scale and lab-scale studies have suggested that corrosion occurs via a Cl-catalyzed mechanism involving cyclic chlorination and oxidation of metals, the so-called active oxidation. This mechanism, initially suggested for corrosion in
waste-fired incinerators [89–91], has been observed in biomass-fired boilers [30,101,104] and also in laboratory investigations under conditions related to biomass firing [64,111,112].

The active oxidation mechanism considers that HCl resulting from either direct reaction of alkali chloride deposits with oxides (reaction 2.14) or sulphation of alkali chlorides (reaction 2.11), or HCl that is present in the gas phase, is oxidized to Cl₂ according to reaction 2.17. Chlorine is transported through fast diffusion pathways to the oxide/metal interface where it reacts with the alloying elements (M) to form metal chlorides (reaction 2.18). The high vapour partial pressures of metal chlorides result in their evaporation away from the oxide/metal interface. Volatile metal chlorides are converted to their corresponding oxides if they encounter sufficient oxygen partial pressures upon migration away from the oxide/metal interface. In such conversion, Cl₂ is released, and thus plays a catalytic role in the overall process.

\[
2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{Cl}_2(g) + \text{H}_2\text{O}(g) \quad (2.17)
\]

\[
\text{M}(s) + \text{Cl}_2(g) \rightleftharpoons \text{MCl}_2(s) \quad (2.18)
\]

The released Cl₂ may reinitiate further chlorination, or be transported away in the gas phase depending on the gas boundary conditions. In Figure 2.13, the possible steps involved in the active oxidation mechanism are schematically illustrated.

**Figure 2.13.** Schematic illustration of possible steps involved in the active oxidation mechanism [157].
The precise preferential transport pathway for chlorine, such that a reducing environment that stabilizes formation of metal chlorides at the oxide/metal interface, is still not fully understood. Lab-scale studies have suggested that this may occur via electrochemical migration through oxide grain boundaries [75,135,164]. In this mechanism, electronic current produced by metal reduction at the oxide/metal interface (reaction 2.19) facilitates reduction of adsorbed oxygen molecules at the oxide/gas interface. Depending on the presence (reaction 2.20) [135] or absence (reaction 2.21) [75] of an alkali chloride deposit, alkali hydroxides or water, respectively, develop. Chloride ions are consequently released from both of these reduction processes.

\[
M \rightleftharpoons M^{2+} + 2e^- \quad (2.19)
\]

\[
2KCl + \frac{1}{2} O_2 + H_2O + 2e^- \rightleftharpoons 2KOH \text{(ads)} + 2Cl^- \text{(ads)} \quad (2.20)
\]

\[
2HCl(\text{ads}) + \frac{1}{2} O_2(\text{ads}) + 2e^- \rightleftharpoons H_2O(\text{g}) + 2Cl^- \text{(ads)} \quad (2.21)
\]

The metal cations and chloride anions are transported through the oxide grain boundaries and form metal chlorides (reaction 2.22) at positions where they meet.

\[
M^{x+} + xCl^- \rightleftharpoons MCl_x(s) \quad (2.22)
\]

The steps in this corrosion mechanism are schematically illustrated in Figure 2.14 [135].

### 2.4 Strategies to mitigate high temperature corrosion under biomass firing conditions

The report in reference [165] outlines many approaches that have been employed to control corrosion in biomass fired boilers. In general terms, these approaches can be classified into three categories:

- a. modifications in boiler design
- b. fuel/gas phase chemistry modifications to favour deposition of non-corrosive species
- c. improvement of the materials corrosion resistance.

Certain modifications can be implemented in boiler designs to minimize corrosion of superheater tubes. Investigations have revealed that changing the location of the superheaters to a position where less deposition of alkali chlorides occurs, can minimize the rate of superheater corrosion [165]. Also, design modifications may involve the use of replaceable superheaters, or the operation of final superheaters at high steam temperatures with fuel from a less corrosive source [165].

Addition of sulphates to the combustion zone, or co-combustion of biomass with high S-containing fuels provides another alternative to minimize the corrosion rate of superheaters. This is based on the ability of the corrosive alkali chlorides to be converted to the relatively less corrosive alkali sulphates in the gas phase prior to condensation on the superheaters [96,103,166,167]. Also, biomass pretreatment by
washing or pyrolysis at moderate temperatures provide an avenue to extract the corrosive alkali metals and chlorides [165,168,169].

Figure 2.14. Schematic illustration of the mechanistic steps involved in KCl-induced corrosion at high temperatures [135].
It still remains a challenge to develop materials that can completely withstand corrosion in biomass fired boilers. Assessment of materials both in full-scale and lab-scale conditions (sections 2.2.1 and 2.2.2.4) show that almost all investigated alloys/coatings sustain corrosion attack, although to varying degrees. TiAlN and enamel coatings according to results in [161] are promising coating materials that may need to be further explored for applications in biomass fired boilers. Investigations involving Fe-Cr steels have pointed out possible positive effect of alloying with Si and Al, on the corrosion induced by KCl [152,170]. Surface rich layers of these elements (Si or Al) obtained by various surface modification approaches were evaluated in the present work as alternative material solutions for reducing corrosion in biomass fired power plants. These results are contained in chapter 6.
Chapter 3 – Experimental procedure and characterization techniques

Deposit composition and gas phase chemistry are essential factors that can influence corrosion attack during biomass firing in power plants (cf. chapter 2). Correspondingly, the nature of corrosion under biomass firing conditions is more complex compared to the relatively straightforward oxidation of metals at high temperatures. Laboratory exposure for understanding corrosion mechanisms must consider influences of both the corrosive deposit and the flue gas chemistry to closely mimic the conditions experienced by superheaters in biomass fired power plants. However, the corrosion products that result from such exposures will be complex, with respect to both composition and morphology. Innovative characterization methods are therefore necessary to comprehensively study biomass induced corrosion.

This chapter presents details of the experimental set-up utilized in the present work to mimic biomass induced corrosion on a laboratory scale. In addition, it introduces the various characterization techniques that were applied, and highlights their complementary information content, which finally allows comprehensive characterization of the resulting corrosion products.

3.1 Laboratory scale simulation of biomass induced corrosion

3.1.1 Coating samples with a synthetic deposit

Laboratory scale investigations in this work involved deposit coated samples that were high temperature exposed to various gas mixtures relevant for understanding corrosion during biomass firing in power plants. Deposits close to the fireside surface of superheaters in biomass fired power plants are enriched in KCl, K₂SO₄, or a combination of these (chapters 1.2 and 2.1.3) [23,24,27]. However, investigations in this work were carried out only with synthetic KCl deposits, because from a corrosion standpoint, KCl is the most aggressive specie. In addition, reactions of KCl with S-containing species in the gas phase originating from biomass firing will lead to the formation of K₂SO₄ in a manner that replicates the conditions close to surfaces of superheaters in power plants.

KCl particles having size distribution of 32-63 μm were applied as synthetic deposits. The salt (with assay, ≥ 99%) was sourced from Sigma. Different coating techniques have been tested and evaluated with the aim of applying reasonable and uniform quantities of deposits homogeneously distributed on the sample surface. With the prior knowledge that deposit/corrosion product melting may occur during corrosion exposures, the concave side, instead of the convex side of test specimens were coated with the deposit. Deposit coating on the concave side of test specimens was also chosen to ensure that deposits do not detach from the samples during corrosion exposure.
The coating techniques evaluated included:

a. spray coating with KCl-isopropanol solutions using atomizers, and
b. coating with KCl-isopropanol slurries by means of a spatula.

As shown in Figure 3.1, technique (a) results in non-uniform coverage of samples with the deposit. Moreover, significant amount of deposits (mostly in the middle of the sample) was only achieved after several spray rounds because the curved sample geometry prevents deposition at the sample edges. The bottleneck in this technique lies in the fact that the spray nozzle of the atomizer is frequently blocked by deposit particles. In addition, the thickness of the deposit obtained by this technique was practically unsuitable for deposit characterization after corrosion exposures.

On the contrary, application of the deposit slurry using a spatula (technique b) proved to be able to deposit relatively uniform and significant amounts of the deposit on the samples with good reproducibly (Figure 3.1b). Further, this application technique gives deposits of reasonable thickness after drying (about 1mm on average) which could also be characterized as a compact layer after the corrosion exposures, and hence, was utilized in the present work for coating samples with KCl deposits.

![Figure 3.1](image.png)

**Figure 3.1.** Deposits applied by different techniques on samples. (a) Inhomogeneous deposit distribution on a sample surface resulting from application via spray coating with an atomizer. (b) Thick and uniform deposit obtained by coating the sample surface with a slurry using a spatula, after drying the slurry a thick deposit is obtained.

### 3.1.2 High temperature exposures

In this work, the general gas compositions given in Table 3.1 were utilized to mimic the conditions relevant when firing biomass (straw) in power plants. The straw-firing (also termed oxidizing-
chlorinating-sulphidizing) gas composition resembles full scale gas measurements in a Danish straw fired power plant [111], but the concentration of HCl is set to represent the worst scenario. In addition to this complex composition, the gas mixture was systematically modified to understand the effect of gas chemistry on corrosion during biomass firing. This modification resulted in classification of gas species into: oxidizing, oxidizing-sulphidizing and oxidizing-chlorinating gas mixtures, under which the experiments in chapters 5.1-5.3 were conducted.

With the exception of H2O, the concentrations of the gas components in Table 3.1, as obtained with mass flow controllers, are given on a dry basis. In the laboratory, mass flow controllers were applied for regulated feed of the required gases from their respective stock bottles into the reaction chamber containing the samples. For gas mixtures involving H2O vapour, this specie is incorporated into the mixture by bubbling of the desired gas (without SO2 and HCl) through a thermally regulated water bath.

Table 3.1. Composition of the gas mixture utilized in the laboratory, to replicate the relevant gas phase chemistries during biomass firing in power plants.

<table>
<thead>
<tr>
<th>Classification</th>
<th>HCl</th>
<th>SO2</th>
<th>CO2</th>
<th>O2</th>
<th>N2</th>
<th>H2Ob</th>
</tr>
</thead>
<tbody>
<tr>
<td>Classifiers:</td>
<td>ppmv</td>
<td>ppmv</td>
<td>vol %</td>
<td>vol %</td>
<td>vol %</td>
<td>vol %</td>
</tr>
<tr>
<td>Straw firing</td>
<td>400</td>
<td>60</td>
<td>12</td>
<td>6</td>
<td>82</td>
<td>3</td>
</tr>
<tr>
<td>Oxidizing</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Oxidizing-Sulphidizing</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Oxidizing-Chlorinating</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
</tbody>
</table>

a Except for H2O, concentrations are given on a dry basis.

In addition, selected experiments were carried out with 13.4 vol % H2O for addressing the effect of gas phase chemistry.

High temperature exposure of deposit coated samples under the gas atmospheres in Table 3.1, permits reasonable simulation of the conditions in real life. These conditions were achieved using a dedicated corrosion test rig (Figures 3.2 and 3.3), which is available at CHEC. This dedicated corrosion test rig consists of a mixing panel, a high temperature reactor unit, and a flue gas cleaning system.

\[\text{CHEC (Combustion and Harmful Emission Control), is a research centre under the Department of Chemical and Biochemical Engineering at the Technical University of Denmark.}\]
In the gas mixing panel, mass flow controllers are used to regulate the concentration of gas species in the inlet gas mixture, which is bubbled through a thermally regulated water bath, to incorporate the desired H₂O vapour content into the final inlet gas stream. In this work, the total gas flow rate was 1000 mL/min. An electrically heated horizontal furnace containing five quartz tubes makes up the high temperature
reactor unit. The gases exiting these reactors are passed through the cleaning unit, before final exit into the exhaust system.

Details of laboratory experimental investigations carried out to realize the objectives of this project are summarized in Table 3.2. Further details on this are presented in the experimental sections of subsequent chapters.

### 3.1.3 Investigated materials

In this work, the austenitic stainless steel, TP 347H with fine grained (FG) microstructure was employed for investigations that focused on the comprehensive characterization of corrosion products. The same material was employed for investigations addressing the effect of gas phase chemistry, time and temperature variations on corrosion. To understand the effect of alloying elements and grain size, the fine grained and coarse grained (CG) version of TP 347H, in addition to the austenitic stainless steel, Esshete 1250 were investigated.

The commercial FeCrAl alloy, Kanthal APM and Ni-based superalloy, Nimonic 80A were used for studies assessing the potentials of preoxidation as a surface modification approach to prevent corrosion. SiO<sub>x</sub> coating on TP 347H FG as well as Ni and NiAl coatings on Esshete 1250 were also investigated in this work as potential surface modification approaches. In addition, a nitride layer on a commercial FeCrAl alloy was investigated for a similar purpose. The compositions of these alloys are collected in Table 3.3.

### 3.2 Corrosion product characterization

This section first outlines the basic principles of the characterization techniques applied in the project. This is followed by a description of the procedures in which these techniques were used for characterization of corrosion products in the present work.

#### 3.2.1 Basic principles of characterization techniques

**3.2.1.1 Light optical microscopy**

Microstructural characterization of materials using light optical microscopy (LOM), according to references [171,172], generally bases on the optical principles of image formation, its magnification and resolution. In the basic sense, reflected light from a given sample is converged by an objective lens to form a magnified image which is subsequently converged by a projector lens to give the final magnified image on a screen. Alternatively, the image from the objective lens passes through an eyepiece lens if it is to be viewed directly by the human eyes.
Table 3.2. Summary of experimental details for the laboratory exposures in the present work.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Effect of gas phase chemistry</strong></td>
<td>Investigated material: Deposit (KCl)-coated and deposit-free TP347H FG samples</td>
</tr>
<tr>
<td>Temperature</td>
<td>560 °C</td>
</tr>
<tr>
<td>Time</td>
<td>72 h</td>
</tr>
<tr>
<td>Gas mixtures (with 13.4 vol% H₂O, except for ‘v’)</td>
<td>i. Oxidizing&lt;br&gt;ii. Oxidizing-chlorinating&lt;br&gt;iii. Oxidizing-sulphidizing&lt;br&gt;iv. Oxidizing-sulphidizing-chlorinating (straw firing)&lt;br&gt;v. Straw firing (3 vol% H₂O)</td>
</tr>
<tr>
<td><strong>Effect of time</strong></td>
<td>Investigated material: Deposit (KCl)-coated TP347H FG samples</td>
</tr>
<tr>
<td>Temperatures</td>
<td>560 °C and 600 °C</td>
</tr>
<tr>
<td>Time</td>
<td>at 560 °C: 83.5 h, 168 h, 336 h, 672 h&lt;br&gt;at 600 °C: 83.5 h, 168 h</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>Straw firing (3 vol% H₂O)</td>
</tr>
<tr>
<td><strong>Effect of temperature</strong></td>
<td>Investigated material: Deposit (KCl)-coated TP347H FG samples</td>
</tr>
<tr>
<td>Isothermal exposures</td>
<td>at 560 °C: 83.5 h, 168 h&lt;br&gt;at 600 °C: 83.5 h, 168 h</td>
</tr>
<tr>
<td>Thermal cycling exposures</td>
<td>560 °C (83.5 h) → 600 °C (83.5 h)&lt;br&gt;600 °C (83.5 h) → 560 °C (83.5 h)</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>Straw firing (3 vol% H₂O)</td>
</tr>
<tr>
<td><strong>Effect of preoxidation</strong></td>
<td>Preoxidation: Samples: Kanthal APM and Nimonic 80A</td>
</tr>
<tr>
<td>Conditions</td>
<td>168 h at 900 °C in O₂&lt;br&gt;168 h at 900 °C in O₂ + 10 vol% H₂O&lt;br&gt;168 h at 1100 °C in O₃ (Kanthal APM only)</td>
</tr>
<tr>
<td>Corrosion exposure</td>
<td>Samples: Deposit (KCl)-coated preoxidized and non-preoxidized Kanthal APM and Nimonic 80A samples</td>
</tr>
<tr>
<td>Conditions</td>
<td>168 h at 560 °C under straw firing (3 vol% H₂O) gas mixture</td>
</tr>
<tr>
<td><strong>Others</strong></td>
<td>Investigated materials: Deposit (KCl)-coated samples of relevant alloys and surface engineered materials</td>
</tr>
<tr>
<td>Exposure conditions</td>
<td>168 h at 560 °C under straw firing (3 vol% H₂O) gas mixture</td>
</tr>
</tbody>
</table>
Table 3.3. Composition of the different alloys investigated in the present work

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>TP 347H</td>
<td>Bal.</td>
</tr>
<tr>
<td>Esshete 1250</td>
<td>Bal.</td>
</tr>
<tr>
<td>Kanthal APM</td>
<td>Bal.</td>
</tr>
<tr>
<td>Nimonic 80A</td>
<td>&lt;3.0</td>
</tr>
<tr>
<td>FeCrAl alloy</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Changes in properties of reflected light waves after interaction with samples facilitate materials characterization by LOM (i.e. reflected light optical microscopy). Variations in wavelength and amplitude are the basis for contrast. LOM is able to reveal the microstructure after samples have been etched, because the material’s microstructure responds differently to the etching solution.

3.2.1.2 Scanning electron microscopy
In accordance with references [173,174], the principles of scanning electron microscopy (SEM) are based on the scattering of incident high energy electrons by atoms in a given sample. Such interactions generate secondary electrons (SE) or backscattered electrons (BSE) from the sample, which are collected by
corresponding detectors and used for materials characterization in the SEM. The energies of these ejected electrons differ, and so does the depths from which they are ejected from the sample. SEs result from inelastic scattering and are relatively generated from the near surface regions because of their low energies. On the other hand, BSEs result from elastic scattering and are generated from larger depths because they have higher energies with magnitudes similar with that of the incident electrons.

Topological differences on a sample are commonly revealed using SE signals since they are produced from the near surface regions. The SE detector (Everhart-Thornley detector) provides topographical contrast based on the effect of trajectory, and electron number, on the number of SEs it collects.

Composition contrast in a sample is provided by BSE images. This is based on the high sensitivity of the backscatter coefficient (i.e. the fraction of the number of ejected BSEs to the number of incident electrons) on the atomic number. While regions in a sample containing elements of high atomic number will give more BSEs, the reverse will be the case for regions containing elements of low atomic number. This difference, when translated on different greyscale levels, reveals a contrast between two regions of different chemical composition.

3.2.1.3 Energy dispersive X-ray spectroscopy

The basics of energy dispersive X-ray spectroscopy (EDS) are summarized according to the detailed description in reference [175]. Interactions of incident high energy electrons with matter may also cause ionization of atoms in the sample. The energy decay of the ionized atom involves transition of its electrons from higher energy states to the vacant site on a lower shell, whereby photons in the X-ray region of the electromagnetic spectrum are emitted. The characteristic nature of the emitted X-rays (corresponding to the energy difference between the higher and lower shell) provides a fingerprint for identification of the chemical composition in the region irradiated by the incident electrons. This is based on the ability of a solid state detector to differentiate the different energies (on the basis of the pulse height) of the generated X-rays.

3.2.1.4 X-ray diffraction

X-ray diffraction (XRD) operates based on the elastic scattering of X-rays by atoms in a material. Its basic principles are presented here in accordance with detailed explanations in references [176–179]. X-ray diffraction resulting in diffraction patterns (or diffractograms) is easier understood, in the geometric sense, by considering the scattering of X-rays in a manner analogous to reflection of light. In this consideration, incident X-rays are reflected by atoms arranged in lattice planes in a crystalline material. Constructive interference only occurs if the path (phase) difference (x-y) between the incident radiation and that reflected by atoms in two consecutive planes with interatomic distance (dhkl), is an integer (n) of its wavelength (λ). This condition is expressed in the Bragg equation as given below.

\[(x - y) = 2dhkl \sin \theta = n\lambda \]  

(3.1)
\( \theta \) is the angle the incident radiation subtends with the plane of atoms, and \( hkl \) are miller indices of atomic lattice planes. The occurrence of constructive interference is called diffraction and intensity is measured; in contrast, destructive interference occurs when there are no lattice planes fulfilling Bragg’s equation, thus, in these cases only so-called background intensity is measured. Apart from the reflection mode considered above, XRD can also be carried out in the transmission mode in which the X-ray beam passes through the entire thickness of the sample.

XRD in reflection mode can be carried out either in symmetric or asymmetric diffraction geometries as schematically illustrated in Figure 3.4. In the symmetric diffraction geometry, the diffracting lattice plans are parallel to the surface such that the diffraction vector (\( \vec{g} \)) is parallel to the lattice plan (and surface) normal (\( \vec{n} \)) as illustrated in Figure 3.4a. The penetration depth strongly varies with the diffraction angle, consequently resulting in high penetrations depths (up to about 10 \( \mu \)m for Fe\(_2\)O\(_3\) with Cr-K\( \alpha \) radiation) at high 2\( \theta \) values [180]. As illustrated on the example of layered corrosion products in Figure 3.4b, analysis of thin layered structures is inappropriate with symmetric diffraction geometries due to this rather large penetration depth thus, giving absorption weighted averaging of information from the different layers. In the asymmetric (grazing incidence) diffraction geometry (Figure 3.4c), the incidence angle (\( \gamma \)) is kept fixed throughout the measurement. The diffracting lattice plans are inclined at an angle (\( \psi \)) to the sample surface such that the diffraction vector is tilted from the surface normal by \( \psi \). The penetration depth is considerably lower (with \( \gamma = 5^\circ \), about 1.6 \( \mu \)m for Fe\(_2\)O\(_3\) with Cr-K\( \alpha \) radiation) compared to the symmetric diffraction geometry and it is fairly constant over the whole measurable 2\( \theta \) range [180]. Both issues as well as the possibility of varying the incidence angle make the grazing incidence geometry suitable for depth resolved analysis of thin layers at the surface (Figure 3.4d).

Incident X-rays may be of a specified energy (so-called monochromatic) or distributed in energy (so called white radiation). The former is employed for angular dispersive (AD) diffraction while the later finds use in energy dispersive (ED) diffraction. By applying the energy relation (\( E = \frac{hc}{\lambda} \)) to the Bragg equation above (equation 3.1), the lattice planar spacing (\( d^{hkl} \)) is expressed in the energy scale (\( E^{hkl} \)) for different diffraction lines according to equation 3.2.

\[
d^{hkl} = \frac{hc}{2 \sin \theta} \frac{1}{E^{hkl}} \tag{3.2}
\]

where \( h \) is the Planck’s constant and \( c \) is the speed of light [181]. ED XRD is advantageous in the sense that it yields a multitude of diffraction lines in a single measurement, while the diffraction angle \( \theta \) remains constant [181,182]. In contrast to AD XRD, where non-destructive depth-resolved measurements within the maximum penetration depth are possible applying the grazing incidence geometry in reflection mode, the specific case of ED XRD applying high intense synchrotron radiation in transmission geometry allows to limit the irradiated area such that depth-resolved measurements are possible without (apart from measurement time) any limitation of the depth range (see chapter 4).
Figure 3.4 Illustration of different diffraction geometries and their influence on penetration depths during XRD measurements. (a) Symmetric diffraction geometry and (b) its corresponding high penetration depths. (c) Asymmetric (grazing incidence) diffraction geometry, and (d) its suitability for depth resolved measurements due to limited penetration depths. The different symbols are explained in the text.

Peaks in the diffraction pattern are obtained when the Bragg's condition is fulfilled. The position of these peaks (both in angular and energy dispersive diffraction) depends, according to the Bragg equation, on the lattice planar spacing which is a fingerprint for identification of crystalline materials.

It is important to note that the fundamental principles of LOM, SEM, EDS and XRD exceed that presented in the above sections. These additional details can be found in references [171–179].

3.2.2 Comparison of the different techniques and their complementary nature

LOM has very low resolution (usually about 1 μm), but can give fast information on the grain structure of an exposed material after metallographic sample preparation and subsequent etching. LOM can also serve as a straightforward technique to get an overview of the distribution of corrosion product layers on the cross section of an exposed sample before detailed characterization with SEM. It is therefore useful as a first characterization technique, which, however, should be further supplemented with higher resolution microscopy. Also, LOM does not provide information of the elemental composition or phases present in the corrosion product.
Using both SE and BSE imaging, SEM is suitable for both microstructural and compositional analysis of corrosion products (Table 3.4). SE imaging is very important for both plan view and cross sectional characterization of corrosion products and with field emission gun sources, spatial resolution down to nanometres can be achieved. BSE imaging is also of importance for the characterization of corrosion products resulting from biomass induced corrosion as it can reveal chemical differences and provides a fast indication of the compositional distribution of elements in the complex corrosion products. However, the exact composition or crystalline phases present in corrosion products cannot be revealed by BSE imaging.

EDS gives no information on microstructure of corrosion products. However, it provides information on the elemental composition, both on sample cross sections, and from plan view investigations (Table 3.4). The fact that X-rays are generated from larger depths results in EDS spatial resolution of about 1 μm³. When SEM based characterization is supplemented with EDS, both microstructural and elemental compositional information from the same location of the complex corrosion products become accessible and, thus, supplement each other.

The lattice planar spacing can be used to identify crystalline phases present in a material through XRD. This is achievable by comparing measured diffraction patterns with diffraction standards such as those contained in the Joint Committee on Powder Diffraction Standards (JCPDS). Phase analysis by XRD can be supported if the elemental composition of the measured sample region is known. In this regard, input from EDS essentially complements XRD. In addition, in case of depth dependent changes within the surface near region of a sample, its previous microscopic characterisation by SEM (or LOM) supports the interpretation of XRD results, which reflect absorption weighted information over the actual X-ray penetration depth.

As summarized in Table 3.4, complementarily use of the extractable information from the different techniques provide means through which comprehensive information on the microstructure, chemical composition and crystalline phases in the corrosion products can be obtained.

### 3.2.3 Combination of techniques and applied characterization methodologies

In the present work, two methodologies have been applied for microstructure characterization: a) analysis of cross sections (Method I), and b) plan view analysis (Method II). These methodologies are illustrated in Figure 3.5.

#### 3.2.3.1 Analysis of cross sections (Method I)

Method I employ LOM, SEM and EDS techniques according to conventional two-dimensional characterization carried out on sample cross sections. The use of laboratory, angular dispersive XRD to identify the phases present in the different layers of corrosion products is not possible on cross sections. As a result, Method I was supplemented by additional depth profiling of the crystalline corrosion products using energy dispersive synchrotron diffraction in the transmission mode. Depth profiling is
achieved by translation of a gauge volume defined by the dimensions of slit systems in the beam path, through the sample [182]. This is described further in chapter 4.2. Although the complementary use of all the techniques is achieved via method I, information from LOM, SEM and EDS can be analysed only in two-dimensions as a snap shot of a real 3D microstructure.

Table 3.4. Overview of the possible information provided by the different characterization techniques. Their suitability for cross sectional and plan view investigations is indicated as well.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Extractable information</th>
<th>Suitability?</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Microstructure</td>
<td>Elemental composition</td>
</tr>
<tr>
<td>LOM</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>SEM</td>
<td>✓ (SEs)</td>
<td>✓ (BSEs)</td>
</tr>
<tr>
<td>EDS</td>
<td>✓</td>
<td></td>
</tr>
<tr>
<td>XRD</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\)achieved in transmission mode with the use of narrow slit systems.

Sample preparation for characterization with Method I generally involve the steps outlined in Figure 3.6. After the samples are retrieved from the corrosion test rig, they are cold mounted in an epoxy based resin under vacuum (step 1), such that the morphology of corrosion products is retained as much as possible. After curing of the epoxy resin, the mounted samples are then sectioned under water-free conditions to expose a cross section (step 2) which is again cold mounted under vacuum in a similar resin (step 3). This exposed cross section is metallographically prepared (step 4) to produce a polished surface for subsequent analysis. The metallographic preparation is conducted under water free conditions, hence, necessitating the use of absolute ethanol (99.9 \%, VWR Chemicals) as lubricant during the grinding and polishing processes. This preserved the water soluble parts of the corrosion product and deposit.

Except for the plant exposed specimen described in chapter 4.2, all deposit-coated samples exposed in this work were prepared according to the above outlined procedure before characterization with Method I. If grain structure examination with LOM is of interest, the prepared cross section was etched, otherwise the unetched surfaces were coated with carbon to prevent electrostatic charging during SEM and EDS investigations.
Figure 3.5. The different methodologies applied for characterization of corrosion products.
Figure 3.6. Schematic outline of the preparation steps for sample characterization with Method I.
With Method I, EDS analysis is obtained by mapping an area. To facilitate relationship of these elemental analysis to ED XRD results, a re-quantification procedure which transforms the data in each elemental map into a 1D elemental profile, is applied. This was motivated based on a similar approach in literature [183]. In this re-quantification procedure, the cross section from which the EDS maps were obtained is subdivided into meshes of defined dimensions along the x and y coordinates, as illustrated in Figure 3.7. Elemental compositions from each mesh is re-quantified from the recorded EDS map data using the commercial EDS software (INCA, Oxford), which also implements matrix corrections (the so-called ZAF corrections) for the generated data.

The 1D elemental profile is then obtained by plotting the average elemental composition ($\bar{C}_{xi}$) across a strip of meshes in the x-coordinate at different positions (i). $\bar{C}_{xi}$ is calculated according to equation 3.3

$$\bar{C}_{xi} = \frac{\sum_{p=1}^{n} C_p}{n}$$  \hspace{1cm} (3.3)

where $C_p$ is the elemental composition re-quantified from a mesh at a position $p$ in the y-coordinate, along the considered strip of meshes at position $i$, in the x-coordinate.

3.2.3.2 Plan view analysis (Method II)

Method II complements laboratory AD XRD in the reflection mode with SEM and EDS techniques. This is achieved by successive mechanical removal of the different layers of corrosion product. Plan view comprehensive characterization of the different interfaces revealed by careful removal of the corrosion product layers is obtained by SEM, EDS and AD XRD. Hence, in addition to the two-dimensional
characterizations (Method I), the location or uniformity of the different features on the layers of corrosion products is observed with Method II. In this thesis, Method II is designated the ‘plan view top down’ characterization method.

Characterization with Method II does not involve any form of sample preparation and hence, does not necessitate the use of any lubricant. Characterization of samples after exposure by SEM, EDS and AD XRD starts from investigation of the deposit at the deposit/gas interface. As the deposit layer obtained using the slurry coating (chapter 3.1.1) is thick, it allows the removal of deposits as a compact layer by means of a scalpel. Hence characterization by SEM, EDS and AD XRD is also conducted at the deposit/corrosion product interface. Depending on the nature of corrosion products, subsequent removal of compact layers with a scalpel was carried out. Otherwise, the layers were gently removed as uniformly as possible by means of grinding with SiC paper. In any of these cases, the newly revealed surfaces are characterized by SEM, EDS and AD XRD. After each removal step, the corresponding loss in sample weight was determined. Using an average density of the phases identified by AD XRD, the thickness of the layer removed after each stage was calculated.

Further details on the sample preparation steps, as well as the procedures in which the different techniques were applied for characterization of corrosion products using the different methodologies (Figure 3.5) are described in the experimental section of subsequent chapters.

### 3.3 Thermodynamic calculations

Thermodynamic calculations to support experimental findings in this work were conducted using the commercial thermodynamic calculation software, FactSage [184]. Versions 6.7 and 7.0 of the software were used. In this work, thermodynamic feasibility of relevant reactions was assessed by calculation of Gibbs free energies at the exposure temperatures. In addition, thermodynamic calculations metal-chlorine-oxygen stability diagrams for relevant systems were carried out. The experimental sections of subsequent chapters contain a list of the applied databases.
Summary of results

Chapters 4 – 6 present the results from this study either in the form of published articles or manuscripts.

The objective of chapter 4 is to demonstrate the capability of the two methodologies explained in chapter 3, for the comprehensive characterization of corrosion products formed under biomass firing conditions. The chapter consists of two parts corresponding to characterization of corrosion products resulting from laboratory scale and full scale exposures. The first part (chapter 4.1) is added as a published scientific paper and demonstrates how Method II (the plan view top down method), can be applied to reveal localized information necessary for thorough discussion of biomass induced corrosion mechanism. In the second part (chapter 4.2), Method I (analysis of cross sections) is supplemented with depth resolved energy dispersive synchrotron diffraction (ED XRD), for comprehensive characterization of corrosion products on a plant exposed superheater tube. This method demonstrates the excellent capability of correlating diffraction analysis with elemental and microstructural information, for studying corrosion induced by biomass firing. Chapter 4.2 is presented as a published scientific article.

The focus of chapter 5 is on how different parameters influence biomass induced corrosion mechanism. It reports the results on the effect of gas phase chemistry, time and temperature variations on the corrosion of TP 347H FG using laboratory scale exposures. The effect of gas chemistry is the focus of chapters 5.1 – 5.3. Chapter 5.1 reports the results from exposures conducted under oxidizing and oxidizing-chlorinating gas mixtures. This is followed by chapter 5.2 which compares the exposures under oxidizing-sulphidizing and oxidizing-chlorinating-sulphidizing gas mixtures, to highlight the effect of SO2 during corrosion. Both chapters 5.1 and 5.2 are presented in the form of published scientific articles. Chapter 5.3 which is included also as a published paper addresses the effect of H2O content in the oxidizing-chlorinating-sulphidizing gas mixture, designated as straw-firing gas mixture. In the last part of chapter 5, (chapter 5.4), results from exposures addressing the effect of time and thermal variations are presented. This part is presented in the form of a manuscript, which is still in preparation. In addition to exposures with deposit-coated TP 347H FG samples, deposit-free samples also formed part of the studies in chapters 5.1 – 5.3, revealing that the influence of gas phase chemistry on corrosion is altered by the presence of deposits.

Chapter 6 concentrates on the corrosion performance of preoxidized surfaces, coatings and alternative superheater materials, under laboratory conditions mimicking biomass firing. The chapter is presented in the form of manuscripts which have been submitted or planned for submission. In chapters 6.1 – 6.3, the potentials of preoxidation as a surface modification approach to develop corrosion resistant surfaces, is evaluated. This was with the examples of Al-rich and Cr-T-rich oxide layers formed on commercial alloys, Kanthal APM and Nimonic 80A respectively. Results from the assessment of other standard surface modification approaches such as nitriding, and coatings based on SiOx and Ni-Al, are collected in chapter 6.4. These standard surface modification approaches showed relatively lower corrosion, and in some cases, only local attack, compared to the corresponding unprotected alloy. In the last part of this
chapter (chapter 6.4), the influence of grain boundaries and alloying elements, with the example of Mn, on the corrosion performance of commercial austenitic stainless steels is presented. While Mn was selectively attacked, was no visible effect of grain size on the corrosion of the investigated steels within the studied time frame.

For a quick overview of the experimental conditions in these chapters, the reader is referred to Table 1 below.
Table 1. Overview of experimental conditions for the results presented in this study

<table>
<thead>
<tr>
<th>Project objectives</th>
<th>Methods for characterizing corrosion products</th>
<th>The effect of process parameters</th>
<th>Corrosion performance of alternative materials and modified surfaces</th>
</tr>
</thead>
<tbody>
<tr>
<td>Experimental focus</td>
<td>Laboratory scale exposure</td>
<td>Plant exposure</td>
<td>The effect of chlorine</td>
</tr>
<tr>
<td>Chapter</td>
<td>4.1</td>
<td>4.2</td>
<td>5.1</td>
</tr>
<tr>
<td>Investigated materials</td>
<td>TP 347H FG</td>
<td>TP 347H FG</td>
<td>TP 347H FG</td>
</tr>
<tr>
<td>Deposit (KCl)-coating?</td>
<td>Deposit coated samples</td>
<td>Deposit and non-deposit coated samples</td>
<td>Deposit coated samples</td>
</tr>
<tr>
<td>Exposure time</td>
<td>168 h</td>
<td>30534 h</td>
<td>72 h</td>
</tr>
<tr>
<td>Exposure temperature</td>
<td>560 °C</td>
<td>Steam temperature: 540 °C</td>
<td>560 °C</td>
</tr>
<tr>
<td>Gas mixture</td>
<td>Straw firing</td>
<td>Straw and wood pellets were fired</td>
<td>Oxidizing and Oxidizing-Chlorinating (13.4 vol % H₂O)</td>
</tr>
</tbody>
</table>
Chapter 4 – Methodologies for characterization of corrosion products
4.1 – High temperature corrosion under laboratory conditions simulating biomass firing: A comprehensive characterization of corrosion products

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Abstract

An austenitic stainless steel (TP 347H FG) was coated with a synthetic deposit and exposed, under laboratory conditions simulating straw-firing at 560 °C, for one week. Microscopic, diffraction and spectroscopic techniques were employed for cross-sectional and plan view ‘top-down’ microstructural characterization of the corrosion products. The corrosion products consisted of three layers: i) the outermost layer consisting of a mixed layer of K₂SO₄ and FeₓOᵧ on a partly molten layer of the initial deposit, ii) the middle layer consists of spinel (FeCr₂O₄) and Fe₂O₃, and iii) the innermost layer is a sponge-like Ni₃S₂ containing layer. At the corrosion front, Cl-rich protrusions were observed. Results indicate that selective corrosion of Fe and Cr by Cl, active oxidation and sulphidation attack of Ni are possible corrosion mechanisms.

Keywords: Stainless steel, Biomass, High temperature corrosion, Chlorination, Sulphidation.

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1. Introduction

The increasing CO₂-levels in the atmosphere have necessitated the use of renewable energy sources such as biomass, for ‘CO₂ neutral’ heat and power production. Power plants in Denmark are currently firing biomass (straw and wood) as a substitute for fossil fuels, mainly coal. Biomass is considered CO₂ neutral since it recaptures the CO₂ released during combustion through photosynthesis within a short period of time (≈10⁰ years), compared to the time for coal seam formation (≈10⁶ years). Furthermore, the widespread availability of biomass makes its utilization for heat and power production a viable energy source. Despite these encouraging attributes, the chemistry of biomass is quite different from that of fossil fuels [12,185,186]. Fuels with a high content of K and Cl are usually labelled troublesome since they form low-melting, sticky deposits leading to slagging and fouling problems. Moreover Cl plays a vital role in the catastrophic corrosion observed in heat exchangers (superheaters) in biomass-fired boilers, especially those utilizing straw [137,164].

Since biomass contains significant amounts of flame-volatile alkali metal salts [13–15,19], the ash deposit challenges from combustion of these fuels differ considerably from fossil fuels. Through diffusion, thermophoresis, condensation or inertial impaction, gaseous alkali species, alkali-rich aerosols and fly ash particles are able to form thick deposits on cooler parts of the heat exchangers, where heat is transferred from the hot flue gas into the steam cycle [8,78,187,188]. These aerosol particles consist mainly of potassium chloride (KCl) and potassium sulphate (K₂SO₄) [20,21], which are two species known to cause significant operational challenges due to fouling and corrosion of heat exchangers [22].

To lessen the corrosion of superheater components, the outlet temperature of the final superheater is kept relatively low, i.e. at or below approximately 540 °C in Denmark. This result in a lower efficiency of the power plants compared to coal-firing plants. Thus, there is a strong need for alternative solutions to corrosion problems in order for biomass to remain an economically viable energy source. This task is anchored on comprehending fully the mechanisms involved in the corrosion process. This will guide the development of alloyed materials which can be utilized as superheaters in boilers firing biomass.

Full-scale corrosion tests have been carried out in power plants in order to ascertain corrosion rates and mechanisms. Generally, the high corrosion rate observed during straw-firing is attributed to the following active oxidation mechanism caused by Cl [24,101,189]. Sulphation of the condensed KCl close to the superheater tubes generates Cl. This penetrates the initial oxide layer and reacts with the alloying elements giving rise to metal chlorides. At the oxide/alloy interface, these metal chlorides possess high vapor pressures and hence vaporize to the oxide/gas interface, where they become oxidized due to sufficient oxygen partial pressures at these locations [8,104]. Part of the Cl liberated from this oxidation is able to diffuse back to the corrosion front where it reacts again with the alloy, thereby propagating the corrosion process. However, the unavoidable variations in operating temperatures and fuel type tend to complicate the assessment and thus hinder full understanding of this mechanism. As a result, laboratory-scale studies are employed to study corrosion under well-controlled (although often greatly simplified)
conditions with a focus on specific parameters. Simplified laboratory-scale corrosion studies using synthetic deposits (KCl, NaCl, CaCl₂, etc.), and in some cases, under HCl- or H₂O-containing gaseous atmospheres, have revealed the respective roles of K and Cl in initiating and catalyzing the corrosion of alloys under oxidizing conditions [75,114,116,117,130,135,137,153,164,190–192]. The results from characterization of corrosion products from most of these laboratory studies point towards an active oxidation type of mechanism. However, few studies [8,111,112,193] have investigated both the influence of the flue gas and the synthetic deposit in order to discover more information regarding the corrosion mechanisms under such realistic, but complex conditions. Comprehensive characterization is difficult with standard metallographic techniques due to the heterogeneous nature of corrosion products from such studies and the fact that many of the chloride containing products are water soluble.

The mechanistic conclusions from both full-scale and laboratory-scale studies are often based on Light Optical Microscopy (LOM), Scanning Electron Microscopy (SEM) and chemical elemental analysis (by Energy Dispersive Spectroscopy - EDS), on metallographically prepared sample cross sections [111,193], or on plan view of exposed samples [135,164]. A weakness of this approach, is that localized and sub-surface features arising from the corrosion process tend to be obscured if they are absent along the examined cross section, or if they are localized in a few microns area, and thus important information which could aid understanding is lost. Consequently, it is desirable to optimize the approach towards characterization of the corrosion products through a combination of cross-sectional, and a plan view ‘top-down’ technique. For combining site-specific local analysis with an increased area/volume of the investigated sample part, supplementary X-ray diffraction (XRD) analysis provides an additional advantage. Furthermore, XRD will enable a thorough phase analysis of crystalline corrosion products and thus complement the elemental analysis by EDS.

This paper reports on the application of both cross-sectional and a plan view ‘top-down’ complementary characterization methods for systematic analysis of high temperature corrosion of an austenitic stainless steel (TP 347H FG) after laboratory exposure to straw-firing gaseous conditions under a synthetic deposit in the laboratory. Corrosion products were investigated as a function of distance from the original deposit surface, based on both cross section and plan view analysis, combined with stepwise removal of the corrosion products. The complementary information obtained from microscopy (by LOM and SEM), elemental analysis (by EDS) and qualitative phase analysis (by XRD), allowed the depth-resolved characterization of corrosion products. This comprehensive characterization helped to effectively discuss the corrosion mechanisms under the exposure conditions.

2 Experimental

2.1 Sample preparation and high temperature exposure

A fine grained (FG) austenitic stainless steel (TP 347H FG) tube with the composition shown in Table 1 was investigated. The tube was sectioned into rings of width 1 cm. From these rings, arc shaped
specimens with an average internal surface area of 1.2 cm$^2$ were cut. These tube pieces were degreased in acetone and then ethanol, in an ultrasonic bath prior to synthetic deposit coating.

**Table 1.** EDS measured chemical composition (in wt.%), of the as-received austenitic stainless steel (TP 347H FG) investigated

<table>
<thead>
<tr>
<th></th>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Fe</th>
<th>Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.4</td>
<td>18.1</td>
<td>2.0</td>
<td>10.3</td>
<td>68.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>

The concave side of the curved tube pieces was covered with a synthetic deposit of pure KCl (Sigma, ≥ 99%). For this purpose, a deposit slurry was prepared by mixing 32 – 60 μm sized KCl particles with 2-propanol. The slurry was applied such that, after solvent evaporation, a uniform coating of about 52.1 mg cm$^{-2}$ of the deposit was obtained on the surface. The use of deposit slurries is in accordance with the EU guidelines [142,194] for hot corrosion testing, and also enhances effective simulation of high temperature corrosion under alkali chloride deposits as observed in power plants.

High temperature exposure of the coated specimen was carried out in a corrosion test rig [8,112] consisting of an electrically heated horizontal furnace, a gas mixing panel and a flue gas clean-up system. A schematic sketch of the corrosion test-rig is shown in Fig. 1. The test-rig contains five quartz tubes which allow five exposures under a similar gas environment (in the present work, only one distinct exposure condition is considered). Mass flow controllers were employed to regulate the concentration of the respective gases making up the simulated flue gas.

Table 2 presents the gas composition employed to simulate the flue gas composition during straw-firing, as measured in a Danish power plant firing straw [111]. The concentration of HCl used is a worst case level as the average concentration in straw-firing is approximately 70 ppm. To ensure a uniform gas flow rate in each reactor, ball flow meters were also connected at the exit of each reactor. The KCl coated specimens were exposed at 560 °C for 168 hours in the corrosion test-rig.

Additionally, in a separate experiment to investigate the possibility of K$_2$CrO$_4$ sulphation under the simulated straw-firing condition, as-received K$_2$CrO$_4$ particles were exposed to the same flue gas composition used to simulate straw-firing at 560 °C for 168 h.
Figure 1. Schematic illustration of the corrosion test rig employed for the high-temperature exposure. The electrically heated horizontal furnace contains 5 quartz reactors, which allows for 5 simultaneous experiments under similar flue gas conditions. Only 1 (out of the 5) flue gas cleaning systems have been shown.

Table 2. Composition of the (dry) flue gas employed to simulate straw firing conditions

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration in flow</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>82 vol.-% (dry)</td>
</tr>
<tr>
<td>O₂</td>
<td>6 vol.-% (dry)</td>
</tr>
<tr>
<td>CO₂</td>
<td>12 vol.-% (dry)</td>
</tr>
<tr>
<td>SO₂</td>
<td>60 ppmv (dry)</td>
</tr>
<tr>
<td>HCl</td>
<td>400 ppmv (dry)</td>
</tr>
</tbody>
</table>

2.2 Characterization of exposed samples

After cooling to room temperature, the exposed samples were investigated by microscopic (LOM, SEM), and diffraction based (XRD) techniques, in addition to chemical compositional analysis (EDS). The comprehensive characterization of the exposed samples involved both a cross-sectional approach and a plan view ‘top-down’ approach through removal of corrosion products.

For cross-sectional investigation, an exposed sample was first mounted in epoxy under vacuum, which ensured a rather tight embedding and preserved the sample morphology. The embedded sample was further sectioned along its length-axis, and subsequently re-embedded with the cut surface facing downwards in order to access the sample’s cross section. The final embedded sample was ground and
polished according to standard metallographic sample preparation procedure, but under water-free conditions. As a substitute, absolute ethanol (VWR chemicals, 99.9%) was utilized during grinding and polishing to preserve the water-soluble corrosion products.

Plan view ‘top-down’ analysis was carried out on exposed samples without any embedding. Microscopic, spectroscopic and diffraction based characterizations were first carried out directly on the surface of the exposed sample and then, combined with removal of various layers of the corrosion product. A schematic sketch showing the directions and locations from which the characterization stages were undertaken is shown in Fig. 2.

A scalpel and at larger depths, SiC paper were used to remove the synthetic KCl deposit and the resulting corrosion products. In cases where large deposits and corrosion product layers could be removed as compact pieces, the underside of these was also investigated. This removal is a dry process which does not involve solvents of any kind. The weight difference after each removal step was monitored for estimating the removed layer thickness assuming a homogenous layer distribution. A related approach had earlier been employed for XRD stress analysis of oxide phases on the steam side of superheater tubes [180].

The reaction product resulting from the additional separate exposure of K₂CrO₄ to straw-firing conditions was characterized by SEM, EDS and XRD.

### 2.3 Characterization techniques

Cross-sections of the exposed samples were examined by means of LOM (OLYMPUS GX 41) to investigate the microstructure, thickness and morphology of the various corrosion products. The
metallographically prepared samples were etched by swabbing with glyceregia for ca. 6 sec and afterwards rinsed with deionized water before LOM investigations.

SEM was employed for both cross section and plan view characterization of the exposed samples. Both secondary electron (SE) and backscattered electron (BSE) images were used to obtain information on the morphology and chemical composition of the corrosion products. A SEM (FEI, Inspect S and JEOL, JSM 5900) operated with an acceleration voltage of 15 keV was used.

Elemental analysis of corrosion products was carried out, both on cross sections and as plan view measurements, applying an Oxford Inca EDS system. The EDS system was connected to the SEM, which was also operated with an acceleration voltage of 15 keV during EDS-analysis.

X-ray diffraction was carried out on the concave sample surface, both directly after exposure and after the various removals of the corrosion products. XRD was carried out using a diffractometer (D8 Discover) from Bruker AXS operated in grazing incidence geometry, with a point focused incident X-ray beam using a polycap optics system to converge the beam. The investigations were undertaken such that the sample length-axis (i.e. the longitudinal axis of the tube) with uniform sample height becomes parallel to the diffraction plan and thus eliminates the possibility of shielding the X-Ray beams. Measurements after the various layer removals were carried out with an X-ray incidence angle of 3°, giving a constant penetration depth less than 1.3 μm within the range of measured diffraction angles (2θ = 30 – 135°) for the applied Cr-Kα radiation. Measurements directly on the as-exposed sample surface, i.e. before any layer removal, were performed with an incidence angle of 5°. However the penetration depth cannot be determined accurately due to the unknown absorption characteristics of the porous salt deposit. The sketch in Fig. 2 shows the different locations at which XRD investigations were carried out. For XRD measurements on the reaction products from the exposure of K₂CrO₄, the conventional Bragg-Brentano diffraction geometry was used with Cr-Kα radiation.

3. Results

3.1 Characterization across the cross section of the exposed sample

The microstructure of the sample cross section (cs), as observed with SEM using a BSE detector, is shown in Fig. 3a. From the micrograph, three layers of corrosion products (layer 1-cs to layer 3-cs) can be identified and magnified views of these different layers are presented in Figs. 3b and 3c. The thickness of these corrosion product layers is inhomogeneous. However, results from thickness measurements from 30 locations across the exposed sample cross section, showed the average thickness to be 31.3 ± 6.8 μm, 18.5 ± 7.8 μm and 10.8 ± 2.6 μm for layer 1-cs, layer 2-cs and layer 3-cs, respectively. To supplement microscopic analysis, EDS elemental mapping was also carried out (Fig. 4), to show the distribution of alloying elements or deposit/flue gas constituents within the corrosion product.
The chemical composition of the three distinct layers of the corrosion products, which were identified by microscopy (Fig. 3), can be visualized in the EDS maps (Fig. 4). From the EDS maps, layer 1-cs consist of a mixed layer as already indicated by the contrast in the micrograph (see Fig. 3) and contains mainly K, Fe, S and O. A discontinuous band of Cl is observed above layer 1-cs. Layer 2-cs is revealed to consist of Fe, Mn, Cr, and O (see Fig. 4). This layer contains severe cracks as well as several voids, i.e. the layer possesses high porosity. Close to the bulk alloy, the sponge-like layer (layer 3-cs) is observed from the EDS maps to consist of Ni and S. This sponge-like layer is non-uniform and exhibits an irregular interface with the bulk of the alloy (Fig. 3c).

Upon etching the sample cross section with glyceregia, the microstructure of the steel below layer 3-cs was revealed as shown in Fig. 5. Selective attack along the grain boundaries is observed close to the corrosion front and is marked in the micrograph.
Figure 4. SEM image (upper left) and EDS elemental maps showing the chemical composition of the corrosion products across the cross section of the exposed sample.

Figure 5. LOM micrograph showing the microstructure of the exposed sample cross section below the corrosion products after etching with glyceregia. Grain boundary attack is marked.
It is pertinent to mention that these corrosion product layers shown in the micrographs (Figs. 3 and 4) are observed directly below the initial (KCl) deposit. The embedding of the sample in epoxy to preserve the morphology of the corrosion products for cross-sectional examination obscures some information about the chemistry and morphology of the deposit after high temperature exposure. This is a result of interference from the embedding matrix during chemical elemental analysis, as well as the detachment of some of the deposit particles during metallographic preparation.

### 3.2 Depth-resolved characterization combined with successive layer removal

Plan view investigations by SEM (carried out at locations (i) and (ii) in Fig. 2) revealed the morphology of the synthetic deposit after exposure, as shown in Fig. 6. Small particle clusters are observed to accumulate around the initial KCl (deposit) particles. At the deposit/flue gas interface (Fig. 6a), the small particle clusters appear to have totally coated the initial deposit surface, while at the deposit/corrosion product interface (Fig. 6b) these particles appear as attachments to the initial deposit particles. EDS-analysis (see Table 3) on these particle clusters shows the presence of S in addition to K and Cl, thus, suggesting the sulphation of the initial synthetic deposit. The measured concentrations of K, S and O from EDS-analysis indicate the formation of K$_2$SO$_4$.

The diffractograms in Fig. 7 were recorded by XRD on the exposed sample, both at the deposit/flue gas interface and at the deposit/corrosion product interface (points (i) and (ii) in Fig. 2). Apart from KCl, K$_2$SO$_4$ can be identified on both measured sites (according to Joint Committee Powder Diffraction Standard (JCPDS) cards; 41-1476 and 83-681 for KCl and K$_2$SO$_4$ respectively).

**Figure 6.** BSE micrographs showing the deposit particles, after high temperature exposure viewed both from (a): the flue gas/deposit interface and (b): the deposit/oxide layer interface (corresponding to locations (i) and (ii) in Fig. 2). Results from EDS-analysis on the selected regions are presented in Table 3.
Table 3. Elemental composition of selected regions at the flue gas/deposit interface (see Fig. 6a), determined by EDS-analysis

<table>
<thead>
<tr>
<th>Region</th>
<th>Element (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O</td>
</tr>
<tr>
<td>1</td>
<td>38.2</td>
</tr>
<tr>
<td>2</td>
<td>18.7</td>
</tr>
</tbody>
</table>

XRD phase identification thus supports the EDS-data with respect to the sulphation of the initial deposit to yield K₂SO₄ (see results in Table 3). However, the additional detection of KCl by XRD (in conjunction with identification of K and Cl by EDS) also suggests incomplete sulphation of the deposit particles during exposure.

Figure 7. XRD phase analysis on the synthetic deposit, both at the flue gas/deposit interface and at the deposit/corrosion product interface, (i.e. points (i) and (ii) in Fig. 2).

Similar to the observation of distinct layers in the cross section analysis (-cs layers), also the plan view analysis revealed that the corrosion product consists of several layers (-pv layers). Two distinct layers of corrosion products were identified underneath the initial synthetic deposit. Fig. 8 shows the microstructures of these layers, as observed from the initial deposit/flue gas interface, and the interface between the first two layers of corrosion product (points (iii) and (iv) in Fig. 2). SE and BSE micrographs respectively reveal morphological and chemical contrast between these layers. An overview of both layer 1-pv and layer 2-pv is shown in Figs. 8a and 8b.
Figure 8. BSE (left column) and SE (right column) micrographs from plan view analysis showing layer 1-pv and layer 2-pv of the corrosion product (as viewed from the deposit/corrosion product interface – points (iii) and (iv) in Fig. 2), after the synthetic deposit has been removed. Results from EDS-analysis
on the marked regions are presented in Table 4. In (a) and (b), the two layers of corrosion products can be seen. Magnified BSE and SE images are shown for layer 1-pv in (c) and (d) and from different locations for layer 2-pv in (e)-(h).

Layer 1-pv (Figs. 8c-d) when viewed from point (iii) in Fig. 2, is observed to consist of isolated clusters of round-shaped particles lying on a continuous layer. The morphology of this continuous layer suggests that it has been partly molten. The continuous partly molten layer on layer 1-pv is also observed to contain embedded particle strands. Through EDS-analysis (see Table 4), the isolated clusters of round-shaped particles (region 2 in Fig. 8c) are found to be abundant in K, S and O. Conversely, on the partly molten continuous layer (region 1 in Fig. 8c), the major identified elements were K, Cl, O and Fe. Layer 1-pv (Figs. 8c-d) could correspond to layer 1-cs (cf. Fig. 3) which comprised of K, Fe, S and O, as observed from cross-sectional characterization of the exposed sample. From the plan view ‘top-down’ characterization method, it is observed that layer 1-cs could have been formed locally, rather than as a continuous layer as observed in the micrograph in Fig. 3. This highlights the need for complementing both characterization approaches for thorough characterization of corrosion products.

### Table 4. Elemental composition of selected regions at the deposit/corrosion product interface (see Fig. 8), determined by EDS-analysis

<table>
<thead>
<tr>
<th>Image</th>
<th>Region</th>
<th>Element (wt.-%)</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Figure 8c</td>
<td>1</td>
<td>6.6</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>34.0</td>
</tr>
<tr>
<td>Figure 8e</td>
<td>3</td>
<td>25.9</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>26.6</td>
</tr>
<tr>
<td>Figure 8g</td>
<td>5</td>
<td>22.5</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>22.2</td>
</tr>
</tbody>
</table>

The microstructure of layer 2-pv shown in Figs. 8e-h is more complex. SEM and EDS investigations on this layer were carried out from the direction indicated by point (iv) in Fig. 2. On some locations, faceted Fe-rich structures were observed (see Figs. 8e-f and Table 4). Surrounding these faceted structures, Fe-rich blade-like hollow structures containing appreciable amounts of Cr are also observed. These hollow shaped structures existed in a networked type of arrangement. Some faceted structures can also be identified within these structures. Other locations on layer 2-pv comprised of coral-like arrangement of particles (Figs. 8g-h). Whisker-like protuberances are observed within these coral-like arranged particles. EDS-analysis disclosed this layer to consist of O, Fe, Cr, K and Cl (see Table 4).

Fig. 9 presents the microstructure of the corrosion products beneath the synthetic deposit, but as viewed from the interface between layer 2 and layer 3. Directions from which the investigations were carried out
are indicated as points (v) and (vi) in Fig. 2. Similar to the observation from Figs. 8a-b, two layers (layer 1-pv and layer 2-pv) of corrosion products are observed in the micrograph in Fig. 9a.

Figure 9. BSE micrographs showing the morphology of the corrosion products (as viewed from the interface between layers 2 and 3 of the corrosion product –indicated by points (v) and (vi) in Fig. 2), after the synthetic deposit has been removed. Two distinct layers of corrosion products are observed in (a) and magnified images are shown in (b)-(d). EDS results from selected regions on the micrographs are presented in Table 5.

The first layer (layer 1-pv) consists of segregated dark regions (Fig. 9b) amidst a brighter region having a partly molten and sintered morphology (Fig. 9c). This is similar to that observed in Fig. 8a-b. Within the segregated dark regions on layer 1-pv, bright particle strands are seen to accumulate around, and on the dark round-shaped particles. EDS-analysis showed the composition of this segregated dark regions to include O, S, K, and Fe, with minor amounts of Cl and Cr (see Table 5). The bright particle strands are similarly observed on the partly molten and sintered regions in layer 1-pv (Fig. 9c). The elemental composition of the partly molten and sintered region was determined by EDS-analysis to consist of Cl, K and O, with minor amounts of Cr and Fe (Table 5). This observation reiterates the incomplete sulphation of the initial deposit particles under the exposure conditions. The second layer is observed to
comprise of large facetted structures lying on a continuous layer (see Fig. 9d). The morphology of this layer shows non continuous regions in the form of platelets. The large facetted structures were identified by EDS-analysis (see Table 5) to contain O and Fe with a minor amount of Cr (1.6 wt.-%). On the continuous layer, O, Fe and high amounts of Cr (46 wt.-%) were identified by EDS-analysis. Minor amounts of Si, Ni, Mn, Nb, S, K and Cl were also identified on this layer in concentrations < 2 wt.-% (Table 5).

Table 5. Elemental composition of selected regions at the interface between corrosion product layers 1 and 2 (see Fig. 9), determined by EDS-analysis

<table>
<thead>
<tr>
<th>Image Region</th>
<th>Element (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O  S  Cl  K  Cr  Mn  Fe  Si  Ni  Nb</td>
</tr>
<tr>
<td>Figure 9b 1</td>
<td>38.7 17.5 0.3 39.5 - - 4.0 - - -</td>
</tr>
<tr>
<td>Figure 9c 2</td>
<td>3.2 - 46.2 45.7 0.8 - 4.1 - - -</td>
</tr>
<tr>
<td>Figure 9d 3</td>
<td>28.0 - - - - 1.6 - 70.4 - - -</td>
</tr>
<tr>
<td>Figure 9d 4</td>
<td>22.6 - 0.9 0.5 46.4 1.0 25.1 0.8 0.4 1.9</td>
</tr>
</tbody>
</table>

Figure 10. X-Ray diffractogram from the removed corrosion product beneath the synthetic deposit, i.e. from the interface between layers 2 and 3 of the corrosion product (point (vi) in Fig. 2). XRD results from the interface between corrosion product layers 2 and 3 are shown in Fig. 10. XRD was carried out on the removed corrosion product from the direction indicated as point (vi) in Fig. 2. Phase identification is not straightforward for the present oxides, because slight variations of the chemical composition as well as the presence of macrostresses considerably cause deviations of the measured peak position compared to the theoretical data from the JCPDS for possible phases. However, in addition to
K₂SO₄ and KCl (in agreement with Fig. 7), Fe₂O₃ (JCPDS card 33-664) and Cr-containing spinel (JCPDS card 34-140) were identified.

The change in microstructure of the third layer of corrosion product (layer 3-pv), from the layer surface (L3S) towards the bulk of the alloy is shown in Fig. 11. Characterization of this layer was carried out from the direction indicated as point (vii) in Fig. 2. A combination of the weight change after each removal step, and the density of the prevalent phases identified enabled an estimation of the thickness of the removed layer. EDS revealed high Ni and S concentrations (36.6 wt.-% Ni and 11.3 wt.-% S) on the surface of layer 3-pv (see region 2 in Table 6). Also in larger depth of 9.1 μm from L3S, EDS revealed (not shown here) that S is associated with Ni along the alloy grain boundaries.

Figure 11. BSE micrographs showing microstructure changes of the internal corrosion regions revealed by successive removal of the porous layers starting from the original interface between layer 2-pv and layer 3-pv (Fig. 11a, i.e. point (vii) in Fig. 2). The associated depths shown in b)-d), have been estimated from the weight of the removed corrosion products and the densities of the prevalent phases identified by XRD measurements. EDS results of the marked regions are given in Table 6.

64
Table 6. Elemental composition of selected regions on layer 3-pv of the corrosion product (see Fig. 11), determined by EDS-analysis

<table>
<thead>
<tr>
<th>Image</th>
<th>Region</th>
<th>Element (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Figure 11a</td>
<td>1</td>
<td>13.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>20.1</td>
</tr>
<tr>
<td>Figure 11c</td>
<td>3</td>
<td>1.6</td>
</tr>
</tbody>
</table>

*The determined Si concentration could have been influence by residual Si from the grinding process.*

Protrusions very rich in Cl (13.5 wt.-%) are observed locally on layer 3-pv (see Fig. 11a-b). Fe, Cr, Si and low amounts of K (≤ 1 wt-%) were also identified by EDS-analysis on this layer. Empirically, the amount of K observed is too low to chemically balance both Cl and SO₄²⁻ anions. Interestingly, relative to the concentration of other cations, and the concentration of Ni in the bulk alloy (cf. Tables 1 and 6), only Ni enrichment is observed within the protrusions (up to 40 wt-%). This observation suggests that the observed Cl is possibly, chemically associated with Ni. With further progress towards the bulk of the sample, the corrosion attack is seen to proceed through grain boundary attack (Figs. 11c-d). Metal oxides (FeCr₂O₄ and Fe₂O₃) are also identified by XRD on the surface and sub-surface regions of layer 3-pv (Fig. 12). However, the intensities of peaks from these phases are observed to decrease, as the bulk of the alloy is approached through removal of the corrosion product. Additionally, diffraction from nickel sulphide (Ni₃S₂) (JCPDS card 73-698) was recorded in the diffraction patterns as a function of distance from the surface of layer 3-pv. After an initial increase of the diffracted intensities of Ni₃S₂-peaks, they finally disappear as the bulk of the alloy is approached, which indicates that this phase is only located in a fairly thin region. Peaks from the γ-Fe phase, are seen to dominate with progress towards the bulk of the sample, indicating that the selective corrosion attack region becomes thinner during the course of the removal. No metal chloride phase could be identified from the XRD-measurements, probably because these phases exist only locally within the porous Ni-rich layer, as revealed by SEM (Figs. 11a-b).
Figure 12. X-Ray diffractograms for various removals of layer 3-pv corresponding to the micrographs in Fig. 11. The associated depths have been estimated from the weight of the removed corrosion products and the densities of the prevalent phases identified by XRD.

In Fig. 13, a schematic summarizing the results from characterization of the corrosion product is shown. Results from both cross-sectional and plan view ‘top-down’ characterization methods showed that, the first layer (layer 1) was composed of partly molten KCl, segregates of K₂SO₄ and some Fe-oxide strands. Layer 2 was found to contain Fe₂O₃ and Fe₂CrO₄. In the selective attacked region (layer 3), Ni₃S₂ was identified. Metallic Cl-rich protrusions were also identified in this layer.

3.3 Reaction product from the exposure of K₂CrO₄

Characterization of the reaction product arising from the exposure of K₂CrO₄ to straw-firing conditions revealed the formation of alkali metal sulphates. Characterization of the reaction products both by EDS-analysis and XRD showed the presence of K₂SO₄ in the reaction product (see Fig 14 and Table 7). The observation of Na-containing phases in the diffractogram was due to Na impurities present in the as-received K₂CrO₄, as indicated in the specification sheet [195].
Figure 13. Schematic illustration of the prevalent corrosion products identified from both cross-sectional and plan view ‘top-down’ characterization methods.

Figure 14. Exposure of K$_2$CrO$_4$ to straw-firing conditions: (a) BSE micrograph of the reaction product. The corresponding EDS-analysis is presented in Table 7. (b) X-Ray diffractogram.
Table 7. Elemental composition of selected regions on the corrosion product resulting from exposure of K₂CrO₄ to straw-firing conditions (cf. Fig. 15a), determined by EDS-analysis

<table>
<thead>
<tr>
<th>Image</th>
<th>Region</th>
<th>Element (wt.-%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O</td>
</tr>
<tr>
<td>Figure 15a</td>
<td>1</td>
<td>33.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>31.9</td>
</tr>
</tbody>
</table>

4. Discussion

High temperature corrosion observed on superheater tubes during biomass firing is widely accepted to be caused by KCl, which condenses on heat exchanger surfaces. The catastrophic corrosion observed is frequently explained by the active oxidation mechanism catalyzed by Cl [24,101,138,186]. Initiation and sustaining mechanisms for the corrosion process are still being discussed in literature [75,135,138,141,192]. For Cr-containing alloys under oxidizing conditions, the K-induced breakaway corrosion of the initial protective Cr₂O₃ layer has been reported as the initiation process (equation 1) [114,115,164].

\[
\text{Cr}_2\text{O}_3(s) + 4\text{KCl}(s) + 2\text{H}_2\text{O}(g) + \frac{3}{2}\text{O}_2(g) \rightarrow 2\text{K}_2\text{CrO}_4(s) + 4\text{HCl}(g)
\]  

The above reaction depletes the alloy of Cr, and thus results in the formation of a non-protective iron-rich oxide layer according to equation 2.

\[
(\text{Cr}_{1-x}\text{Fe}_x)_2\text{O}_3(s) + 4\text{KCl}(s) + \frac{3}{2}\text{O}_2(g) + 2\text{H}_2\text{O} \\
\rightarrow x\text{Fe}_2\text{O}_3(s) + 2(1-x)\text{K}_2\text{CrO}_4(s) + 4\text{HCl}(g)
\]  

The HCl generated from this reaction is able dissociate under oxidizing conditions to give Cl₂(g) (equation 3) [104,138,156], which migrates through the porous oxide (possibly through grain boundaries), to the metal bulk where it chlorinates the metal alloying elements, to generate metal chlorides.

\[
2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Cl}_2(g) + \text{H}_2\text{O}(g)
\]  

\[
\text{M}(s) + x\text{Cl} \rightarrow \text{MCl}_x(s)
\]  

The diffusion of chlorine can also progress through an electrochemical route involving the reduction of Cl at the scale surface and the oxidation of the metal below the scale surface [75,135,192].

68
However, in atmospheres containing SO$_2$(g) (similar to experimental conditions of the present work), the sulphation of KCl is possible (equation 5), and thus the initiation as well as the overall corrosion mechanism may be different. By means of the plan view ‘top-down’ characterization approach applied in the present work, it is observed that the initial synthetic deposit consisting of pure KCl(s), becomes sulphated both at the flue gas/deposit and at the ‘initial’ deposit/oxide interface, after exposure to an SO$_2$ containing flue gas (see Figs. 6 and 7).

\[
2\text{KCl}(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g) \quad (5)
\]

Difference in the flue gas concentration at the deposit/flue gas and deposit/corrosion product interfaces, might be a reason for the greater sulphation of the deposit particles at the deposit/flue gas interface. The sulphation of KCl will proceed with the adsorption of SO$_2$ on the KCl particles, forming the SO$_3$ intermediate, according to a Langmuir adsorption model as proposed for NaCl sulphation [196,197]. The round-shaped cluster accumulations (identified to be K$_2$SO$_4$ particles), around the KCl particles observed in Fig. 6, suggest that the K$_2$SO$_4$ must have formed through an adsorption process and thus supports the above mechanism. In Figs. 6 and 7, KCl was also identified in addition to K$_2$SO$_4$, thereby suggesting an incomplete sulphation. Some experiments have reported incomplete sulphation of KCl particles exposed to simulated straw firing conditions [111], or a reduced sulphation of smaller sized KCl particles due to low porosity of the deposit, which limits effective transport of the flue gas through the entire deposit [112]. Nevertheless, the sulphation of KCl will generate HCl (equation 5), which would also catalyze the rapid corrosion of the alloy, since such reaction has been reported to also favor the chlorination reaction (equation 4) [104].

Furthermore, it is possible that under straw-firing conditions, the resulting K$_2$CrO$_4$ from equation (1) formed during the early stages of the corrosion process, becomes converted to K$_2$SO$_4$ according to equation 6.

\[
4\text{K}_2\text{CrO}_4(s) + 4\text{SO}_2(g) \rightleftharpoons 4\text{K}_2\text{SO}_4(s) + 2\text{Cr}_2\text{O}_3(s) + \text{O}_2(g) \quad (6)
\]

The above reaction could account for the absence of K$_2$CrO$_4$ often identified in reports in literature for similar austenitic stainless steels (see for example [22,118,153]), in the present corrosion products, despite the extensive characterization process employed. Although the Reaction 6 is thermodynamically favourable ($\Delta G = -683$ kJ(T = 500 °C) and -617 kJ(T = 600 °C)) [198], it is still unknown if the initiation process under straw-firing conditions proceeds according to the route in equation (1) and (2), which results in K$_2$CrO$_4$-formation, or through the additional stage according to equation (6). To substantiate this, pure K$_2$CrO$_4$ crystals were exposed in the present work to similar conditions simulating straw-firing. Results from the characterization of the reaction products from such exposure highlighted the presence of K$_2$SO$_4$ in the reaction product (see Fig 14 and Table 7), thereby suggesting that the initiation stage of the corrosion process could proceed through the attack by KCl on the initially formed Cr$_2$O$_3$ and a
subsequent transformation of the resulting K₂CrO₄ to the stable K₂SO₄, or directly through the sulphation of KCl.

Plan view investigations below the sulphated deposit showed a fused layer rich in K and Cl, containing strands rich in Fe. This was also observed together with round-shaped particle agglomerates rich in K and S. The morphologies of these structures show that they have been partly molten (Figs. 8c, 8d, 9b and 9c). However, both KCl and K₂SO₄ exhibit melting temperatures above 560 °C. A potential explanation for such melts at 560 °C could be the formation of a eutectic, since neither pure KCl, nor K₂SO₄ can melt in the temperature range considered in the present experiments. The ability of KCl to form low-melting eutectics with transition metal chlorides in the temperature range (200 – 500 °C) has been reported previously [24,141]. With the depletion of Cr in the oxide and subsurface regions, due to reaction with K, according to equation (1), Fe-chloride formation from the chlorination reaction in equation (4), becomes thermodynamically favourable, and thus the formation of a eutectic melt with KCl below 560 °C is possible. In a melt phase, the rate of sulphation is significantly enhanced and more Cl is generated, which is able to penetrate the porous oxide layer and induce further chlorination of alloying elements [100,111,112].

The resulting metal chlorides formed by the chlorination reaction (4) are stable at the (reducing) oxide/alloy interface, and thus possess high equilibrium vapor pressures [156]. Identification of metal chlorides, on local points close to or at the corrosion front between layer 3 and the bulk alloy (Figs. 11a-b, 12) affirms the stability of these species at such reducing locations. This as well confirms the role of Cl in the active oxidation mechanism. Earlier work has also identified metal chlorides at the corrosion front [128,131,153,199]. However, depending on the vapor pressure of the metal chloride, these species are able to evaporate and become oxidized upon reaching regions with relatively high oxygen potentials, according to equation (8).

\[
\text{MCl}_x(s) \rightleftharpoons \text{MCl}_x(g) \quad (7)
\]

\[
y\text{MCl}_x(g) + \frac{z}{2} \text{O}_2(g) \rightleftharpoons \text{M}_y\text{O}_z(s) + y\text{Cl}_x(g) \quad (8)
\]

Part of the released Cl from the oxidation is able to migrate back through the resulting porous oxide to the corrosion front where it reactivates the chlorination reaction. It is worth noting that the Cl-activity (and thus, the Gibbs free energy) required for the chlorination of metal alloying elements at the corrosion front depends on the alloying element [104,156,200]. Ni is known to require a higher Cl activity (compared to Fe and Cr) in order to form the corresponding Ni-chloride [76]. This difference in Cl-activity may explain the significant increase in Ni-concentration observed within layer 3 of the corrosion product (see Figs. 4, 11 and Table 6). The Ni-rich, sponge-like layer must thus have been formed due to selective chlorination and oxidation of Cr and Fe from such regions, consequently leaving the most stable species (Ni) behind as a skeleton.
Dissimilarities in oxygen partial pressure, for the metal chloride to metal oxide transformation in equation (8), as well as the volatility of the metal chlorides, will determine the hierarchical and morphological arrangement of the resulting oxide layers. CrCl₂ has been reported to possess lower vapor pressure than FeCl₂ [104, 156], thus it is realistic to observe a Cr-rich oxide close to the bulk alloy, and a Fe-rich oxide close to the flue gas/corrosion product interface. Such differences in metal chloride vapor pressures would also explain the identification of Fe in the corrosion product layers located at regions with higher oxygen partial pressures (see Figs. 4, 8c, 9b and the tables therein). Thematically, the identification of 1 wt.-% of Si on the surface of layer 3-pv indicated the precipitation of Si-oxide at such locations with low oxygen partial pressure, because of the low oxygen partial pressure required for oxidation of Si-chloride [156]. The Mn band observed in the EDS maps in Fig 4 is located above the Cr band because of the higher oxygen partial pressured required for conversion of Mn-chloride to Mn-oxide. Both cross-sectional and plan view ‘top-down’ characterization of the corrosion products by EDS-analysis showed that the lower region of the oxide layer (layer 2) contains predominantly Cr. Fe rich particles were located mostly within the sulphated K₂SO₄ and KCl partly molten layer (layer 1-pv) on the top regions of layer 2-cs (and layer 2-pv), and even at the deposit/corrosion product interface, thereby confirming that higher oxygen partial pressures are required for the conversion of Fe-chloride. Despite the dependence of metal-chloride to metal-oxide conversion on oxygen partial pressure, XRD-diffraction results do not show the separate formation of the two metal (Fe and Cr) oxides. This could be because the Cr-oxide formed is too thin to be detected by XRD, despite the grazing incidence measurements employed in the current study. On the other hand, it is possible that the similar rhombohedral crystal structures of Cr₂O₃ and Fe₂O₃ would facilitate the formation of the spinel [FeCr₂O₄], as identified by XRD phase analysis (Fig. 10).

Interestingly, the successive removal and characterization of the sponge-like layer, (layer 3) of the corrosion product, using both XRD and EDS have shown that S also exists together with Ni in this layer and can be attributed to the Ni₃S₂ phase as confirmed by XRD phase analysis. Identification of Ni₃S₂ in the corrosion product indicates that, apart from active oxidation of the alloy exposed to straw-firing conditions, sulphidation may be an attack mode on the non-reacted nickel. The Ni sulphidation is observed to also proceed within the region of selective corrosion along grain boundaries (see Fig 11). The identification of sulphidation induced attack in corrosion products resulting from coal firing, as well as co-firing of straw with coal has been reported [103], and the responsible mechanism for sulphidation attack on Ni has been discussed by several authors [201–204]. For direct reaction between S and the metal, it is a requirement for the equilibrium partial pressure of S to be higher than that of the dissociation of the resulting metal sulphide. Additionally, the stability region of the metal oxide should overlap with that of the S partial pressure. Under such conditions, S from the flue gas can diffuse through the porous corrosion product layers to form the metal sulphide below these layers. The presence of metal alloying elements with high affinity for oxide formation (such as Cr) will catalyze the sulphidation attack by enhancing the transfer of S via direct reaction of SO₂ with the oxide former [201,203]. Another possible mechanism will involve direct transport of molecular SO₂ through cracks and pores in the corrosion
product layers (layer 1 and 2), to the sponge-like Ni rich layer of the corrosion product (layer 3). At such position, the oxygen potential is relatively low and thus presents a non-oxidizing atmosphere which would facilitate the sulphidation reaction [201]. Seiersten and Kofstad [202], suggested that the sulphidation of Ni might involve the NiSO₄ intermediate, which converts to the sulphide at lower temperatures. However, such mechanism is expected to result in the formation of NiO and Ni₃S₂ in a 4:1 ratio. The formed NiO from outward diffusion of Ni often leads to detachment of the scale. However, the Ni₃S₂ containing layer (layer 3) observed in the present study showed no signs of detachment (see Fig 3c), thus it is unlikely that the sulphidation attack reported here proceeded according to the mechanism involving the NiSO₄ intermediate.

In summary, the present results from both cross-sectional and the plan view ‘top-down’ characterization of corrosion products, resulting from laboratory scale experiments, indicate that both active oxidation and sulphidation corrosion mechanisms operate during straw-firing.

5. Conclusions

Corrosion products on an austenitic stainless steel (TP 347H FG) exposed to simulated straw-firing conditions under laboratory conditions have been investigated. Thorough characterization of the complete surface region of the exposed sample was achieved from both cross section analysis and a plan view analysis in combination with removal of the corrosion products. Complementary results were revealed from microscopic (LOM, SEM), spectroscopic (EDS) and diffraction analysis (XRD) as a function of distance from the initial deposit surface.

In particular the depth-resolved (plan view ‘top-down’) characterization approach revealed interesting features such as the formation of a KCl melt layer below the initial deposit and the local formation of Cl-rich melts at the corrosion front which are not always visible from cross sections only.

The combination of both the way of characterization (cross section and plan view as a function of depth) and the various characterization methods (LOM, SEM, EDS, XRD) revealed unique results, which are used to further validate the corrosion mechanisms under straw-firing conditions.

Based on the present results it is suggested that the sulphation of KCl as well as the formation of a KCl-Fe-chloride melt within the sulphate could be responsible for the generation of Cl to sustain the active oxidation mechanism.

The morphology and chemistry of the corrosion products show that for an austenitic stainless steel, both Cr and Fe are easily attacked by Cl according to the active oxidation mechanism.

Ni is not readily attacked by Cl and is left as a sponge-like layer due to selective oxidation of Cr and Fe. However, sulphidation of this unreacted nickel can occur.
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References

References cited in this paper are collected in the general reference list of the thesis.
4.2 – Complementary methods for characterization of corrosion products on a plant exposed superheater tube

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Abstract

In this work, complex corrosion products on a superheater tube exposed to biomass-firing were characterized by the complementary use of energy-dispersive synchrotron diffraction, electron microscopy and energy-dispersive X-ray spectroscopy. Non-destructive synchrotron diffraction in transmission geometry measuring with a small gauge volume from the sample surface through the corrosion product, allowed depth-resolved phase identification and revealed the presence of (Fe,Cr)\textsubscript{2}O\textsubscript{3} and FeCr\textsubscript{2}O\textsubscript{4}. This was supplemented by microstructural and elemental analysis correlating the additional presence of a Ni-rich-austenite phase to selective removal of Fe and Cr from the alloy, via a KCl-induced corrosion mechanism. Compositional variations were related to diffraction results and revealed a qualitative influence of the spinel cation-concentration on the observed diffraction lines.

\textbf{Keywords:} Stainless steel; (Synchrotron) X-ray diffraction; SEM; High temperature corrosion; Chlorination; Spinel.
1. Introduction

Although combustion of biomass provides a ‘CO$_2$ neutral’ means of energy generation, this fuel gives operational challenges during combustion in power plants [8,105,205]. The high alkali chloride content in biomass causes fast corrosion of superheaters due to the formation of corrosive deposits (rich in KCl) as well as the presence of corrosive species in the flue gas (HCl, SO$_2$, etc.) [19,21,25,206]. In particular, operation at lower steam temperatures (~ 540 °C) to control the rate of corrosion limits the electrical efficiency of biomass-fired power plants [31]. The development of corrosion resistant alloys and coatings relies on detailed understanding of the underlying corrosion mechanisms. For corrosion under biomass firing (i.e. alkali chloride containing) conditions, a comprehensive characterization of corrosion products is among the prerequisites for understanding the associated high temperature corrosion mechanisms.

Corrosion products resulting from exposure to alkali chlorides in power plants are often heterogeneous and may be up to several hundreds of micrometres thick. Thus, the use of conventional characterization techniques is not straightforward. In addition, the solubility of some of the corrosion products in water-based lubricants raises challenges during sample preparation prior to characterization. Laboratory exposures studying the influence of specific parameters on corrosion of samples with simplified geometries have successfully used advanced characterization techniques (for example, transmission electron microscopy [125], auger electron spectroscopy [124], chronoamperometry [207], etc.) to characterize corrosion products or monitor their formation in-situ [192]. Such advanced techniques are difficult to use for plant exposed samples not only because of the complex morphology of corrosion products originating from real plant exposure but also due to challenging sample geometries.

Some studies have attempted to characterize the corrosion products on plant exposed test superheaters or probes [24,31,94,95,100,101,104]. In these studies, the complex morphology of corrosion products restricted the characterization to light optical and scanning electron microscopy as well as energy dispersive X-ray spectroscopy, mostly carried out on cross sections of samples. Although X-ray diffraction strongly supplements microscopy and elemental analysis, only few studies have attempted to identify the crystalline corrosion product phases on real superheater tubes by this technique. The low penetration depth (several micrometres only) of the employed conventional X-ray sources in such studies limited the analysis to the very near surface region of the corrosion products thereby detecting mostly KCl and K$_2$SO$_4$ [94,95] and prevented detailed phase analysis of the fairly thick corrosion products.

It has recently been demonstrated by some of the present authors that complex corrosion products resulting from laboratory exposure mimicking that in biomass-fired power plants, can be comprehensively characterized by the complementary use of scanning electron microscopy, energy dispersive X-ray spectroscopy and X-ray diffraction with conventional X-ray sources in combination with successive layer removal [208]. Though time consuming, the reported top-down plan view method revealed results that aided understanding of the deposit-gas interactions as well as the role of chlorination and sulphidation as corrosion mechanisms. Aiming for a methodology for comprehensive
characterization of corrosion products on real superheater tubes exposed to biomass firing in power plants, the present work demonstrates the capability of using energy-dispersive synchrotron diffraction in transmission geometry for non-destructive depth profiling of complex and bulky corrosion products on a plant exposed superheater tube. The results were complemented with scanning electron microscopy and energy dispersive X-ray spectroscopy and contribute to understanding of the corrosion mechanisms on samples obtained from a biomass firing power plant.

2. Experimental

2.1. Sample history

The investigated sample originated from a superheater loop in a biomass suspension fired 350 MWth - boiler (Amager Power Station, Unit 1) located in Denmark. The superheater had been operated for 30534 hours. During this period the outlet steam temperature was approx. 540 °C and the fuel used was straw and wood pellets. The superheater has an outer diameter of 38 mm and a wall thickness of 6.3 mm. It consists of austenitic stainless steel TP 347H in a fine-grained version (FG), which is one of the commercially applied materials. The chemical composition is given in Table 1.

Table 1. Chemical composition (in wt. %) of TP 347H FG determined by energy dispersive X-ray spectroscopy. A fusion thermal conductivity unit LECO CS230 was used for the measurement of the carbon content [149].

<table>
<thead>
<tr>
<th></th>
<th>Fe</th>
<th>Si</th>
<th>Mn</th>
<th>Cr</th>
<th>Ni</th>
<th>Nb</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bal.</td>
<td>0.4</td>
<td>2.0</td>
<td>18.2</td>
<td>10.1</td>
<td>0.6</td>
<td>0.057</td>
<td></td>
</tr>
</tbody>
</table>

A ring of the exposed superheater was cut with a saw from longer tube sections under dry conditions. This was then ‘cold-embedded’ in epoxy under vacuum to avoid spallation of corrosion product layers during experimental investigations and sample handling. By means of grinding under water-free conditions (using absolute ethanol, 99.9%, as lubricant) to reduce removal of water soluble phases of the corrosion products, the thickness of the embedded ring was reduced to 3 mm.

2.2. Depth-resolved energy-dispersive synchrotron diffraction

2.2.1 Experimental setup of diffraction measurements

Depth profiling of the corrosion products by diffraction applying synchrotron radiation was carried out at the Energy Dispersive Diffraction (EDDI) materials science beamline at the Berlin synchrotron storage ring (BESSY II). The sample investigated was a 3 mm thick ring obtained from the exposed superheater tube as described in section 2.1.
Unlike the angle-dispersive diffraction mode, the energy-dispersive diffraction is carried out at a fixed diffraction angle and generates a multitude of diffraction lines during one measurement at fixed diffraction angle [182]. For the present study, the diffraction angle was set to $2\theta = 6^\circ$. A snapshot of the diffractometer setup applied for depth profiling is shown in Figure 1a and schematically illustrated in Figure 1b.

Figure 1. Snapshot (a) and schematic illustration (b) of the setup applied for depth profiling by means of energy-dispersive synchrotron diffraction at the EDDI beamline, BESSY II.

The highly brilliant and high intense synchrotron radiation enables measurements in transmission geometry through the 3 mm thick sample of the present study, and it further allows the use of small gauge volumes, resulting in good spatial resolution [181]. The gauge volume was defined by additional narrow slit systems in the primary and secondary beam paths as shown in Figure 1b (for details, see [182,209–211]). The dimensions of these slits in the axial and equatorial direction were 10 μm and 300 μm, respectively.

Unique depth-resolution was achieved by defined z-translations of the sample relative to the gauge volume in step sizes of 4 μm. As the gauge volume height of 10 μm is larger than each single sample displacement, successively recorded energy-dispersive diffraction spectra partly cover the same sample regions. As a result, each measurement was assigned its corresponding depth as the sliding average over the 4 μm of sample displacement.

At each sample position z, energy-dispersive diffraction spectra covering the range of up to 120 keV were measured with an acquisition time of 150 s per displacement step, thus, per spectra recorded at a specific depth. Subsequent analysis considered diffraction lines between 20-85 keV which covers the most efficient photon flux in energy-dispersive experiments at EDDI [182]. Starting at the surface (defined by the first diffraction signal from the sample), depth-resolved measurements were carried out...
through the entire corrosion product until the original bulk alloy was reached. This measurement procedure was applied on two locations along the sample ring (tube): on the windward side (so-called position 12 o’clock) of the tube and on a position located 270 ° from the windward side (position 9 o’clock). These positions are schematically illustrated in Figure 2.

![Figure 2. Schematic illustration of the tube circumference showing positions on which investigations were carried out.](image)

**2.2.2 Analysis of the measured energy-dispersive diffraction spectra**

With the aforementioned procedure for non-destructive depth-resolved energy-dispersive synchrotron diffraction analysis of the corrosion product on different locations of the superheater tube, hundreds of diffraction spectra were measured subsequently as a function of depth. The recorded spectra were evaluated using an analysis procedure programmed in MATLAB and provided by the EDDI beamline scientists. Prior to peak profile fitting, the measured diffraction profiles were corrected for instrumental effects, which implied corrections of the Wiggler spectrum, dead time correction and intensity corrections according to slight changes of the ring current during the measurements. Absorption correction was applied for Fe as the main absorbing component, whereas an absorption correction for each individual phase was not applied due to obvious changes of the phase fractions within the corrosion product. The measurement of a reference sample consisting of Au powder revealed an excellent alignment status of the diffractometer, thus, no additional instrumental correction of the diffraction line positions was necessary.

The background was subtracted by manual assignment of the background positions for each diffraction line in the spectra. Diffraction peaks were fitted using a pseudo-Voigt profile function, which provided the position $E_{\text{hkl}}$ of all diffraction lines hkl in the various spectra. The respective lattice planar spacings $d_{\text{hkl}}$ were calculated according to
\[ d^\text{hkl} = \frac{hc}{2\sin \theta} \frac{1}{E^\text{hkl}} \]  

(1)

(h is the Plank’s constant, c is the speed of light and \( \theta \) corresponds to half of the applied constant diffraction angle) [212], which allowed qualitative phase analysis throughout the corrosion product.

2.3. Electron microscopy and energy dispersive X-ray spectroscopy

In addition to depth profiling by means of energy-dispersive synchrotron diffraction, Scanning Electron Microscopy (SEM) analysis was carried out on the same positions along the superheater circumference where depth profiling by diffraction was done. Gamma ray irradiation indicator labels were used to keep track of the positions where depth profiling was undertaken and at exactly these positions on the sample’s cross section, the microstructure of corrosion products was investigated with a backscatter electron detector in a SEM (Quanta ESEM FEG, FEI) using an acceleration voltage of 15 keV. Prior to SEM investigations, the sample was coated with carbon.

An energy dispersive X-ray spectrometer (Oxford instruments, 80mm², X-Max, SDD) attached to the SEM was used for chemical analysis of the corrosion products. Energy dispersive X-ray spectroscopy (EDS) analysis was carried out with an acceleration voltage of 15 keV. Analysis involved both elemental mapping and elemental re-quantification from the acquired maps using the Aztec and INCA software (Oxford instruments), respectively. The elemental re-quantification involved division of investigated cross sections into 10 μm thick meshes along the direction parallel to the surface of the corrosion product (the y-coordinate), as shown in Figure 3. The length of these meshes corresponds to the full length of the investigated micrograph, which amounts to several hundreds of micrometers. At 10 μm equidistant positions (\( i \)) along the direction perpendicular to the surface of the corrosion product (the z-coordinate), the average concentration of an element, \( \bar{C}_{z_i} \), is re-quantified from the corresponding strip of the mesh. \( \bar{C}_{z_i} \) is plotted as a function of distance along the z-coordinate to obtain a reliable 1-dimensional profile of the concentration of various elements averaged over several hundreds of micrometers compared to the conventional EDS line scan and point measurement procedures, which represent local snapshots not being representative for samples with inhomogeneous elemental distribution [183].
Figure 3. Schematic illustration of the division of a cross section into meshes used for re-quantification of elemental composition from the measured EDS maps.

3. Results

3.1. Non-destructive depth profiling with energy-dispersive synchrotron diffraction

3.1.1. Measurements on the windward side (position 12 o’clock)

The crystalline phases present at different depths of the sample were revealed from subsequent diffraction measurements with controlled displacement (step size = 4 μm) of the sample in z-direction. The evolution of these phases as a function of depth on the windward side (position 12 o’clock) is represented by the contour plot in Figure 4. At the near surface regions (< 150 μm), detected corrosion product phases comprise of (Fe,Cr)2O3 (designated as M2O3, where M = Fe and Cr), spinel FeCr2O4 (designated as M3O4, with M = Fe and Cr), KCl and NiCl2. The diffraction lines corresponding to the spinel phase are observed to extend deeper into the corrosion product (> 150 μm) thereby suggesting that the corundum phase ((Fe,Cr)2O3) is predominantly located in the near surface regions while the spinel (FeCr2O4) is the dominant phase in the middle of the corrosion product. Figure 4 shows that two competing austenite phases are present at different depths. Diffraction lines corresponding to a Ni-rich austenite phase (designated as $\gamma^{Ni}$) were observed deeper in the corrosion product (from about 150 μm). These diffraction lines disappear with the emergence of diffraction lines from the austenitic stainless steel bulk (designated as $\gamma$) which then extends into the bulk of the alloy.
Figure 4. Phase evolution as a function of depth within the corrosion product on the windward side (position 12 o’clock). M = Fe and Cr in the phases designed as M₂O₃ and M₃O₄.

In Figure 5, changes in peak positions (in the energy scale) as a function of depth are revealed for the identified phases. The near surface region, the middle of the corrosion product and the bulk alloy are denoted as regions I, II and III, respectively. A slight increase in the diffraction line position (ΔE ~ 0.1 keV) with depth was observed for the corundum diffraction lines, in the near surface region where this phase was dominant. This is shown on the example of (M₂O₃)₀₁₂ in Figure 5a. Diffraction lines of the spinel phase shift to lower energy values with increasing depth (indicated as S₁ in Figure 5b and also visible in Figure 5c). As the gauge volume was scanned from the middle of the corrosion product into the bulk alloy (from region II to III), it is observed that the (M₃O₄)⁴₀₀ diffraction line disappears, while the (γ)¹¹¹ diffraction line appears. Down to approximately 250 μm within the middle of the corrosion product (region II), diffraction lines corresponding to the Ni-rich austenite phase (γNi) shifted to lower energy values (ΔE ~0.2 keV) (see Figure 5d for the (γNi)²₀₀ diffraction line). Afterwards, the position of these diffraction lines gradually shifted to higher energy values until approximately 500 μm, where the Ni-rich austenite disappears and only diffraction lines corresponding to the bulk alloy (γ) were recorded and dominate within the bulk of the alloy.
Figure 5. Evolution of the diffraction line maxima for various phases of the corrosion product observed on the windward side (position 12 o’clock). M = Fe and Cr in the phases designed as M$_2$O$_3$ and M$_3$O$_4$. In (c) and (d), after approximately 500 μm, the (M$_3$O$_4$)$_{400}$ and (M$_3$O$_4$)$_{311}$ diffraction lines, respectively, disappear while those of (γ)$_{111}$ and (γ)$_{200}$ appear. The regions I, II and III denote the near surface region, middle of the corrosion product and the bulk alloy, respectively.

3.1.2. Measurements on position located 270° from the windward side (position 9 o’clock)

It is expected that variations in factors such as the deposition rate, flue gas temperature, superheater configuration, etc. may cause differences in the type of corrosion products and the degree of corrosion around the tube circumference. However, results from depth profiling at position 9 o’clock (Figure 6a) reveal the presence of the same oxide phases, but with different extension in depth compared with the corrosion products on position 12 o’clock (cf. Figures 4 and 6). At position 9 o’clock, the corundum phase (M$_2$O$_3$) was predominant in region I of the corrosion product (< 50 μm), while the spinel (M$_3$O$_4$) phase was predominant within region II of the corrosion product, and extended into region III, presumably in the form of grain boundary attack. Although distinct diffraction lines corresponding to the Ni-rich austenite phase (γ$^{Ni}$) were not observed on position 9 o’clock, the phase seem to be present, because it caused large asymmetries in the (γ)$_{111}$ and (γ)$_{200}$ diffraction lines due to overlap of diffraction lines for the two different austenite phases (see for example, Figure 6b).
Figure 6. (a) Phase evolution as a function of depth within the corrosion product on the position located 270° from the windward side (position 9 o’clock). (b) Asymmetry in the (γ)_{111} diffraction line as a result of overlap with the Ni-rich austenite (γ^{Ni})_{111} diffraction line. (c) Variation in diffraction line maxima for the spinel phase M₃O₄. M = Fe and Cr in the phases designed as M₂O₃ and M₃O₄.

Fitting of the spinel diffraction lines to a pseudo Voigt function (Figure 6c) showed that the energy position of intensity maxima of these lines varied with depth and two remarkable steps were observed. These steps are indicated as S1 and S2 in Figure 6c for both the 311 and 440 diffraction lines of M₃O₄.
Both diffraction line maxima shift first to lower energy (S1), and thereafter, exhibit a shift (S2) to higher energy as the scan proceeds from the middle of the corrosion product towards the bulk alloy.

### 3.2. Microscopic investigation and elemental composition of corrosion products

#### 3.2.1. Microstructure of corrosion products

Backscattered electron (BSE) imaging is excellent for the characterization of corrosion products under complex atmospheres because the contrast originates from differences in atomic number of elements in the corrosion product and, thus, gives a hint on the various phases. This is reflected in the cross-sectional BSE micrographs in Figure 7, which show the microstructure of corrosion products on position 12 o’clock of the superheater. Differences between the atomic number of elements included in the corrosion products, and the bulk alloy, are expected to result in contrast differences (Figure 7a). In this case, the bulk alloy (γ) with a higher atomic number appears brighter compared to the corrosion product, as a result of generation of a higher fraction of backscattered electrons from this region. An approximately 300 μm thick corrosion product layer extends into the bulk alloy, where selective attack of the alloy grain boundaries is visible. The corrosion product appears to have cracked in a direction parallel to the corrosion product/bulk alloy interface.

![Figure 7](image)

**Figure 7.** BSE micrographs showing: (a) an overview of the corrosion product observed on the windward side (position 12 o’clock), and (b, c): magnified images of marked regions in (a).

Based on the resulting contrast differences in micrographs showing magnified views of the corrosion product (Figure 7b, c), a phase with a higher atomic number is revealed. This appears in the form of islands (in the near surface region, Figure 7b) and as porous regions between the middle of the corrosion product.
product and the region of grain boundary attack (Figure 7c). This (high atomic weight) phase present in the corrosion product (i.e. the bright islands/regions) refers to the Ni-rich austenite ($\gamma^{\text{Ni}}$) phase, as was also observed from energy-dispersive synchrotron diffraction (Figure 4).

Microscopic investigations also show that the microstructure of corrosion products was qualitatively similar on different locations around the tube. Thus, the same type and morphology of phases was observed, although the overall thickness of the corrosion product appears to be different, which agrees with suggestions based on the diffraction results discussed above. This is illustrated with the corrosion product in Figure 8, for position 9 o’clock (i.e. 270° from the windward side), which is similar to that on position 12 o’clock (Figure 7). The presence of a phase with a higher atomic number in the corrosion product is visible in the insert in Figure 8a. Moreover, as was observed on position 12 o’clock (cf. Figure 7), the corrosion products on position 9 o’clock also progressed into the bulk alloy through regions that outline the alloy grain boundaries, thus suggesting grain boundary attack. However, a lower thickness (approximately 150 μm) of compact corrosion product is observed on position 9 o’clock, but with a deeper (>500 μm) internal attack along the grain boundaries. Microscopic investigations on position 9 o’clock also revealed the propagation of cracks through the attacked alloy grain boundaries (Figure 8b) in addition to severe disintegration within the Ni-rich porous regions.

![Figure 8](image.png)

**Figure 8.** BSE micrographs showing: (a) an overview of the corrosion product observed on position 9 o’clock, and (b) crack propagation along the attacked alloy grain boundaries. Insert in (a) show regions with a brighter contrast attributed to the Ni-rich austenite ($\gamma^{\text{Ni}}$) phase.

### 3.2.2. Compositional analysis of corrosion products

Microstructure information on locations where both depth profiling by diffraction, and microscopic investigations were carried out was further supplemented by EDS analysis. Thus, EDS contributed to
verification of the conclusions based on diffraction and microscopy, and revealed good agreement between the various methods.

The elemental composition of corrosion products observed on position 12 o’clock and 9 o’clock, respectively, are presented in EDS maps in Figure 9a and b. The maps show that the corrosion products comprised mainly Fe, Cr and O (i.e. a Fe-Cr containing oxide). Additionally, local accumulation of S and Cl is observed in the corrosion products (although clear identification of sulphides/sulphates by energy-dispersive diffraction was difficult due to severe overlap with diffraction lines of metal oxides). EDS also indicates that K is present in the corrosion product. Close examination of the Ni and O maps on both positions reveal that Ni was incorporated in the corrosion product in a metallic form, rather than as an oxide. The metal (Ni) is scantly distributed (or absent, Figure 9b) in the near surface regions, but becomes abundantly present from the middle of the corrosion product towards the region of grain boundary attack.

![Figure 9](image)

**Figure 9.** EDS maps showing the distribution of elements in the corrosion product observed on (a) the windward side (position 12 o’clock), (b) on the position located 270 o from the windward side (position 9 o’clock).

Using the elemental re-quantification method as described in section 2.3, variations in the (average) elemental concentration in the corrosion products were revealed as a function of depth (Figures 10a and b). In particular, the high averaged Ni concentration (~28 wt. %) in the middle of the corrosion product (cf. Figure 10a), is in good agreement with distinct identification of diffraction lines attributed to the Ni-rich austenite ($\gamma^{\text{Ni}}$) phase on position 12 o’clock by energy-dispersive diffraction depth profiling (cf. Figure 4). In contrast, on position 9 o’clock (Figure 10b), the measured average Ni concentration is lower (< 20 wt. %) in the middle of the corrosion product, which explains the observed asymmetry in the $\gamma$ diffraction lines (Figure 6b) as the lattice spacing for both austenite phases is less different with reduced
Ni content and, in addition, a lower phase fraction would also cause low intensities of the $\gamma^{\text{Ni}}$ diffraction lines.

![Graph showing depth profile of average composition of selected elements in the corrosion product.](image)

Figure 10. Depth profile of the average composition of selected elements in the corrosion product observed on (a) the windward side (position 12 o’clock) and (b) on the position located 270 o from the windward side (position 9 o’clock) obtained through the elemental re-quantification method from the maps in Figures 8a and 8b, respectively, (note the difference in x-axis scales).

Variations in Fe and Cr concentrations across the corrosion product follow opposing trends, and in addition, differ for the different positions investigated (Figure 10). On position 12 o’clock, the average Fe concentration increases in the near surface region (40 to 47 wt. %), but gradually decreases to ~28 wt.
% in the middle of the corrosion product before increasing to the bulk alloy value (~62 wt. %). In contrast, the average Cr concentration decreases (to ~10 wt. %) in the near surface region, before a steep increase to ~23 wt. % in the middle of the corrosion product. Afterwards, the Cr concentration drops to ~ 7 wt. % in the middle of the corrosion product before increasing to its nominal bulk alloy concentration (~18 wt. %). On position 9 o’clock (Figure 10b), the variation in average Fe and Cr concentrations in the near surface region is similar to that observed on position 12 o’clock (cf. Figure 10a). However, the variation in average concentration of these elements in the middle of the corrosion product is different from the trend observed on position 12 o’clock. After a decrease to ~29 wt. %, the average Fe concentration shows a steady increase to ~55 wt. % before approaching the bulk alloy value (~62 wt. %). Concurrently, a steep increase in average Cr concentration from ~6 to 24 wt. % in the middle of the corrosion product is observed. The Cr concentration is maintained at this value in the middle of the corrosion product before gradually decreasing to the bulk alloy value. The relationship between these trends and the changes in energy position of diffraction lines is discussed in the next section.

4. Discussion

Results presented in section 3 illustrate the capability of energy dispersive synchrotron diffraction in the applied transmission geometry with small gauge volume, for depth-resolved characterization of the complex and thick corrosion products observed after high temperature corrosion of superheaters during biomass-firing. Results from depth profiling by diffraction are supplemented with microscopy results by SEM and chemical element analysis by EDS. In the following subsections, these results will be discussed by first suggesting the possible corrosion mechanism and subsequently explaining how this leads to the observed variation in elemental composition within the corrosion products.

4.1. High temperature corrosion under biomass-firing conditions and mechanism of corrosion attack

The high content of alkali-chlorides in deposits formed during combustion of biomass in power plants is chiefly responsible for the severe corrosion attack on superheaters (see for example, [138] and the references therein). KCl (present in the deposit) can either react: (a) directly with the oxide of the alloying elements, M, according to the reaction: $\text{M}_2\text{O}_3(s) + 4\text{KCl}(g) + 2\text{H}_2\text{O}(g) + \frac{3}{2}\text{O}_2(g) \rightleftharpoons 2\text{K}_2\text{M}_\text{O}_4(s) + 4\text{HCl}(g)$, or (b) with gaseous species in the flue gas ($\text{SO}_2$) in accordance with the reaction: $2\text{KCl}(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O} \rightleftharpoons \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g)$, to generate Cl-bearing species (HCl).

As the oxide forming element is consumed by reaction with KCl (option (a) above), the formation of a protective oxide is suppressed under biomass-firing conditions. HCl resulting from either of the above reactions can dissociate to produce Cl [156] which propagates the corrosion attack. Alternatively, direct dissociation of the KCl can serve as a potential source of Cl to propagate the corrosion attack [135]. Propagation primarily involves reaction of Cl (chlorination) with the alloying elements ($\text{M}(s) + x\text{Cl} \rightleftharpoons \text{MCl}_x(s)$). This may proceed by Cl transport through surfaces of cracks and pores in the corrosion product.
[131], oxide grain boundaries [135] or the alloy grain boundaries since they provide faster diffusion pathways. Microscopy results indicate that the corrosion attack predominantly propagated through the alloy grain boundaries (Figures 7 and 8) and, as a result, caused the severe grain boundary attack.

The thermodynamic favourability of chlorination [76] influences the selective nature of corrosion attack. Ni-rich islands and porous regions observed by microscopy (Figures 7 and 8), and high Ni concentrations observed by EDS (Figure 10) are in agreement with thermodynamic stipulations [76], and attributed to selective attack due to the higher driving force for the chlorination of Fe and Cr compared to Ni. In particular, the identification of a Ni-rich austenite phase $\gamma^{\text{Ni}}$ from depth-resolved diffraction (Figure 4) can be explained by the thermodynamics on the chlorination reaction which results in selective attack of Cr and Fe. Similarly, the development of a Ni-rich austenite phase on the same steel due to selective Fe and Cr attack was also observed under controlled laboratory conditions [213]. The variation in the diffraction line positions of $\gamma^{\text{Ni}}$ (Figure 5d) within the corrosion product hints at a non-linear dependence of its lattice parameter on the Ni concentration. Nonlinear variation of the lattice parameter with Ni concentration has similarly been observed in fcc Fe-Ni alloys with varying Ni contents [214].

4.2. Oxide phase partitioning in the corrosion product

The fate of metal chlorides formed from the chlorination reaction is dependent on their volatility as well as the oxygen partial pressure ($p_{O_2}$) at locations where they are formed. The interplay between these factors will influence phase partition of oxides in the corrosion products which may be difficult to analyse in bulky corrosion products. Generally, the metal chloride of Fe (FeCl$_2$) exhibits higher partial pressures than that of Cr (CrCl$_2$) within the estimated metal temperatures of the investigated sample (below 600 °C) [76]. Similarly, the $p_{O_2}$ required for conversion of the FeCl$_2$ to Fe-oxides is higher than that for a similar conversion of CrCl$_2$. It therefore follows that the corrosion product will be partitioned into Fe-oxides at the near surface regions, and Cr-oxides close to the bulk alloy (i.e. at the corrosion front). However, analysis and comparison of results from depth-resolved diffraction analysis and EDS reveal that oxides of these elements (Fe and Cr) are not clearly partitioned in the corrosion product (cf. Figures 4, 5 and 10a, b). Deposit shedding is a common phenomenon occurring naturally or artificially induced in power plants, and may cause descaling of the initially formed oxides, thereby exposing the internal oxides to the corrosive atmosphere [188]. This may be responsible for the observed deviation of oxide composition from the ideal segregation into an external Fe-rich and internal Cr-rich oxide.

Alternatively, the possibility of Cr to be incorporated in iron oxide may cause solid solutions of Cr-Fe-O [215,216]. Interestingly, in accordance with influencing factors stated above, depth profiling by energy-dispersive diffraction (cf. Figure 4) shows that in the near surface region, the oxide phase was a solid solution of Cr in the iron oxide Fe$_2$O$_3$ (Cr$_{x}$Fe$_{2-x}$O$_3$, corundum) while the middle of the corrosion product consisted of a solid solution of Cr in Fe$_3$O$_4$ (FeCr$_{y}$Fe$_{2-x}$O$_4$, spinel). Thus, a possible gradient in $p_{O_2}$ allowed formation of spinel in the middle of the corrosion product. For the corundum phase, an increase in Cr fraction causes a reduction in its lattice parameter [216,217] and explains the slight shift
of corresponding diffraction lines observed in Figure 5a. However, for the spinel phase, the effect of Cr fraction on the lattice parameter is not straightforward. In the Cr rich spinel (x=2 in FeCrₓFe₂₋ₓO₄), Cr³⁺, due to its high octahedral stabilization energy [218–220], preferentially occupies octahedral sites, thus, preserving a normal spinel structure with Fe²⁺ ions in tetrahedral sites. In the Fe-rich spinel, (x=0 in FeCrₓFe₂₋ₓO₄), structurally equivalent positions become occupied by different atoms such that Fe³⁺ ions are distributed between octahedral and tetrahedral sites resulting in an inversed spinel structure [221,222]. A deviation from Vegard’s law follows this difference in crystal structure and causes a nonlinear variation of the lattice parameter from Fe₃O₄ to FeCr₂O₄ (Figure 11a) [217]. Proper elemental analysis revealing cation valences would be required to follow this effect [223], but is beyond the capability of EDS employed in this study. However, to facilitate a qualitative explanation for the shifts in energy position of the spinel diffraction lines (cf. Figures 5 and 6), the amount of Cr in the spinel (x) is estimated using the relationship, \( x = \frac{3k}{1 + k} \) where \( k = (\text{Cr}/\text{Fe}) \) in at. % (Figure 11b, c). This qualitative estimation (see Appendix for details) reveals that x varies between 0.4 and 1.3 with progression into the middle (< ~200 μm) of the corrosion product. Such increase in Cr content in the FeCrₓFe₂₋ₓO₄ system, causes an increase in lattice parameter, in accordance with values reported in [217] and [224] (Figure 11a). Interestingly, this is also in accordance with a shift to lower energies (S1 in Figures 5b and 6c) observed for the diffraction lines of the spinel phase, suggesting that a change from purely inverse, to a mixture of both inverse and normal spinel occurs when progressing towards the middle of the corrosion product [217]. For x values ranging from ~ 0.6 to ~ 1.5, a mixture of inverse and normal spinel is favoured [217,224], hence, the subsequent variation in x observed deeper in the corrosion product should not provoke significant changes in the energy position of the spinel diffraction lines. However, a further shift to higher energies (S2 in Figure 6d) observed for the spinel diffraction lines in position 9 o’clock, possibly implies that x values approached a value of 2, and indicate a change from mixed spinel to the normal Cr-rich spinel (FeCr₂O₄). This clearly highlights an under estimation of the amount of Cr in the spinel, at position 9 o’clock, at locations deeper in the corrosion product since the estimation does not take into account some metallic Fe rich regions present in these locations (Figure 9b).
Figure 11. (a) Dependence of the lattice parameter ‘a’ on the Cr content ‘x’ for the FeCr$_x$Fe$_{2-x}$O$_4$ system according to values reported in [217]. Estimated variation of ‘x’ with distance in the corrosion product on (b) the windward side, ‘position 12 o’clock’, and (c) the position located 270 $^\circ$ from the windward side, ‘position 9 o’clock’.

Although the presence of stresses in the corrosion product will contribute to the observed shifts in diffraction line positions, the steep variation in chemical composition revealed by EDS suggests that the shifts are possibility due to chemical gradients in the corrosion products. This effect clearly will complicate any analysis of the stress condition in the corrosion product and was not attempted in the present study.

5. Conclusions

Corrosion products on a plant exposed superheater tube were studied with the complementary use of energy-dispersive synchrotron diffraction, SEM and EDS. The techniques allow for comprehensive characterization of the rather complex corrosion products resulting from biomass-firing.
By sample displacement in small steps in the z-direction relative to a constrained gauge volume, depth profiling of corrosion product phases is feasible by means of energy dispersive synchrotron diffraction in transmission geometry. This technique reveals the predominant corrosion product phases and in addition, captures the possible effect of compositional changes on their crystallographic properties. In particular, the presence of a Ni-rich austenite phase resulting from the selective corrosion attack of Fe and Cr from the bulk alloy was clearly revealed with synchrotron diffraction depth profiling.

Corrosion products that formed on different positions on the superheater tube varied quantitatively (in terms of thickness), but not qualitatively (composition and morphology of phases). The qualitative agreement in the chemical composition, phase formation and morphology of the corrosion product along the circumference of a superheater tube, as demonstrated in the present study with the example of two locations (12 o’clock and 9 o’clock),

The corrosion product was mainly the Cr$_x$Fe$_{2-x}$O$_3$ corundum phase in the near surface region, while the FeCr$_x$Fe$_{2-x}$O$_4$ spinel phase dominated in larger depth of the corrosion scale. Results from all techniques agreed in revealing the presence of Ni-rich regions within the corrosion product due to KCl-induced selective attack of Fe and Cr from the alloy. Thus, Ni based materials may offer better corrosion resistance to biomass-induced corrosion.

Observation of severe grain boundary attack was only captured through morphological investigations with SEM, whereas diffraction analysis cannot relate detected phases to their location and local distribution within the measured volume. Therefore, it is suggested that a comprehensive characterization should involve complementary techniques, which should each be applied on the same location, as carried out in the present study.

By further supplementing both diffraction depth profiling and SEM characterisation with elemental analysis by EDS, chemical variations within phases in the corrosion product can be revealed. This approach permitted a qualitative analysis of the effect of chemical gradients on the crystal lattice parameter of spinel identified in the corrosion product and thus, may be extended for characterization of complex corrosion products in other related environments.

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Appendix

The amount of Cr in the spinel FeCr$_x$Fe$_{2-x}$O$_4$, from the measured atomic fraction of Fe and Cr by EDS analysis can be estimated as follows.

Let Fe$^a$ and Fe$^b$ represent the trivalent and divalent Fe ions in the spinel respectively. The mole fraction of each cation in the spinel can then be written as:

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cr</th>
<th>Fe$^a$</th>
<th>Fe$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole fraction</td>
<td>x</td>
<td>1</td>
<td>2 - x</td>
</tr>
</tbody>
</table>

Assuming the trivalent and divalent Fe ions are both accounted for in the EDS measurements, the mole fraction of the cations can be rewritten as:

<table>
<thead>
<tr>
<th>Cation</th>
<th>Cr</th>
<th>Fe$^{a+b}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole fraction</td>
<td>x</td>
<td>3 - x</td>
</tr>
</tbody>
</table>

The ratio of Cr ion to the total Fe ions can be defined as:

\[
\frac{\text{Cr}}{\text{Fe}^{a+b}} = k = \frac{x}{3 - x} \tag{A.1}
\]

Upon rearranging we get

\[
x = \frac{3k}{1 + k} \tag{A.2}
\]
Chapter 5 – The influence of process parameters on corrosion mechanisms
5.1 – Effect of flue gas composition on deposit induced high temperature corrosion under laboratory conditions mimicking biomass firing. Part I: Exposures in oxidizing and chlorinating atmospheres

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Abstract

In biomass fired power plants, deposition of alkali chlorides on superheaters, as well as the presence of corrosive flue gas species, give rise to fast corrosion of superheaters. In order to shed light on the corrosion mechanism under this complex condition, the influence of flue gas composition on high temperature corrosion of an austenitic superheater material under laboratory conditions mimicking biomass firing was investigated. Isothermal high temperature exposures at 560 °C for 72 h with deposit (KCl)-coated and deposit-free austenitic stainless steel (TP 347H FG) samples was conducted. Exposures were conducted under both oxidizing and oxidizing-chlorinating atmospheres, and the resulting corrosion products were comprehensively studied with Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDS) and X-ray Diffraction (XRD) techniques. The results show that deposit-free samples suffer grain boundary attack only in an oxidizing-chlorinating atmosphere, otherwise corrosion results in formation of a duplex oxide. Corrosion attack on deposit-coated samples was higher than on deposit-free samples irrespective of the gaseous atmosphere. Specifically, severe volatilization of alloying elements occurred on deposit-coated samples under oxidizing-chlorinating atmosphere due to enhanced impact of KCl and HCl.

Keywords: High temperature corrosion, Biomass, Stainless steel, SEM, XRD, Oxidation, Chlorination, Metal chlorides.

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1 Introduction

High temperature corrosion of superheater tubes limits the efficiency of biomass fired power plants due to restriction of the outlet steam temperatures to a maximum of 540 °C during combustion of herbaceous biomass, like straw [31,205]. The corrosion problems arise from release of K-, S-, and Cl-species during combustion of biomass-based fuels [14,15,20,225], leading to formation of KCl-rich deposits (in the case of straw) along superheater tubes. This challenge has prompted investigations to reveal the mechanisms behind the corrosion attack. Studies have been approached either from a full-scale perspective of tubes exposed in the power plants, or from laboratory scaled exposures simulating the conditions observed in superheater sections of power plants.

Full-scale corrosion studies [24,26,31,94,101,104,199] often involve the use of either air or water cooled probes, test superheaters or sections welded into the existing superheater, in order to compare the performance of different materials. These studies provide information on the nature of corrosive deposits formed on the samples, allowing the deposit chemical composition to be correlated with the observed corrosion attack. From such studies, a Chlorine-induced attack originating from the deposit has been suggested to be responsible for the high-temperature corrosion rates observed [104]. In some studies [103], sulphidation has been identified when co-firing biomass with a fossil fuel. Although realistic information on the rate of corrosion attack are provided by full-scale corrosion studies, the complex fluctuating operating conditions (temperature, fuel type, boiler load etc.) in power plants limit systematic study of the corrosion mechanisms to a certain degree. Also, the very complex morphology of corrosion products resulting from such full-scale studies, in addition to the continuous shedding of deposits/corrosion products, does not straightforwardly allow the use of advanced characterization techniques which could help understand the underlying corrosion mechanisms.

On the other hand, laboratory scale studies [111,112,155,191,192,226] are usually dedicated to investigate specific parameters influencing corrosion. Results from such studies have highlighted the obscured role of K (in KCl deposits) in the early stages of the corrosion attack for high alloyed stainless steels [191]. The corrosivity of other species (for example, NaCl, CaCl2, K2CO3, etc.) has also been extensively investigated [116,117,153,190] in order to validate the role of the alkali metal in the corrosion attack. However, most laboratory scale studies oversimplify the corrosive atmospheres and consider single influences instead of the synergetic effects existing under real plant conditions. As a result, conclusions from these studies are not fully applicable to the complex situations in real power plants [226] since they do not take into account the simultaneous influence of parameters such as the flue gas and deposit composition including possible variations of these.

The influence of flue gas composition on the corrosion of superheater materials has been considered in some laboratory investigations [53,75,124,125,128,130,137,140,227–231]. Some of these studies were carried out on samples without a deposit [53,75,125,128,130,228], with high concentrations of the investigated flue gas species [230,232], or at temperatures above the actual superheater steam
temperatures during biomass (straw)-firing [124,127,231]. To gain improved understanding of the corrosion mechanisms relevant to biomass-firing conditions, systematic laboratory scaled studies under conditions reasonably mimicking biomass firing are thus required. Such studies will help to bridge the gap between results from full-scale high temperature corrosion studies and those from simplified laboratory scale studies where fundamental understanding of the corrosion mechanisms has been established.

In the present work, the influence of flue gas composition on the high temperature corrosion of a superheater material (austenitic stainless steel, TP 347H FG) was systematically investigated under conditions similar to actual biomass firing. Corrosion exposures were carried out in a dedicated furnace, which allows mimicking biomass firing conditions in the laboratory. The flue gas concentrations corresponds to the highest concentration measured in a power plant firing biomass [26,233]. The investigation addressed both the effect of the flue gas, and its interaction with the deposit during the corrosion attack. To this end, some samples were coated with KCl before the corrosion exposure. Material characterization was carried out by both cross-sectional and plan-view ‘top-down’ depth-resolved analysis of the corrosion products. In the first part of this study (Part I, present paper), results from corrosion exposures of both deposit-coated and deposit-free samples to oxidizing and oxidizing-chlorinating gas mixtures are reported. In the accompanying paper (Part II, same journal volume) [234], results from exposure of deposit-coated and deposit-free samples to sulphidizing gas mixtures (with and without HCl) are presented and discussed in detail.

2 Experimental

2.1 High temperature corrosion exposure

A tube of fine grained austenitic stainless steel TP 347H FG, commonly applied as superheaters in biomass-fired power plants, has been used for the investigation. The following chemical composition of the superheater tube was obtained by energy dispersive spectroscopy (EDS): 18.1 wt% Cr, 10.3 wt% Ni, 2.0 wt% Mn, 0.5 wt% Nb, 0.4 wt% Si with Fe as balance. Using Fusion thermal conductivity unit LECO CS230, a carbon content of 0.057 wt% has been identified for this material [149]. From the tube, rings with a width of 10 mm (longitudinal direction of the tube) were cut and further segmented such that arc-shaped samples of length 14.6 mm were obtained. The wall thickness of the tube, thus the height of the samples, was 7.4 mm. The tube segments were ultrasonically degreased in acetone, cleaned in ethanol and dried. The tube segments were used in the as received condition with no form of surface preparation. Some of the samples were coated with KCl, while other samples remained without any KCl on the surface. For coating the samples with a KCl deposit, crushed KCl with a particle size of [32 – 63 μm] (Sigma ≥ 99%) was mixed with 2 – propanol and the resulting slurry was applied on the sample surface to give a final deposit thickness of 1 mm. By using deposit slurries to coat the samples, a good and uniform contact between the deposit and the alloy surface is established after evaporation of the volatile solvent. In the power plant, the deposit forms on the convex (fireside) of the superheater tube, however
in the lab-scale exposure the concave surface was KCl coated to ensure consistent contact between the deposit and sample throughout the exposure.

A dedicated corrosion test rig was employed for the high temperature corrosion exposures (Figure 1). The rig consists of a gas inlet/mixing unit which employed gas cylinders of specific composition and concentrations, an electrically heated furnace and a gas clean-up unit. The desired gas composition was obtained by controlling the flow rate of each gas component using mass flow controllers to result in either (a) an oxidizing or (b) an oxidizing-chlorinating gas mixture. The oxidizing gas consisting of 6 vol% O₂ and 12 vol% CO₂ was saturated with 13.4 vol % H₂O vapour by passing the gas mixture through a thermally regulated water bath maintained at 52 °C. For some exposures, this humid gas mixture was also mixed with 400 ppmv HCl to give an oxidizing-chlorinating gas. For both mixtures, the gas mix was fed through a preheated gas channel into the furnace and N₂ was employed as a carrier gas.

**Figure 1.** Schematic representation of the corrosion test rig used for high-temperature exposures.

Samples were placed in quartz reactors in the horizontal furnace with a minimum separation distance of 50 mm, in order to minimize gas shielding effects. Both deposit-coated and deposit-free samples were exposed to each of the gas mixtures. Table 1 summarizes the experimental conditions applied in the present study. High temperature corrosion exposures were carried out isothermally at 560 °C for 72 h. The test temperature was chosen to mimic the superheater outer surface metal temperature of biomass-fired plants operating at a steam temperature of 540 °C [31]. After each exposure, the samples were cooled inside the reactors under a flow of N₂.
Table 1. Summary of the experimental conditions investigated.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Deposit coated?</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ia</td>
<td>Yes</td>
<td>Oxidizing gas: O₂ – 6 vol % (dry), CO₂ – 12 vol % (dry), N₂ – 82 vol % (dry), H₂O – 13.4 vol %</td>
</tr>
<tr>
<td>Ib</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>IIa</td>
<td>Yes</td>
<td>Oxidizing-chlorinating gas: HCl – 400 ppmv (dry), O₂ – 6 vol % (dry), CO₂ – 12 vol % (dry), N₂ – 82 vol % (dry), H₂O – 13.4 vol %</td>
</tr>
<tr>
<td>IIb</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>

2.2 Characterization of corrosion products

A combination of two methodologies for comprehensive characterization of the corrosion products were applied: (i) characterization of cross-sections and (ii) a plan view ‘top-down’ method involving stepwise mechanical removal of the corrosion product layers [208]. In both cases, complementary methods of materials characterization including microscopic, spectroscopic and diffraction techniques were used.

For cross-sectional investigations, a two-stage mounting procedure was employed for metallographic preparation. To retain the morphology of the corrosion products and the deposit, samples were mounted in epoxy under vacuum after exposure. The mounted samples were then sectioned under dry conditions in order to access the cross sections. In the second stage mounting, the sectioned samples were mounted in epoxy under vacuum with the exposed cross-section facing downwards. Afterwards the mounted samples were prepared according to standard metallographic techniques down to 1 μm polishing using a diamond suspension. Due to the solubility of some of the corrosion products in water, absolute ethanol (VWR Chemicals, 99.9 %) was utilized as a lubricant in the metallographic preparation process, and samples did not get in contact with water.

The plan view ‘top-down’ characterization approach was employed to supplement results from cross-sectional investigations. This reveals more detailed information on the corrosion products as some morphological features are obscured during the metallographic preparation process [208]. Plan view investigations on deposit coated samples started directly on the exposed deposits at the gas-deposit interface and proceeded with successive characterization of newly revealed surfaces after stepwise mechanical removal of the corrosion products using a scalpel or SiC paper. As a huge amount of results are revealed from this characterization method, selected results are presented here to supplement the cross section analysis.

Comprehensive characterization of the corrosion products was achieved by the complementary use of scanning electron microscopy (SEM) imaging, energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). Microstructure analysis with SEM (Inspect S, FEI) with an acceleration voltage of 15 keV was employed for both cross-sectional and plan view investigations; surfaces were coated with
carbon prior to microscopic characterization on cross sections. Micrographs were recorded using the
cr backscatter electron detector (BSE). EDS (Oxford instruments) coupled to the SEM was used for
elemental analysis of the corrosion products using an acceleration voltage of 15 keV. Because of the
heterogeneous morphology of the corrosion products, EDS results less than 1 wt% were not considered
from plan view investigations.

Qualitative phase identification of corrosion products was conducted by XRD. The diffractometer
(Bruker AXS, D8 Discover) was equipped with a Cr-Kα radiation source, and measurements were carried
out in the grazing incidence mode (GI-XRD) with a fixed incidence angle (γ) of 2°. Measurements were
carried out on the original surfaces and after stepwise removal of the corrosion products, where the
thickness of the removed layers was larger than the X-ray penetration depth. For XRD measurements on
deposit-free samples, γ = 5° was used, in order to cover a larger depth since no further corrosion product
removal was carried out for these samples. Due to the curved geometry of the samples, the incident
radiation was converged into a point focused beam using a polycap optic system and samples were placed
such that the incident beam was not shielded by the sample curvature.

Thermodynamic calculations were performed with the commercially available FactSage software
[184,235] to support the experimental results. Equilibrium calculations were performed using the Fact
53, FT Misc and FT pulp databases. The calculations were based on minimizing the Gibbs free energy
of the system considered.

3 Results

3.1 Deposit (KCl) coated samples exposed to an oxidizing gas mixture (Experiment Ia)

Figure 2 shows the cross section of samples coated with KCl, after exposure to an oxidizing gas mixture;
the two micrographs are representative of the corrosion morphologies observed. A compact double
layered corrosion product was formed on some locations (Figure 2a). The outer layer (layer 1) of the
corrosion product is observed to contain porosities. On some locations on the cross section (Figure 2b),
very large voids are present above layer 1. Variations in contrast, observed in the lower layer of corrosion
product (layer 2) suggest a difference in chemical composition within this layer. Below layer 2, corrosion
attack proceeds into the bulk alloy preferentially through the grain boundaries.
Figure 2. Micrographs showing cross-sections of deposit-coated samples exposed to an oxidizing gas mixture (i.e. experimental condition Ia). (a) Regions with lesser porosity in the corrosion product and (b) regions containing large voids and severe grain boundary attack. Double-headed arrows 1 and 2 indicate the different layers of corrosion product.

Elemental compositions of the corrosion product layers are revealed by the EDS maps shown in Figure 3. From these, it can be seen that Fe and O are the predominant elements in layer 1, whereas layer 2 of the corrosion product is enriched in Cr, Ni and O. From the Ni and O maps (Figure 3a), it is observed that in some points, Ni is not associated with O. Further, the Ni maps reveal that this element is mostly enriched at the lower regions of layer 2, and separates this layer from the bulk alloy. Interestingly, Cl is also identified in some locations in layer 2 of the corrosion product, probably in association with the alloying elements Fe, Cr and Ni. In some locations (micrographs not shown here), Cl rich features were observed to have precipitated from some positions in layer 2. The EDS maps in Figure 3 also show that both Cr and O were the predominant elements on locations that seem to mark the grain boundaries (although samples were not etched), hence suggesting that the grain boundaries were attacked.

In Figures 4-6, results from the plan view ‘top-down’ characterization are presented. Because the deposit could be lifted up from the sample surface as a compact layer, it was examined from both the gas/deposit and the deposit/corrosion product interfaces; in contrast, these interfaces are usually damaged during preparation of a sample cross-section. Plan view characterization of the deposit both from the gas/deposit and deposit/corrosion product interfaces showed no additional features on the deposit particles (Figure 4) and EDS analysis also confirmed that the deposit contains only Cl (52.5 wt %) and K (47.6 wt %) after the exposure. The micrographs in Figure 5 show the topography of layer 1 of the corrosion product after removal of the deposit. Corrosion products on the surface of layer 1 are observed as heterogeneous protrusions, mostly around the deposit particles. EDS analysis suggests that these protrusions existed in two kinds:
**Figure 3.** EDS maps showing the distribution of various elements in different regions (a) and (b) (cf. Figure 2) of the corrosion products on deposit-coated samples exposed to an oxidizing gas mixture (i.e. experimental condition Ia).

**Figure 4.** Plan-view microstructure of deposit particles observed from the (a) gas/deposit interface and (b) deposit/corrosion product interface after removal of the deposit, after exposure to an oxidizing gas mixture (experimental condition Ia).
(i) Fe-rich oxide (Figure 5a) and (ii) K-Cl-Fe-O rich accumulations (Figure 5b). Consistent with the elemental analysis, the contrast observed in the micrographs also suggests a difference in elemental composition of the accumulations. In the K-Cl-Fe-O rich accumulations, the small particles exhibit the same contrast as the KCl particles, compared with the surrounding features which appear brighter. In Figure 5c, these K-Cl-Fe-O features are observed to accumulate around the deposit particles. Conversely, Figure 5d shows that some regions of layer 1 existed as a compact Fe-rich oxide layer, consistent with the compact layer shown in Figure 2a.

**Figure 5.** Plan view micrographs showing layer 1 of corrosion products on a sample exposed to the oxidizing gas mixture (experimental condition 1a) after removal of the deposit. (a-c) indicate heterogeneous regions of the corrosion product, and (d) compact region of the corrosion product. Elemental composition of the selected areas in wt% is: Region 1: O-27.2, K-3.5, Cr-2.8, Mn-3.4 and Fe-61.2. Region 2: O-25.7, Cl-14.2, K-15.4, Cr-2.3, Mn-2.1 and Fe-39.7. Region 3: O-27.5, Cr-1.3, Mn-2.1 and Fe-68.3.
The corrosion product layer observed after partial removal of layer 1 (Figure 6) still showed the presence of Fe and O. In addition, some local features rich in Cr and K as well as Cl were also observed. The identification of K and Cr indicates the presence of K$_2$CrO$_4$, which is likely to form under experimental condition Ia [149,191]. With further removal of layer 1, the Cr-rich inner layer of the corrosion product (layer 2) is observed as shown in Figure 7a. In line with observations from cross-sections (Figure 3), Cl rich features were also observed on some locations in this layer. The elemental maps in Figure 7a show that layer 2 consists of Cr, Ni, Fe and O. Also, Ni is seen to be enriched along the grain boundaries. In larger depth, as observed after continued removal of layer 2, preferential attack along the grain boundaries is observed (Figure 7b). At the corrosion front where grain boundaries have been attacked, EDS maps show that Cr and O are enriched along such grain boundaries.

Figure 8 shows results from GI – XRD measurements, recorded with successive mechanical removal of the corrosion product layers. The diffractogram recorded on layer 1 reveals that Fe$_2$O$_3$ (Joint Committee on Powder Diffraction Standards, JCPDS card 33-664) and KCl (JCPDS card 41-1476) are the crystalline phases present in this layer of the corrosion product. Fe$_2$O$_3$ and spinel – FeCr$_2$O$_4$ (JCPDS card 34-140) are phases identified after partial removal of layer 1, as well as in layer 2. When the region of grain boundary attack is approached, the spinel phase and austenite phase (JCPDS card 33-397) become the only identifiable phases in the diffractogram, while the latter phase predominates as the corrosion front/bulk alloy is reached.
Figure 7. Plan-view micrographs and EDS elemental maps of (a) layer 2 of corrosion product and (b) the region of grain boundary attack close to the corrosion front after removal of layer 2 on a sample exposed to an oxidizing gas mixture (experimental condition Ia).

Figure 8. X-ray diffractograms showing the crystalline phases in the various layers of the corrosion product on a deposit-coated sample exposed to an oxidizing gas mixture (experimental condition Ia). The peak at 68°2θ (see arrow) corresponds to α'-Fe, which originates from a phase transformation of γ-Fe due to mechanical removal of the bulk alloy.
3.2 Deposit-free samples exposed to an oxidizing gas mixture (Experiment Ib)

A double layered oxide was observed on the deposit-free samples after exposure to an oxidizing gas mixture, and there was no grain boundary attack (Figure 9a). The thickness and continuity of the outer and inner layer (layers 1 and 2, respectively) varied along the sample surface. The plan view micrograph in Figure 9b also confirms the discontinuous nature of the corrosion product. EDS elemental mapping on the cross section revealed that the outer layer (layer 1) is enriched in Fe and O while Cr and O become predominant in the inner layer (layer 2). Additionally, Ni is observed in the lower part of layer 2, and is enriched at its interface with the alloy bulk. At the discontinuous regions of the corrosion product, localized Cr enriched oxide is noticed above the alloy bulk. This is consistent with the plan view elemental mapping (Figure 9b), revealing Cr to be enriched at the interface between the Fe rich oxide islands.

![Figure 9](image_url)

**Figure 9.** (a) Cross-section and (b) plan-view micrographs with corresponding EDS maps showing elemental composition of the corrosion products resulting from exposure of deposit-free sample to an oxidizing gas mixture (i.e. experimental condition Ib). Double-headed arrows (1) and (2) indicate the different layers of corrosion product.
Results from GI – XRD measurements on the deposit-free sample exposed to an oxidizing gas mixture are shown in Figure 10. The identified crystalline phases are Fe₂O₃ (JCPDS card 33-664) and FeCr₂O₄ (JCPDS card 34-140). The austenite peaks present in the diffractogram are attributed to the alloy bulk, which contributes to diffraction due to the thin corrosion product.

![X-ray diffractogram showing the predominant crystalline corrosion product phases on a deposit-free sample exposed to an oxidizing gas mixture (experimental condition Ib).](image)

**Figure 10.** X-ray diffractogram showing the predominant crystalline corrosion product phases on a deposit-free sample exposed to an oxidizing gas mixture (experimental condition Ib).

### 3.3 Deposit (KCl) coated samples exposed to an oxidizing-chlorinating gas mixture (Experiment IIa)

The micrographs in Figure 11 show the typical cross-sections of deposit-coated samples, after exposure to an oxidizing-chlorinating gas mixture (i.e. experimental condition IIa in Table 1). Generally, three layers can be observed from the cross sections: layer 1 (in Figure 11a) is a very inhomogeneous and porous upper layer observed on some regions of the exposed sample, while it was absent on other locations on the sample (cf. Figure 11b). Layer 2 (in Figure 11a and b) is a compact layer which partly cracked during metallographic sample preparation. Layer 3 (in Figure 11b) refers to localized selective attack together with further attack along grain boundaries of the alloy. The predominant elements in these 3 layers are shown by EDS maps in Figure 12. In layer 1 of the corrosion products, Fe and O are the predominant elements, with some Mn and Ni. K and Cl are identified in localized areas. Layer 2 is enriched in Cr and O. In the regions designated as layer 3 of the corrosion product, there is localized depletion of Fe and Cr, with a corresponding enrichment of Ni in these areas. Regions that suffered grain boundary attack contained Cr, Ni, Cl and O (Figure 12b).
Figure 11. Cross-sections showing the corrosion product on deposit-coated sample exposed to an oxidizing-chlorinating gas mixture (i.e. experimental condition IIa). (a) Regions with bubble-like heterogeneous morphology and (b) relatively compact layers of corrosion product. Double-headed arrows 1, 2 and 3 indicate the different layers of corrosion product.

Figure 12. EDS maps showing the elemental composition of the corrosion products (cf. Figure 11) resulting from exposure of deposit-coated samples to an oxidizing-chlorinating gas mixture (i.e. experimental condition IIa).
In Figures 13 and 14, selected results from the plan view ‘top-down’ characterization are presented. At the gas/deposit interface (Figure 13a), the initial deposit of KCl is observed to retain its morphology, and only K and Cl were identified by EDS analysis. In contrast, at the deposit/corrosion product interface, the deposit appears to have partially melted because the faceted appearance is replaced by a smooth surface (Figure 13b). Additionally, some particles are observed to have accumulated on the deposit. EDS analysis at the deposit/corrosion product interface showed the deposit to contain (in wt %): Fe – 5.2, O – 9.8, Cl – 43.2 and K – 41.8.

Figure 13. Plan view microstructure after exposure of deposit-coated samples to an oxidizing-chlorinating gas mixture (experimental condition IIa) showing the deposit at (a) the gas/deposit interface and at (b) the deposit/corrosion product interface. (c and d) correspond to layer 1 of corrosion product observed below the initial deposit.
Figure 13c shows the plan view microstructure of layer 1 of the corrosion product after removal of the deposit. The observed heterogeneous and bubble-like morphology from plan view characterization is consistent with that observed in the cross-section in Figure 11a, and possibly, originates from removal/entrapment of gaseous species below this layer. Layer 1 consists of a mixture which contains a molten phase as revealed from the magnified micrograph in Figure 13d. EDS analysis showed that in addition to metal oxides of Fe, Cr and Mn, the mixture also contained K and Cl in the following concentration (in wt %): Fe – 33.7, Mn – 4.9, Cr – 1.6, O – 20.2, Cl – 20.0 and K – 19.6.

Figure 14. Plan view microstructure of layer 3 showing (a) the Ni rich layer resulting from selective attack, (b) Cl rich structures observed on some locations in layer 3. Grain boundary attack and the elemental composition close to the corrosion front is shown in (c). The sample was exposed to an oxidizing-chlorinating gas mixture (experimental condition IIa).
The plan view micrographs in Figure 14 show the microstructure of layer 3. Figure 14a clearly shows that this layer was very porous with a corresponding elemental composition of (in wt %): Ni – 64.6, Fe – 14.7, Cr – 7.2, Si – 1.5 and O – 9.8. At some locations on this layer, Cl containing protrusions were observed (Figure 14b). Elemental analysis on these features revealed the following composition (in wt %): Ni – 17.1, Fe – 34.9, Mn – 1.1, Cr – 8.3, O – 24.4 and Cl – 14.1. At positions close to the corrosion front, as revealed by further removal of the corrosion product, the corrosion attack is observed to proceed preferentially along the grain boundaries (Figure 14c). EDS maps show that Cr, Ni and O are enriched along the grain boundaries whereas Fe is depleted.

X-ray diffractograms showing the major crystalline phases of the corrosion products are presented in Figure 15. Measurements on layer 1 of the corrosion product (Figure 13c) detected the crystalline phases Fe₂O₃ (JCPDS card 33-664), FeCr₂O₄ (JCPDS card 34-140) and KCl (JCPDS card 41-1476). Whether or not other alloying elements are in solid solution with identified phases cannot be determined, because the observed slight offset of measured peak positions compared to the theoretical ones can originate from both chemical variations and internal stresses.

**Figure 15.** X-ray diffractograms showing the predominant crystalline phases in different layers of corrosion product after exposure of a deposit-coated sample to an oxidizing-chlorinating gas mixture (experimental condition IIa).

On layer 3 (the porous Ni rich layer), two austenite phases (JCPDS cards 33-397 and 33-945) are observed in the diffractogram. One of them originates from austenite containing about 75 wt% of Ni and corresponds to the high concentration of Ni identified in layer 3 by EDS analysis. Solid solution of Ni in
austenite should provoke an increase in lattice constant [236] which would shift the (γ-Fe-75 wt% Ni) peaks to a lower 2θ value. However, because this effect reverses at higher Ni concentrations (> 40 wt% Ni) [214], the actual Ni concentration in layer 3 (64.6 wt. % Ni) shifts the peak of (γ-Fe-75 wt% Ni) to higher 2θ values relative to that of (γ-Fe-11 wt% Ni) (Figure 15). As the corrosion front is approached, only peaks originating from austenite with 11 wt% Ni (JCPDS card 33-397), corresponding to the bulk alloy, are recorded by XRD.

3.4 Deposit-free samples exposed to an oxidizing-chlorinating gas mixture (Experiment IIb)

High temperature corrosion of deposit-free samples under an oxidizing-chlorinating gas mixture did not result in formation of heterogeneous corrosion products as observed on deposit-coated samples (cf. Figures 16 and 11a). Instead, after the exposure of deposit-free samples, a double layered corrosion product formed (Figure 16a).

Figure 16. Corrosion products after exposure of deposit-free samples to an oxidizing-chlorinating gas mixture (experimental condition IIb). (a) Cross-section and (b) plan-view micrograph. (c) Cross-section EDS maps showing elemental composition of the corrosion products. (d) Plan view EDS maps showing elemental distribution below a spalled region. Double-headed arrows 1 and 2 indicate the different layers of corrosion product.

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Corrosion attack under this condition is seen to progress into the bulk of the alloy in the form of grain boundary attack. EDS maps in Figure 16c reveal that the double layered corrosion product is enriched in Fe and O in the outer layer, layer 1, whereas Cr and O become predominant in the inner layer, layer 2. It is also observed that Ni is enriched in the lower parts of layer 2 which extends into regions of grain boundary attack, enriched in Cr and O. Additionally, Ni enrichment is observed adjacent to the regions where grain boundary attack occurred.

Similar to the observation on the sample cross-section, plan view investigation (Figure 16b) did not reveal any heterogeneous layer of corrosion product. Instead, the corrosion products consisted of blade like structures on the sample surface (similar to Figure 5d and 9b). EDS analysis on regions where the corrosion product partly spalled off (Figure 16d) confirm the double layer formation of an outer Fe-O layer, and an inner Cr-O rich layer (i.e. layer 1 and layer 2, respectively). Interestingly, Cl rich features were also observed around the interface between layer 2 and the bulk alloy.

From qualitative phase analysis using GI-XRD (Figure 17), Fe₂O₃ (JCPDS card 33-664) and FeCr₂O₄ (JCPDS card 34-140) were the major crystalline corrosion products identified on the deposit-free sample exposed to the oxidizing-chlorinating gas mixture. The additional presence of Fe₃O₄ (JCPDS card 73-698) is likely, but its theoretical peak positions are close to the ones for FeCr₂O₄, moreover, the solubility of Cr in iron oxides may favour formation of FeCr₂O₄.

![Figure 17. X-ray diffractogram showing the crystalline corrosion product phases on a deposit-free sample exposed to an oxidizing-chlorinating gas mixture (experimental condition IIb).](image-url)
3.5 Extent of corrosion attack

For comparison of the corrosion attack on deposit-coated and deposit-free samples after exposure to the different gas mixtures, the depths of the internal attack (thicknesses of layer 2 or 3, or the total thicknesses of layer 2 and 3) were measured on more than 20 positions on each of the exposed samples. The measurement considered the depth of the observed internal and/or grain boundary attacked regions on the specimens (depending on the exposure condition and the resulting corrosion product, cf. Figures 2, 9, 11 and 16a) because these layers formed below the original metal interface. The box chart in Figure 18 presents the statistical distribution of measured thicknesses (note the difference in scale). Generally, it is observed that a deeper internal attack occurred on deposit-coated samples than on deposit-free samples irrespective of the flue gas composition. For the deposit-free samples in particular, the measured mean and maximum thicknesses show that more corrosion attack occurred after exposure to the oxidizing-chlorinating gas mixture. However, in the case of the deposit-coated samples, the mean thicknesses of internal/grain boundary attacked regions were similar. The thickness of layer 1 could not be assessed in the same way due to the increased porosity and heterogeneity from interaction between the oxide and the deposit (see Figures 2 and 11).

![Figure 18](image)

**Figure 18.** Thicknesses of the resulting internal/grain boundary attack (layers 2 and 3) after exposure to different gas mixtures. The maximum and minimum thicknesses are represented by the marks above and below each box. Location of 50% of the distribution is shown by the horizontal bar in each box whereas the round dots represent the mean thicknesses. The standard deviation from the mean is represented by the horizontal edges of the box. At least 20 positions on the exposed samples were measured to obtain the distribution.
4 Discussion

Experimental results revealed the influence of the gas composition on both the extent of the corrosion attack and the morphology of the various corrosion layers. Generally, severe corrosion was observed on all samples coated with a KCl deposit, compared to deposit-free samples. In Table 2, the corrosion products observed on deposit-coated and deposit-free samples are summarized.

**Table 2.** Summary of corrosion products after exposure of deposit-coated and deposit-free samples to the different gas mixtures.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Deposit appearance</th>
<th>Corrosion product morphology, phase and chemical composition</th>
</tr>
</thead>
</table>
| Ia (oxidizing gas mixture) | No observable change | Layer 1: Compact/partly molten heterogeneous (Fe$_2$O$_3$ - KCl)  
Layer 2: Fe – Cr – Ni – O (Fe$_2$O$_3$, FeCr$_2$O$_4$).  
Grain boundary attack, Cl – rich protrusions |
| Ib (oxidizing gas mixture) | - | Discontinuous double-layered (Fe$_2$O$_3$, FeCr$_2$O$_4$)  
Layer 1: Fe – O enriched  
Layer 2: Cr – Ni – O enriched |
| IIa (oxidizing-chlorinating gas mixture) | Partly molten at the deposit/corrosion product interface | Layer 1: Mostly partly molten and heterogeneous (Fe$_2$O$_3$ - KCl)  
Layer 2: Fe – Cr – O (Fe$_2$O$_3$, FeCr$_2$O$_4$)  
Layer 3: (Ni-rich (75 wt%) phase).  
Grain boundary attack, Cl – rich protrusions |
| IIb (oxidizing-chlorinating gas-mixture) | - | Double-layered (Fe$_2$O$_3$, FeCr$_2$O$_4$)  
Layer 1: Fe – O enriched  
Layer 2: Cr – Ni – O enriched.  
Grain boundary attack, Cl – rich accumulations |

For the deposit-coated samples, Fe$_2$O$_3$ were observed in the first layer of corrosion product (i.e. below the deposit) together with KCl with a morphology indicating that melting of KCl had occurred. It is also generally observed that the elemental composition of the second/third layer of corrosion products, the occurrence of grain boundary attack depended on the absence/presence of a deposit as well as the composition of the gas mixture. In addition, the deposit morphology after the exposures depended on the
composition of the gas mixture. These experimental results suggest that corrosion was primarily affected by KCl and secondarily by the additional presence of HCl in the gas mixture. The impact of these species in relation to the observed corrosion products are discussed in the following sections.

4.1 The influence of KCl on the corrosion process

Results from experiment Ia show that even in the absence of a secondary corrosive species such as HCl in the gas mixture, the deposit (KCl) can initiate significant corrosion of the alloy (cf. Figures 2, 3 and 9). Corrosion of the deposit-free sample exposed to an oxidizing gas mixture resulted in a discontinuous double-layered corrosion product (Figure 9), and the morphology of such corrosion product is consistent with a solid state diffusion oxidation mechanism (involving CO2 and/or H2O) in which the faster transport of Fe results in an external Fe-rich oxide, while Cr forms an inner oxide layer due to its relatively higher affinity to oxygen as well as its slow diffusion in the spinel phase [38,41]. The thinner chromium rich oxide observed in local areas (Figure 9b) is due to the formation of a Cr rich oxide as diffusion of Cr through the grain boundaries is higher than in the bulk grain at lower temperatures similar to that in the present study. Formation of Cr2O3 hence results in slower oxidation rates in these areas [62].

For the deposit-coated samples, plan view investigation show that heterogeneously distributed Fe2O3 and KCl have formed below the initial deposit after exposure to an oxidizing gas mixture. Under oxidizing conditions, potassium from KCl is capable of disrupting the initial protective Cr2O3 layer on the sample (reaction 1), leading to Cr depletion and subsequent development of a non-protective layer [137]. The reaction has been reported to be more favourable in the presence of gaseous KCl [127].

\[
\text{KCl(s)} + \frac{1}{4} \text{Cr}_2\text{O}_3(s) + \frac{3}{8} \text{O}_2(g) + \frac{1}{2} \text{H}_2\text{O}(g) \rightleftharpoons \frac{1}{2} \text{K}_2\text{CrO}_4(s) + \text{HCl}(g) \quad (1)
\]

For reaction 1, the Gibbs free energy (\(\Delta G^\circ\)) at 560 °C is 36.57 kJ/mol (KCl) [184,235]. This reaction can give a HCl partial pressure (\(p_{\text{HCl}}\)) of \(6.15 \times 10^{-4}\) atm, which by dissociation according to reaction 2 results in a chlorine partial pressure (\(p_{\text{Cl}_2}\)) of \(9.10 \times 10^{-7}\) atm [184,235].

\[
2\text{HCl}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{Cl}_2(g) + \text{H}_2\text{O}(g) \quad (2)
\]

For reaction 2, the Gibbs free energy (\(\Delta G^\circ\)) at 560 °C = -2.37 kJ/mol (Cl2) [184,235].

Identification of K-Cr rich regions in the corrosion products (Figure 6) suggests that reaction 1 indeed occurred and also agrees with results in the literature [138,191,192]. The corrosion attack initiated by K is intensified since HCl released from (1) can dissociate into Cl2 (reaction 2) and is transported through the porous oxide or via an electrochemical mechanism, to the bulk alloy where it chlorinates the alloying elements (M), according to reaction 3 [75,156].

\[
\text{M(s)} + x\text{Cl} \rightleftharpoons \text{MCl}_{x}(s) \quad (3)
\]
It is worth noting that KCl itself can also act as a chlorine source according to the electrochemical mechanism described in reference [135]. The transition metal chlorides resulting from reaction 3 generally possess high vapour pressures at high temperatures and are consequently volatile. These species are oxidized to the corresponding metal oxides if they encounter environments containing sufficient amounts of oxygen (according to reaction 4).

\[ yMCl_x(g) + \frac{Z}{2}O_2(g) \rightleftharpoons M_yO_z(s) + yCl_x(g) \]  

(4)

When both oxygen and chlorine are present in the corrosive gas, metal-oxygen-chlorine phase stability diagrams (predominance diagrams) helps to predict the stable phase(s) under specific oxygen and chlorine partial pressures. The predominance diagram is based on the minimization of the systems total Gibbs free energy as a function of oxygen and chlorine partial pressures. In the present work, such diagrams calculated for Fe, Cr and Ni using the commercial software package FactSage and are superimposed in Figure 19 [184,235]. It is important to note that for the Fe-Cl2-O2 diagram, the line separating solid metal chloride and gas metal chloride phases, only represents the maximum limit for the solid metal chloride because volatile metal chlorides may exit at chlorine partial pressures below this limit [157,237]. According to Figure 19, Cr and Fe will require a lower Cl2 partial pressure for chlorination relative to Ni, which requires \( p_{Cl_2} > 10^{-11}\) atm.

![Figure 19](image.png)

**Figure 19.** Superimposed predominance diagrams for the M-Cl-O system at 560 °C showing the stability regions for oxides and chlorides of major alloying elements in the investigated material, M. (M = Cr-blue, Fe-black, Ni-red). Calculations were performed with FactSage [184,235] using the Fact PS, FT oxide, FT salt and FT pulp databases.
However, because CrCl₂ formation (as well as its transformation to Cr₂O₃) occurs at relatively lower O₂ partial pressures, it is reasonable that only the metal oxides (chlorides) of Fe are observed close to the corrosion product/deposit interface (with high O₂ partial pressures) since the FeCl₂→Fe₂O₃ transformation occurs at higher O₂ partial pressures. Results from cross sectional and plan view investigations (cf. Figures 2, 3, 5 and 8) are in good agreement with the thermodynamic calculations as Fe₂O₃ was mostly observed in layer 1 below the deposit, whereas the spinel (FeCr₂O₄) was observed in layer 2. The identification of Ni in layer 2 of corrosion products (the spinel) is explained by the effect of Ni in the spinel, where it promotes lower partition of alloying elements [62]. On the other hand, the identification of metallic Ni in the corrosion products could be because it requires the highest Cl₂ partial pressure for chlorination (pCl₂ > 10⁻¹¹ atm, Figure 19).

The selective progression of corrosion attack along the grain boundaries corresponds to the faster diffusion of corrosive species along the grain boundaries. In addition, it has been reported that preferential attack of Cr-carbides [104,186] present at the grain boundaries could favour selective progression of corrosion attack through the grain boundaries. In line with thermodynamics of the chlorination-oxidation process, high volatility of metal chlorides of Fe and faster transport through grain boundaries supports Fe depletion along the attacked grain boundaries (Figure 3 and 7b).

The morphology of KCl and Fe₂O₃ rich corrosion products (on deposit-coated samples exposed to an oxidizing-chlorinating gas mixture) indicate partial melting of KCl during the exposure and is consistent with the observation that after exposure, the deposit could be removed from the sample surface as a compact layer and not as individual particles (Figure 13b). The transformation of the deposit particles to such molten morphologies is attributed to the ability of FeCl₂ to lower the melting temperature of KCl (772 °C) because the KCl-FeCl₂ system forms a eutectic point at 355 °C [184,235], which is below the temperature at which the present exposures were carried out. Such phase transformation (solid → liquid) will exacerbate the corrosiveness of the deposit due to enhanced contact between the sample surface and the corrosive deposit, thus promoting further chlorination of the alloying elements. The corresponding oxidation of dissolved Fe (i.e. FeCl₂) in such melts accounts for Fe₂O₃ identification in the KCl-Fe₂O₃ mixture.

In general, the corrosion attack observed on deposit-coated samples reflects the interplay between K and Cl. However it has to be noted that Cl plays a special role in the corrosion attack, as part of this species released from reaction (4) possess the tendency of propagating the corrosion attack by re-initiating reaction (3). Thus, K has one role – breakdown of Cr₂O₃, while Cl has two – formation of a melt on the sample surface and increased generation of HCl, thus, propagating the reaction at the corrosion front. The role of K is not exclusively necessary to initiate chlorination of the alloy since deposit-free samples exposed to the oxidizing-chlorinating gas mixture also suffered chlorination related corrosion attack (cf. Figure 16).
4.2 The influence of HCl on the corrosion process

From the severe attack on deposit-free samples after exposure to an oxidizing-chlorinating gas mixture (see Figures 16 and 18), it is obvious that the addition of HCl to the gas mixture triggered corrosion through a mechanism different from that described for deposit-free samples exposed to an oxidizing gas mixture. Considering a complete dissociation of the original 0.035 vol % HCl present in the flue gas, according to the Deacon reaction (2) [132,156], chlorine partial pressure \( (p_{Cl_2}) \) of \( 2.91 \times 10^{-7} \) atm can be generated at 560 °C [184,235]. Thermodynamically (Figure 19), this can initiate the chlorination of Cr, Fe and Ni under low oxygen partial pressures in accordance with the mechanisms discussed in section 4.1. Indeed, the observed morphology and composition of the corrosion products (Figures 16 and 17) agree reasonably with thermodynamic predictions. As a result of the chlorination reaction, accumulation of Cl-rich features was observed at the corrosion front (Figure 16d). The observed corrosion products are also in good agreement with those from related previous studies [130,227,228,238–240] and the identification of metallic Ni in the EDS maps (Figure 16c) can either be due to its easier incorporation in the spinel [62] or because the actual Cl2 partial pressure at the corrosion front was too low (< \( 10^{-11} \) atm) for chlorination of Ni.

It is clear from the morphology of the corrosion product, that HCl alone is not responsible for formation of the heterogeneously distributed, Fe2O3-KCl partly molten layer observed after exposure of deposit-coated samples to an oxidizing-chlorinating gas mixture. However, with the simultaneous presence of both the KCl deposit and HCl in the gas mixture (experiment IIa), an increased corrosion attack was observed. Although the elemental composition of the corrosion products remains the same as in the absence of a deposit, the morphology of the corrosion products is obviously different (cf. Figures 11-14 and 16). The enhanced formation of the KCl-FeCl2 eutectic mixture (Figure 13d) possibly increased the degree of corrosion attack due to enhanced contact between the sample and the partly molten deposit particles. Consequently, a higher Cl2 partial pressure arising from reactions 1 and 2 in combination with the one present in the flue gas facilitated more chlorination of the alloying elements (reaction 3). In conformity with this (i.e. increased chlorination of the alloying elements, Fe and Cr), deposit particles close to the initial sample surface appeared to have been partly molten (Figure 13b), probably due to formation of a eutectic between the deposit and the volatized FeCl2 (from reactions 3). A manifestation of increased volatilization of metal chlorides resulting from reactions 3 and 4 is the porous, bubble-like and heterogeneous morphology of the Fe2O3-KCl layer 1 as observed from plan-view investigations (Figure 13c). While such layers may have been initiated in the oxidizing gas mixture (experiment Ia) through the process involving K2CrO4 formation (reaction 1), the bubble-like and heterogeneous nature of the layer in experiment IIa clearly indicates that HCl addition to the gas mixture had a significant effect on volatilization of metal chlorides formed during the corrosion process. Increased chlorination and volatilization leading to selective removal of the alloying elements (Fe and Cr) is responsible for the formation of a Ni-rich phase (in layer 3) as identified by XRD.
5 Summary and conclusions

Systematic investigations of the high temperature corrosion of an austenitic superheater material (TP 347H FG) at 560 °C under conditions relevant for biomass firing in thermal power plants show that both deposit (KCl) particles and the corrosive flue gas composition affect the corrosion process. Based on the results from this study, the following conclusions can be deduced:

1. The alloy suffers corrosion attack under all the conditions investigated.

2. More severe corrosion attack occurs on KCl-deposit coated samples compared to the deposit-free samples when exposed to the same gaseous mixture.

3. Corrosion attack on deposit-free samples exposed to an oxidizing gas mixture follows the conventional oxidation mechanism leading to a double-layered oxide. No grain boundary attack occurs under this condition. However, the presence of a KCl deposit significantly changes the corrosion attack due to the influence of both K and Cl. Selective attack of Cr along the grain boundaries occurs after such exposure.

4. HCl in the flue gas significantly enhances the chlorination of alloying elements leading to formation of volatile metal chlorides. In the absence of KCl, this effect results in a typical Cl-induced type of corrosion attack (chlorination) progressing through the grain boundaries.

5. When KCl is present on the sample, addition of HCl to the gas mixture increases the formation of a corrosive FeClx-KCl eutectic, and hence, increases the selective attack of the thermodynamically favoured species (Fe and Cr). This leads to formation of a Ni-rich phase close to the corrosion front. The corrosion products resulting from this attack are highly porous and heterogeneous due to severe volatilization of the formed metal chlorides.

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The references cited in this manuscript are collected in the general reference list of the thesis.
5.2 – Effect of flue gas composition on deposit induced high temperature corrosion under laboratory conditions mimicking biomass firing. Part II: Exposures in SO₂ containing atmospheres\textsuperscript{v}

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Abstract

In biomass fired power plants, the fast corrosion of superheaters is facilitated by the presence of corrosive flue gas species, for example, SO₂, which are released during combustion. To understand the role of the gas species on the corrosion process, comparative laboratory exposures of deposit (KCl)-coated and deposit-free austenitic stainless steel (TP 347H FG) samples to gas mixtures containing SO₂ was carried out, under conditions relevant to biomass-firing. Exposures were conducted isothermally at 560 °C for 72 h, in oxidizing-sulphidizing, and oxidizing-sulphidizing-chlorinating gas mixtures containing 60 ppmv SO₂. Scanning Electron Microscopy (SEM), Energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) techniques were complimentarily applied to characterize the resulting corrosion products. A partially molten K₂SO₄-layer formed on KCl coated specimens, and corrosion resulted in localized broad pits containing sulphides and oxides. The severe pitting attack was decreased by the presence of HCl in the gas mixture.

Keywords: High temperature corrosion, Stainless steel, Sulphation, Chlorination, Sulphidization, Metal chlorides.

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1. Introduction

Although current environmental awareness calls for a shift towards greener energy sources, combustion of biomass (especially straw) in power plants is still challenging due to various operational difficulties such as slagging and fouling, and corrosion in the boiler [8,101]. This is because the chemical composition of biomass-based fuels differs considerably from that of fossil fuels, resulting in much higher corrosion rates [104]. Typically, biomass-based fuels contain high contents of potassium (K) and chlorine (Cl) [225] and during combustion, release of these species leads to deposition of alkali chloride-rich deposits on superheaters [8]. Prompted by this challenge, a number of investigations have focused on studies related to KCl-induced corrosion of superheater materials (see for example [138,165,191,208,226]). Generally, investigations have revealed that both the alkali metal cation and chloride anion participate in the fast corrosion of investigated alloys. Specifically, the alkali metal cation, potassium, has been reported to play the crucial role in disrupting the formation of protective chromium-rich oxide during the initiation stages of corrosion attack [137,191,226]. These results are based on studies under fairly oxidizing conditions with gas mixtures comprising of oxygen (O2) and water (H2O) vapour. However, results from full-scale investigations [27,100,104] have shown the presence of sulphur containing corrosion products in addition to KCl and oxides of the alloying elements. Such observations emphasize the importance of including other gaseous species in laboratory investigations to enable a closer simulation of conditions in the boiler.

Organically or inorganically bound sulphur in the fuel is also released as sulphur (IV) oxide (SO2) during combustion, in the devolatilization and char combustion stages [8,13,14]. The concentration of SO2 in the flue gas can influence both the formation of deposits and corrosion of superheaters. It is reported that SO2 can react in the gas phase with potassium chloride (KCl) vapour to form potassium sulphate (K2SO4) nuclei for further condensation of KCl [8,21]. Despite its importance, the role of SO2 with respect to corrosion of superheaters under biomass-firing conditions is still not fully understood. Studies have shown that conversion of KCl to K2SO4 due to the presence of SO2 in the gas reduces the corrosion attack [127,230,241]. This was justified on the basis that K2SO4 has lesser tendency to cause formation of potassium chromate (K2CrO4) and therefore will not prevent formation of the protective chromia (Cr2O3) scale. However, it has to be noted that in some of these studies [114,230], (probably) due to the formation of hydrogen chloride (HCl) from the conversion of KCl to K2SO4, a higher mass gain of samples was recorded than that observed while using only K2SO4 as deposits. Some studies [8,90,104] have attributed the ability of (H)Cl generated from the sulphation of alkali chloride deposits to induce cyclic chlorination of alloying elements, as the major process responsible for corrosion of superheaters. However, it has been pointed out that the concentration of SO2 employed for corrosion studies using alkali chloride deposits may influence the effect of the resulting HCl on corrosion. Specifically, while using as high as 15000 ppm of SO2 [232], it was suggested that the observed reduction in corrosion attack was due to preferential sulphation of deposit particles at the gas/deposit interface leading to reduced generation of HCl close to the deposit/alloy interface. This therefore implies that depending on its concentration, SO2 may exert a positive or negative effect on corrosion attack. Based on results from full-scale flue gas
measurements in power plants firing biomass, the maximum SO2-concentration measured before the superheater section as well as in the stack, was below 120 ppm \cite{24,100,242,243}. In addition, the composition of the flue gas is not strictly oxidizing as has been employed in most laboratory investigations addressing the effect of SO2. Therefore it is important to investigate the influence of SO2 on corrosion of superheaters, under gas mixtures similar to biomass boiler conditions in order to understand the related corrosion mechanisms under such conditions.

This paper is the second part of the study addressing the effect of flue gas composition on the corrosion of superheaters in biomass-fired boilers using laboratory scaled investigations. Part I \cite{213} reports on the effect of Cl containing species (in both the deposit and the gas phase) on the corrosion of a superheater material (TP 347H FG). The present paper (Part-II) focusses on the influence of SO2 in the gas phase during corrosion of the same superheater material. In analogy to part-I of this study \cite{213}, the present investigation considers both deposit-free and KCl-deposited samples, and it also addresses the influence of additional HCl in the gas phase, to clarify the effect of the interaction between SO2 and deposit particles on corrosion.

2 Experimental

2.1 High temperature corrosion exposure

An austenitic stainless steel (TP 347H FG) tube with the following chemical composition was used for the experiments: 18.1 wt% chromium (Cr), 10.3 wt% nickel (Ni), 2.0 wt% manganese (Mn), 0.5 wt% niobium (Nb), 0.4 wt% silicon (Si) with iron (Fe) as balance. According to \cite{149}, the alloy has a carbon content of 0.057 wt%. From the tube, rings with a width of 10 mm (longitudinal direction of the tube) were cut and further segmented such that arc shaped samples with arc length of 14.6 mm were obtained. The wall thickness of the tube, i.e. the height of the samples, was 7.4 mm. Prior to corrosion exposures, the samples were cleaned by ultrasonically degreasing in acetone followed by drying in ethanol. Afterwards, samples to be exposed with a deposit were coated with a slurry of the synthetic KCl deposit which was obtained by dispersing 32 – 63 μm sized KCl particles (Sigma, \geq 99\%) in a solution of 2-propanol. Using deposit slurries to coat samples provides a means of obtaining a tight contact between deposit particles and the sample surface, so as to closely mimic the conditions in real superheaters. A final thickness of the KCl-deposit of 1 mm was obtained after drying the coating on the sample. Samples for exposures under deposit-free conditions were directly exposed in the as-cleaned state.

The corrosion test rig utilised is shown in Figure 1 and consists of a gas mixing unit, an electrically heated furnace and a scrubber system for cleaning the flue gas. Using mass flow controllers in the gas mixing unit, the desired concentration of each gas component was obtained. To incorporate 13.4 vol % of water vapour (H2O) in the gas stream, the carrier gas (nitrogen - N2), carbon (IV) oxide (CO2) and oxygen (O2) were all bubbled through a water flask maintained at 52 °C. The final gas stream comprised of a mixture of the humid oxidizing gas (H2O, CO2 and O2), SO2 (and HCl) which was fed into the reactor.
through a preheated gas channel to avoid condensation. The total gas flow rate in the inlet stream was 1000 mL min\(^{-1}\).

**Figure 1.** Schematic representation of the corrosion test rig employed for the high-temperature exposures.

Table 1 summarizes the four different exposures considered in the present study. Under both oxidizing-sulphidizing and oxidizing-sulphidizing-chlorinating gas mixtures, deposit-coated and deposit-free samples were exposed. The oxidizing-sulphidizing-chlorinating gas mixture mimics the condition during straw-firing [111] where the HCl concentration is chosen to reflect the worst case situation. Each experimental condition involved a minimum of 4 samples placed in quartz reactors inside the furnace in positions parallel to the direction of gas flow. Exposures were carried out isothermally at 560 °C for 72 h after which samples were allowed to cool inside the reactors under a flow of N\(_2\).

**Table 1.** A summary of the experimental conditions investigated in the present study.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Deposit coated?</th>
<th>Gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>IIIa</td>
<td>Yes</td>
<td>Oxidizing-sulphidizing gas: SO(_2) – 60 ppmv (dry), O(_2) – 6 vol % (dry), CO(_2) – 12 vol % (dry), N(_2) – 82 vol % (dry) and H(_2)O – 13.4 vol %</td>
</tr>
<tr>
<td>IIIb</td>
<td>No</td>
<td></td>
</tr>
<tr>
<td>IVa</td>
<td>Yes</td>
<td>Oxidizing-sulphidizing-chlorinating gas: HCl – 400 ppmv (dry), SO(_2) – 60 ppmv (dry), O(_2) – 6 vol % (dry), CO(_2) – 12 vol % (dry), N(_2) – 82 vol % (dry) and H(_2)O – 13.4 vol %</td>
</tr>
<tr>
<td>IVb</td>
<td>No</td>
<td></td>
</tr>
</tbody>
</table>
2.2 Corrosion product characterization

For comprehensive characterization of the corrosion products, both cross-sectional and the plan ‘top-down’ approaches [208] were employed. This involved the complementary use of scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD). For cross-sectional characterization of corrosion products, samples were mounted in epoxy under vacuum using a two-stage process (for details of metallographic preparation, see [208]).

In the plan view ‘top-down’ approach, characterization was undertaken directly on surfaces of exposed samples and continued on the successively revealed surfaces after several steps of mechanical removal of the corrosion products with a scalpel or silicon carbide (SiC) paper. This stepwise removal and characterization of exposed surface reveals detailed information that supplements microstructure information obtained from cross-sections. A detailed explanation of this approach in addition to its advantages for characterization of corrosion products is given elsewhere [208].

An Inspect S (FEI instruments) microscope was used for SEM investigations on both cross-sections and plan views. An acceleration voltage of 15 keV was used and imaging was carried out using the backscatter electron detector (BSE) unless otherwise stated. EDS was also carried out in the SEM using an acceleration voltage of 15 keV to determine the chemical composition of the corrosion products. Both Aztec and Inca (Oxford instruments) software were used for EDS analysis. EDS results presented here are limited to concentrations above 1 wt % which are representative for the otherwise heterogeneous corrosion products. For qualitative phase analysis, XRD was carried out as part of the plan view ‘top-down’ characterization, thus, on both the original surfaces and after successive mechanical removal of the corrosion product layers. A Bruker AXS (D8 Discover) diffractometer equipped with a Cr Kα radiation source was used in grazing incidence geometry (GI-XRD, grazing incidence angle, γ = 2°), whereby the X-ray penetration depth was confined to thicknesses lower than that of the removed layer in each case. However in the case of deposit-free samples involving no further removal of the thin corrosion products, the incidence angle (γ) was raised to 5° to increase the X-ray penetration depth and probe more sample volume. Due to the curved geometry of the samples, the incident beam was converged using a polycap optic system into a point focused beam.

In addition to experimental investigations, thermodynamic calculations were performed with FactSage 7.0 [184,235] using the FactPS, FT oxid, FT salt, and FT pulp databases. The calculations were used to support some of the experimental findings and were based on minimizing the Gibbs free energy of the systems considered.
3. Results

3.1 KCl-coated samples exposed to an oxidizing-sulphidizing gas (Experiment IIIa)

From examinations of cross-sectioned deposit-coated samples exposed to the oxidizing-sulphidizing gas mixture (experimental condition IIIa), two different types of corrosion product morphologies were observed (Figure 2a and b). In some areas the corrosion product appears rather homogeneous in thickness with flat topography (Figure 2a), whereas in other regions there is a dome-like appearance (Figure 2b) with corresponding extensive pitting of the alloy.

**Figure 2.** Cross-section of corrosion products showing (a) regions with flat morphology and (b) regions with pitting morphology after exposure of KCl-coated samples to an oxidizing-sulphidizing gas mixture (experiment IIIa). The different types of morphologies in (a) and (b) were equally distributed across the sample cross section. Double-headed arrows 1–3 indicate the different layers of corrosion product. Note that the deposits are not visible in both micrographs.

The different types of morphologies were distributed equally across the sample cross section, thus none of the morphology types was predominant. The corrosion product layers identified in regions comprising each of these morphologies are indicated by double-headed arrows (1-3) in Figure 2. As revealed by the contrast in the micrographs (Figure 2), layer 1 of the corrosion product was present in both types of morphology and is apparently a mixture of two phases. For regions with the flat morphology, layer 2 was
a relatively compact layer while in regions with the dome-like appearance; layer 2 consisted of finely dispersed particles located closer to layer 1, and a mixture of two phases located above the assumed original sample surface. Layer 3 exists as broad pits below the “original” metal surface and was only present in regions with dome-like appearance.

Elemental distribution maps in Figure 3a show that layer 1 in Figure 2a, contains Fe, Mn, K, S, and O. The relatively compact layer 2 in regions with flat morphology (Figure 2a) is revealed by the EDS maps in Figure 3a to contain Fe, Cr and O, with a band of S in the lower part. Local regions enriched in Ni were also present at the interface between layer 2 and the alloy bulk. For regions with pitting attack, the elemental composition of layer 1 was similar with that of layer 1 in Figure 3a, and hence, not repeated here. EDS maps in Figure 3b show that for the regions with pitting attack, the dispersed particles located closer to layer 1 were Fe and O rich. However, the mixture of two phases located above the assumed original sample surface (Figure 2b) are Fe-O rich (darker regions) and Ni-S rich (brighter regions) as revealed by EDS maps in Figure 3b. The broad pits below the “original” metal surface (i.e. layer 3 in Figure 2b) consist of Fe, Cr, S and O (Figure 3b). A Ni enriched band is formed within the alloy adjacent the corrosion front and on some locations, this layer was porous (Figure S1, supporting information).

Plan view investigations on the deposit after the exposure showed the accumulation of faceted particles on the deposit particles (Figure 4a, b), which was not visible in the cross-sections. These accumulations were present both at the gas/deposit and deposit/corrosion product interfaces, but the faceted particles were smaller at the latter interface (Figure 4b). At the gas/deposit interface, EDS analysis showed the faceted particles to consist of K, S and O with the following concentration (wt %): K–41.7, S-18.4 and O–39.9. However, the original deposit particles were not completely covered with the faceted particles at the deposit/corrosion product interface, and therefore EDS analysis showed the presence of about 2.2 wt % Cl.

A secondary electron (SE) plan view micrograph is shown in Figure 4c revealing both flat and dome-like morphologies, beneath the deposit (corresponding to layer 1 in the cross-sections). A close-up BSE micrograph of regions with flat morphology (Figure 4d) gives the appearance of a molten phase with small particles of another composition. Similar to the result from the cross section, EDS analysis showed the presence of (in wt %): Fe–1.9, Mn–6.6, K–38.4, S–16.8 and O–36.3 in this layer.
Figure 3. EDS maps showing elemental composition of the corrosion products resulting from exposure of deposit-coated samples to an oxidizing-sulphidizing gas mixture (experiment IIIa). Double-headed arrows 1–3 indicate the different layers of corrosion product. Note that the composition of layer 1 in (a) is similar in both Figures 2a and b, and hence not repeated in (b).

Figure 5 shows the corrosion product after partial removal of layer 1. From the overview in Figure 5a, the outward grown layers (i.e. layer 2) on regions with dome-like morphology (box b), layer 2 on regions with flat morphology (box c), as well as remnants of layer 1, can all be seen. Similar to the cross section of regions with a dome-like morphology (cf Figure 2b, c), the contrast in the magnified micrograph in Figure 5b also infers the presence of at least two phases, which is consistent with EDS analysis that the bright regions in this layer (area 2 in Figure 5b) are enriched in Fe, Ni, S and O, whereas the darker region consisting of finely dispersed particles (area 3 in Figure 5b) are enriched in Fe and O. Fe-rich larger faceted particles were also identified on some positions adjacent to the finely dispersed particles. Plan view investigations of regions with flat morphology show that a Fe-rich oxide layer exists below layer 1 on regions with a flat morphology, where no internal attack/pitting was observed (Figure 5c).
Figure 4. Plan view micrographs showing deposit particles at (a) the gas/deposit and (b) deposit/corrosion product interfaces after exposure to an oxidizing-sulphidizing gas mixture (experiment IIIa). (c) SE micrograph of layer 1 of corrosion product showing regions with both flat and dome-like (pitting) morphologies, below the initial deposit. (d) A magnified BSE micrograph of the flat regions contained in (c).
Figure 5. Plan view BSE micrograph after exposure of deposit-coated samples to an oxidizing-sulphidizing gas mixture (experiment IIIa) showing (a) an overview and (b,c) close-up microstructures of corrosion product below layer 1 (after partial removal of the layer shown in Figure 4c). Elemental compositions are given in wt%.

In Figure 6, the plan view of the corrosion products on the sample subsurface region is shown. Localized pits are observed in the micrograph corresponding to the internally attacked zones (layer 3) (cf. Figure 2). From the EDS maps, it is observed that these zones are depleted in Fe. In agreement with characterization on the cross section (Figure 3b), Cr, S, O are also present in the pits, and Ni is depleted within the pits but slightly enriched in the alloy adjacent to the pits. No additional feature was observed with further removal of the corrosion product, except for the reduction in size of the localized pits as the bulk of the alloy was approached.
Phase identification through GI – XRD measurements (Figure 7), showed that the predominant crystalline corrosion product in layer 1 is $\text{K}_2\text{SO}_4$ [according to Joint Committee on Powder Diffraction Standards (JCPDS) card 05-613]. In addition, KCl was also identified in layer 1 due to incomplete removal of KCl deposit particles (cf. Figure 4c). On the external corrosion product layer beneath layer 1 (i.e. layers 2), the identified major crystalline phases were $\text{Fe}_2\text{O}_3$ (JCPDS card 33-664) and $\text{Fe}_3\text{O}_4$ (JCPDS card 73-698). Peaks from $\text{K}_2\text{SO}_4$ and KCl are still observed in the diffractogram recorded on the outward grown corrosion products, probably because of the incomplete removal of layer 1 (cf. Figure 5a). The diffractogram recorded on the sample subsurface (layer 3) is seen to contain peaks from $\text{Cr}_2\text{O}_3$ (JCPDS card 38-1479). Sulphides of Ni or Cr as suggested by EDS results in Figures 5 and 6 were not identified with XRD. Because the internally attacked regions are localized and thus the alloy bulk also diffracts, peaks from the austenite phase (alloy bulk) are also present in the diffractogram recorded on layer 3. The additional peak evolving near the austenite-111 peak at about $68^\circ 20$ (indicated by the arrow) originates from the stress-induced austenite transformation to martensite during the mechanical removal process. It is pertinent to note that the possibility of clarifying if oxides of the alloying elements are in solid solution in the identified phases cannot be determined based on the presented XRD results, because of the simultaneous influence of both chemical variations and internal stresses in the corrosion products on the measured peak positions compared to the theoretical diffraction angles of the various phases.

**Figure 6.** Plan view and EDS maps of the internally attacked region (layer 3) after exposure of deposit-coated samples to an oxidizing-sulphidizing gas mixture (experiment IIIa).
Figure 7. XRD diffractograms showing the crystalline phases present in different layers of the resulting corrosion product after exposure of deposit-coated samples to an oxidizing-sulphidizing gas mixture (experiment IIIa).

3.2 Deposit-free samples exposed to an oxidizing-sulphidizing gas (Experiment IIIb)

Figure 8 presents the cross-section and plan-view of the corrosion products after exposure of deposit-free samples to an oxidizing-sulphidizing gas. Compared to the corrosion product on deposit-coated samples, a relatively thin layer of corrosion product formed on deposit-free samples. Elemental maps (Figure 8a) of the O-rich corrosion product show that it is Fe-rich in the upper parts and Cr-rich in the lower parts. In addition, distinct S-containing regions are observed at the lower part of the corrosion product and, together with Ni, at points where the attack has occurred.

The plan view micrograph in Figure 8b show that the corrosion attack was somewhat minimized along the grain boundaries relative to the interior of the grains. By EDS mapping, it was observed that the corrosion products near the grain boundaries are Cr and Ni rich, whereas Fe-rich corrosion products are formed over the interior of the grains.

$\text{Fe}_2\text{O}_3$ (JCPDS card 33-664) and $\text{FeCr}_2\text{O}_4$ (JCPDS card 34-140) were the only crystalline corrosion products identified from GI – XRD measurements (Figure 9). As a result of the thin nature of corrosion products, peaks from the austenite phase (alloy bulk) were also recorded.
Figure 8. (a) Cross-section and corresponding EDS elemental maps, and (b) plan-view of the corrosion products resulting from exposure of deposit-free samples to an oxidizing-sulphidizing gas mixture (experiment IIIb).

Figure 9. XRD diffractogram of a deposit-free sample exposed to an oxidizing-sulphidizing gas mixture (experiment IIIb).
3.3  **KCl coated samples exposed to an oxidizing-sulphidizing-chlorinating gas (Experiment IVa)**

The detailed results from cross-section and plan view characterization of corrosion products from this exposure have been previously reported by the present authors [244], where the effect of the water content in the corrosive gas mixture was addressed. In the present paper, a summary of results is presented to aid comparison with both experimental conditions IIIa in the present work, i.e. without HCl in the gas mixture, and experimental condition IIa in part I of this work [213], without SO$_2$ present in the gas mixture.

In general, three layers of corrosion products were observed below the initial deposit after exposure of deposit-coated samples to a gas mixture mimicking straw-firing, i.e. the oxidizing-sulphidizing-chlorinating gas mixture (Figure 10).

![Figure 10](image-url)  
*Figure 10*. Resulting microstructures of the corrosion product after exposure of deposit-coated samples to the straw-firing gas mixture (experiment IVa). Inserted double-headed arrows indicate the different layers of corrosion product.

The different corrosion product layers are indicated by double-headed arrows in the micrographs shown in Figure 10a and b. Elemental mapping on the cross section (Figure 11a) show that K, S, Fe and O make up the elemental composition of layer 1. Additionally, Cl and K, and Mn and O were identified on some locations in the upper part of layer 1. The elemental composition of layer 2 revealed Fe, Cr and O. As is typical for deposit-induced corrosion, the morphology of the layer 3 was heterogeneous where grain boundary attack, selective attack resulting in porous regions and shallow S-containing pits were typical features observed. EDS mapping (Figure 11b) shows that layer 3 consists of Cr, Ni, S, and O. However,
Ni appears to be enriched in the regions with a porous morphology. Cl was also identified on some locations of layer 3 [244].

Figure 11. EDS maps showing the elemental composition of corrosion products resulting from the exposure of deposit-coated samples to a gas mixture mimicking straw-firing conditions (experiment IVa). Double-headed arrows 1–3 indicate the different layers of corrosion product.

Plan-view investigations showed K, S and O particles around original deposit particles due to partial sulphation of the KCl deposit both at the gas/deposit and deposit/corrosion product interfaces (Figures 12a and b, respectively). Similar to observations on the deposits exposed to an oxidizing-sulphidizing gas (cf. Figures 4a, b), accumulation of the K, S and O containing features occurred to a lesser extent at the deposit/corrosion product interface compared with the gas/deposit interface. Additionally, plan view investigations revealed that layer 1 was also composed of partially sulphated deposit particles on a K₂SO₄–Fe₂O₃–KCl layer (Figure 12c).
3.4 Deposit-free samples exposed to an oxidizing-sulphidizing-chlorinating gas (Experiment IVb)

The plan-view micrograph in Figure 13 shows the corrosion products on a deposit-free sample after exposure to a gas mixture mimicking straw-firing. The contrast in the BSE micrograph suggests that a thicker layer of corrosion products formed mainly on the grain interiors (appearing darker) compared with regions around the grain boundaries, which appears brighter because of a higher fraction of backscattered electrons from the underlying bulk alloy. Similar to the composition of the corrosion products formed on deposit-free samples exposed to an oxidizing-sulphidizing gas (cf. Figure 8b), the corrosion product formed above the grain interiors was also Fe-rich compared with regions around the grain boundaries (Figure 13).
Figure 13. Plan-view microstructure and chemical composition (in wt %) of the corrosion product observed after the exposure of deposit-free samples to a gas mixture mimicking straw-firing conditions (experiment IVb).

3.5 Thickness of corrosion products

Statistical variation in thickness of the first layer of corrosion products (layer 1) resulting from exposure of deposit-coated samples to the different atmospheres are compared in Figure 14. Comparisons of the mean and maximum values show that exposure of deposit-coated samples to an oxidizing-sulphidizing atmosphere results in a thicker sulphate ($K_2SO_4$) containing layer – layer 1. In Figure 14, the depths of internal attack suffered by deposit-coated samples exposed to the different atmospheres are also compared, to obtain a measure of corrosion rate in the different atmospheres. Comparison of the internally attacked layer considered the depth of the broad pits (layer 3 in Figure 2) after exposures under oxidizing-sulphidizing atmospheres, and the thickness of layer 3 (Figure 10) from exposures to straw-firing conditions. It is observed that both the mean and maximum depth of the pits resulting from exposure to an oxidizing-sulphidizing gas surpasses the mean and maximum depth of internal or grain boundary attack resulting from exposure to the gas mixture mimicking straw-firing.
Figure 14. Thicknesses of layer 1 of corrosion product, and the internal attack after exposure of deposit-coated samples to the different gas mixtures. The maximum and minimum values are represented by marks above and below each box, whereas location of 50 % of the distribution is shown by the horizontal bar in each box. Round dots in each box represent the mean value, and the standard deviation from the mean is represented by the horizontal edges of the box. At least 20 positions on the exposed samples were measured to obtain the distribution. Note the difference in the vertical scales.

4 Discussion

From characterization of the samples exposed to the different atmospheres, it is revealed that more corrosion attack occurred on deposit-coated samples compared with deposit-free samples exposed to identical conditions. A summary of the corrosion products identified on deposit-coated samples is presented in Table 2 to aid comparison. A noteworthy observation is that partial sulphation of the deposit particles occurred after exposure to both an oxidizing-sulphidizing gas (Figure 4a, b) and an oxidizing-sulphidizing-chlorinating gas (mimicking straw-firing) (Figure 12a, b). As a result, metal oxides of Fe and Mn, in mixture with K2SO4 were always present in layer 1 of the corrosion product (i.e. below the deposit) with a morphology that indicated formation of a melt phase during the exposure. KCl was present in some cases in layer 1. The elemental composition and morphology of layer 3 of corrosion products after the exposures remarkably depended on the absence/presence of additional HCl in the gas mixture. In the following discussion, the interactions between the alloying elements, deposit (KCl) particles, and the gaseous atmosphere are addressed in terms of their impact on corrosion under conditions relevant to biomass-firing.
Table 2. Summary of corrosion products on deposit-coated samples resulting from exposure to the different gas mixtures.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Deposit appearance</th>
<th>Corrosion product morphology, phase and chemical composition</th>
</tr>
</thead>
</table>
| IIIa (oxidizing-sulphidizing gas mixture) | Partly sulphated at both gas/deposit and deposit/corrosion product interfaces | **Flat morphology**: layer 1: Flat and partly molten, K$_2$SO$_4$ and Fe$_2$O$_3$  
Layer 2: Fe – Cr – rich oxide. Ni and S enrichment in deeper regions  
Layer 3: Broad internal Cr – O – S-rich pits, Cr$_2$O$_3$, Ni enrichment at interface between pits and bulk alloy |
| IIIb (oxidizing-sulphidizing gas-mixture) | Discontinuous Fe-Cr-rich oxide, Fe$_2$O$_3$. Local S enrichment |
| IVa (oxidizing-sulphidizing-chlorinating gas mixture) | Partly sulphated at both gas/deposit and deposit/corrosion product interfaces | Layer 1: Partly molten, K$_2$SO$_4$ and Fe$_2$O$_3$, and KCl  
Layer 2: Fe – Cr – rich oxide, Fe$_2$O$_3$  
Layer 3: Cr – Ni – S – O – rich, grain boundary attack, chlorine rich features |
| IVb (oxidizing-sulphidizing-chlorinating gas mixture) | Discontinuous Fe-Cr-rich oxide, Fe$_2$O$_3$ [244] |

4.1 **SO$_2$ effects in the presence of a KCl deposit**

In part-I of this work, the effect of a KCl deposit on corrosion of samples exposed under oxidizing conditions was discussed [213]. Potassium from the deposits was suggested to disrupt the initial protective layer (Cr$_2$O$_3$) causing the formation of a non-protective Fe-rich layer instead [137]. Subsequently, due to the ability of chlorine species (both from such reaction and the HCl in the gas mixture) to initiate chlorination of alloying elements, selective attack of Fe, Mn and Cr was observed. The reaction between KCl with Cr$_2$O$_3$ may have occurred in the present study. As reported in [127,208], formed K$_2$CrO$_4$ will be quickly sulphated to K$_2$SO$_4$ due to the presence of SO$_2$ in the gas mixtures.
A positive effect of SO₂ has been reported when SO₂ sulphates KCl aerosol particles in the vapour phase, before they condense on vulnerable metallic surfaces (i.e. ‘in-flight’ sulphation) [167,245]. However, heterogeneous (‘in-deposit’) sulphation [246] is considered in the following discussion because this corresponds to the experimental conditions in the present study. This reaction is responsible for the accumulation of K, S and O-rich (K₂SO₄) features around KCl particles and is in agreement with results from full-scale studies [100]. The mechanism behind this is properly discussed in literature [196,197,246].

According to the Deacon process [156], the sulphation of KCl particles under the current experimental conditions will result in generation of pCl₂ which is six orders of magnitude higher than that resulting from K₂CrO₄ formation [184,235]. A pertinent question would be how this ‘in-deposit’ sulphation reaction will influence corrosion of the alloy with respect to the formed sulphate and released HCl. For the deposit-coated samples exposed to gas mixtures containing SO₂, the simultaneous presence of both K₂SO₄ and MₓOᵧ (M = {Fe, Mn}) is observed in layer 1 below the deposits. This therefore suggests that metal (Fe and Mn) chlorides formed due to chlorination (reaction 1) and were converted to their oxides within the sulphate.

\[ M(s) + xCl \rightarrow MClₓ(s) \] (1)

Plan view investigations (Figures 4d and 12c) show that layer 1 has partly been molten although the exposure temperature in this work (560 °C) was considerably lower than the melting temperature of K₂SO₄ (1069 °C), KCl (772 °C) and the KCl-K₂SO₄ eutectic temperature (690 °C) [247]. Interestingly, the KCl-K₂SO₄-Fe₂O₃ system has been reported to show a solidus at 577 °C [26]. It is therefore possible that the metal chlorides generated from reaction 1 during the initial stages of corrosion lowered the melting temperature of the KCl-MeClₓ-K₂SO₄ system below 560 °C. Metal chlorides (especially FeCl₂) are known [26,208,248], and was also observed in part 1 of this study [213] to be able to induce low temperature melt formation. In accordance with increased generation of HCl reported in reference [246], such solid-liquid transformation enhances the rate of the sulphation reaction because KCl sulphates faster in the molten phase. In addition, a better coverage of the sample is provided by the Cl-containing melt, hence, permitting greater dissolution of alloying element by chlorination.

Molten sulphate deposits have the potential of initiating hot corrosion attack at temperatures above 600°C [82]. The morphology of corrosion products formed on KCl deposit-coated samples exposed to oxidizing-sulphidizing gas mixture (Figures 2 and 5) suggests corrosion attack dominated by molten sulphates and in addition, it is similar to that observed for a Co-Cr alloy exposed at temperatures between 600 and 750 °C [249]. However, the absence of K in the large pits (Figure 3b) implies that the mechanism of corrosion attack of the present samples is not solely related to the previously outlined type (II) hot corrosion caused by a related sulphate (Na₂SO₄) [85,249]. Although dissolution of alloying elements in the sulphate melt has been reported [83] as the major mechanism of attack responsible for the formation
of the observed large pits (Figure 2b), a synergistic action between Cl and S may be responsible for the increased corrosion attack after exposure to an oxidizing-sulphidizing gas. Thus, it is suggested that in the Cl-containing melt, dissolution occurred by chlorination (reaction 1) of alloying elements. This is supported by the presence of Ni-rich porous layers on some positions adjacent to the corrosion front (Figure S1, supporting information) because, compared to Fe, Cr and Mn, Ni has a lower driving force for chlorination [56,76,156]. A similar synergistic effect (between Cl and S) has also been observed for corrosion attack under a syngas atmosphere [250] and with sulphate deposits [251] due to the additional influence of chlorides. In addition to the proposed role of both KCl and metal chlorides to assist in low temperature formation of a sulphate containing melt, these Cl-bearing species are also proposed to assist in transportation of alloying elements away from the corrosion front (in the pits) leading to their redistribution above the pits. Some considerations on the mechanisms leading to this complex corrosion attack are further discussed as follows.

Upon chlorination of alloying elements in the melt, volatile metal chlorides with varying stabilities will result [56,76,156]. Specifically, Fe and Ni-chlorides, according to thermodynamic calculations [184,235] will need to encounter sufficiently higher $p_{\text{O}_2}$ (> $10^{-27}$ and $10^{-21}$ atm, respectively), to be converted to the corresponding metal oxides (reaction 2), compared to Cr which will require $p_{\text{O}_2}$ > $10^{-38}$ atm. The requirement of high $p_{\text{O}_2}$ for NiCl$_2$ transformation to the oxide is supported by experimental results in reference [232] as well as its observation on samples after in situ corrosion tests in power plants [252].

$$\text{yMCl}_x(\text{g}) + \frac{z}{2}\text{O}_2(\text{g}) \rightleftharpoons \text{M}_y\text{O}_z(s) + y\text{Cl}_x(\text{g})$$  \hspace{1cm} (2)

In agreement with thermodynamic calculations with respect to $p_{\text{O}_2}$, only Ni- and Fe-containing corrosion products were observed above the pits (Figure 3b). The resulting metal chlorides of these elements were partitioned into Fe-oxide and Ni-sulphide, which is justified on the basis of the corresponding reactions between FeCl$_2$ and NiCl$_2$ resulting from chlorination within the pits, and S-containing species at positions above the pits. The thermodynamic favourability of reaction 3 ($\Delta G^\circ = -85.93$ kJ/mol (NiS) at 560 °C [184,235]) supports favourable partitioning of Ni into the sulphide phase and Fe as the oxide as observed in Figure 3b. (FeS and NiS have been chosen for simplicity).

$$\text{FeS(s)} + \text{NiO(s)} + 0.16\text{O}_2(\text{g}) \rightleftharpoons 0.33\text{Fe}_3\text{O}_4(s) + \text{NiS(s)}$$  \hspace{1cm} (3)

As a result of the porous morphology of the corrosion product in the pits (Figure 2b), transport of SO$_2$ into the pits is also feasible, and in addition to low $p_{\text{O}_2}$ present in these regions, sulphidation of Fe can occur, as confirmed experimentally in the EDS maps in Figure 3b. Moreover, reaction of the resulting Fe-sulphides with Cl species would also result in formation of the volatile Fe-chlorides which will be transported away from the pits in accordance with the active-sulphidation mechanism proposed in reference [253]. Interestingly, the very low $p_{\text{O}_2}$ in the pits is also observed to be sufficient for conversion of any CrCl$_2$ to the oxide.
The morphology of the corrosion products resulting from experiments IIIa and IVa (cf. Figures 2 and 10) as well as the degree of corrosion attack (cf. Figure 14) suggests that with SO₂ in the gas mixture, the type of corrosion attack depends on whether HCl is also present in the gas mixture. The presence of HCl in the oxidizing-sulphidizing-chlorinating gas mixture, (simulating straw-firing) is observed to reduce the thickness of the K₂SO₄ – MₓOᵧ layer (Figure 14), which is probably caused by decreased sulphation of KCl to K₂SO₄. Comparison of corrosion product morphologies (cf. Figures 2 and 10) reveals that the suspected Cl-assisted hot-corrosion attack was greatly reduced in the oxidizing-sulphidizing-chlorinating environment possibly because the sulphate layer was not able to provide a slightly reducing microclimate to facilitate such corrosion attack. However, selective chlorination of Fe, Mn and Cr (reaction 1) occurred and accounts for the formation of porous Ni-rich islands in layer 3 of the corrosion product (Figures 10a and 11b). Furthermore, the tendency of Cl to perpetuate corrosion attack along grain boundaries due to easier diffusion along these paths (as was observed in part I of this study, under oxidizing and oxidizing-chlorinating conditions [213]), is also manifested in the corrosion products. Nonetheless, formation of Cr-rich shallow pits (Figure 10b) similar to those observed from the oxidizing-sulphidizing gas mixture (cf. Figure 2b), in addition to accumulation of S in the lower layers of corrosion product (Figure 11b) also infers that in addition to chlorination, sulphidation has an essential influence on the observed corrosion attack.

From comparison of the results in part I of this study [213], and the present results, it is observed that KCl interaction with metal chlorides always results in melt formation, which increases corrosion attack. However, contrary to the oxidizing and oxidizing-chlorinating conditions, the sulphate layers resulting from sulphation in SO₂ containing gases provides microclimates which facilitate severe pitting attack. To improve the understanding of SO₂ effects on high temperature corrosion involving KCl deposits, as well as the responsible mechanisms, further experiments should be conducted by varying parameters such as SO₂ concentration within ranges relevant to biomass firing, deposit thickness, oxidizing potential of the gas, as well as the use of K₂SO₄ as the initial deposit. Time resolved studies are also necessary to observe corrosion in the initial stages.

4.2  SO₂ effects under deposit-free conditions

The morphology of corrosion products resulting from exposure of deposit-free samples suggests a lesser degree of corrosion attack relative to that on the deposit-coated samples. Interestingly, the corrosion product morphology and composition was similar for deposit-free samples exposed to both oxidizing-sulphidizing gas (cf. Figure 8b) and the gaseous mixture mimicking straw-firing conditions (cf. Figure 13). Comparison of the experimental results after exposures to oxidizing and oxidizing-chlorinating atmospheres in the absence of a KCl deposit (see part-I of this study [213]) with the present results from oxidizing-sulphidizing and straw-firing atmospheres, reveals that the formation of a double layered corrosion product was strongly inhibited after exposures to gas mixtures containing SO₂. This effect could be attributed to strong adsorption of SO₂ on active sites of the sample surface, consequently hampering formation of oxygen containing ions [241]. In line with this, the kinetics of oxidation will be
reduced as a result of the limited adsorption of oxygen bearing species (which generate oxygen containing anions). In addition to the active site blocking effect, adsorbed sulphate species may influence the transport of ions through the oxide grain boundaries. Surface sulphates has been suggested to slow down oxygen ion transport in the grain boundary of hematite, thereby causing an inhibitive effect on the oxidation of Fe \[241\].

On the other hand, previous investigation on the oxidation of FeCr alloys has suggested that the development of a double layered corrosion product facilitated by H ingress into the alloy \[254\], is greatly reduced by the presence of impurity S in the alloy \[255\]. The high affinity of Cr for S promoted its enrichment around segregated S regions, and was mooted to enhance formation of the protective Cr$_2$O$_3$ \[255\]. Interestingly, EDS maps in Figure 8 reveal that after exposure of deposit-free samples to an oxidizing-sulphidizing gas (experiment IIIb), S accumulated in the lower parts of the corrosion products and along the attacked grain boundaries. It is possible that this facilitated formation of Cr-rich oxides which slowed down growth of the double layered oxide observed in SO$_2$ free exposures \[213\].

In all the gas mixtures utilized for exposures in the present study (Table 1), the ratio of $P_{H_2O}$ to $P_{O_2}$ is greater than 1, hence an additional effect of this high $P_{H_2O}$ on corrosion is possible. High $P_{H_2O}$ in the O$_2$ containing gas mixture is known to cause volatilization of Cr oxide in the form of CrO$_2$(OH)$_2$ species even at temperatures below 1000 $^\circ$C, above which oxide volatilization has been suggested to account for accelerated corrosion \[52,137\]. Above 500 $^\circ$C, it has been observed for austenitic stainless steels, that Cr-depleted oxides are consequently formed due to insufficient supply of Cr from the bulk to maintain formation of a Cr-rich oxide \[137\][164]. This effect is also reflected in results observed on deposit-free samples after exposure to oxidizing-sulphidizing and oxidizing-sulphidizing-chlorinating (straw-firing) gas mixtures. Mainly Fe-rich oxides were observed by plan-view investigations (cf. Figures 8b and 13). However, the regions surrounding the grain boundaries show the presence of a thinner Cr-rich oxide which was facilitated by faster transport of Cr through the grain boundaries. In addition to the possible effect of Cr-oxide volatilization, the formation of Fe-rich oxides may have been induced by the ability of OH$^-$ resulting from dissociation of H$_2$O, to promote internal oxidation of Cr, thereby resulting in the outward formation of Fe-rich oxides \[62\].

5 Summary and conclusions

The effects of flue gas composition on high temperature corrosion of a superheater material (TP 347H FG) have been studied, with emphasis on the role of 60 ppmv SO$_2$ in the gas. The following conclusions can be made based on the obtained results.

- SO$_2$ in the gas phase is able to reduce corrosion attack only in the absence of a KCl deposit.

- Deposit-coated samples suffer more corrosion attack compared to their deposit-free counterparts after similar exposure to SO$_2$ containing gas mixtures.
- **SO₂** incorporation into the gas phase causes sulphation of the original KCl deposit particles. A layer comprising mainly of K₂SO₄ and Fe₂O₃ forms below the initial deposit. The Fe₂O₃ in this layer results from conversion of metal chlorides to oxides.

- In the presence of KCl, a chloride-sulphate melt induced by metal chlorides forms, and provokes a Cl-assisted pitting attack. Alloying elements are chlorinated and transported as metal chlorides away from the pits. This type of corrosion attack is severe under an oxidizing-sulphidizing gas atmosphere.

- Additional presence of HCl in the gas mixture (oxidizing-sulphidizing-chlorinating gas mixture) decelerates the pitting attack but initiates grain boundary attack.

- The severe degradation suffered by deposit-coated samples after exposure to an oxidizing-sulphidizing gas mixture hint at possible corrosion problems if ‘in-deposit’ sulphation of alkali chlorides occurs under low p_{O₂} conditions.

**Acknowledgements**

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**References**

The references cited in this manuscript are collected in the general reference list of the thesis.
Supporting Information

**Figure S1.** Microstructure (a and b) and composition (c) of pitting attack resulting from high temperature corrosion of TP 347H FG exposed to an oxidizing-sulphidizing gas mixture at 560 °C for 72 h. The presence of a Ni-rich layer adjacent to the corrosion front is evident from the EDS maps in (c).
5.3 – Effect of water vapour on high temperature corrosion under conditions mimicking biomass firing\textsuperscript{vi}

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Abstract

The variable flue gas composition in biomass-fired plants, among other parameters, contributes to the complexity of high temperature corrosion of materials. Systematic parameter studies are thus necessary to understand the underlying corrosion mechanisms. This paper investigates the effect of water (H\textsubscript{2}O) vapour content in the flue gas, on the high temperature corrosion of austenitic stainless steel (TP 347H FG) under laboratory conditions, to improve the understanding of corrosion mechanisms. Deposit-coated and deposit-free samples were isothermally exposed for 72 h in a synthetic flue gas atmosphere containing either 3 vol % or 13 vol % H\textsubscript{2}O vapour. Comprehensive characterization of the corrosion products was carried out by the complementary use of microscopic, spectroscopic and diffraction based techniques. To evaluate the effect of the exposure time, results were compared to previous results with longer isothermal exposure over 168 h, and indicated that the development of a Ni-rich layer due to selective attack was time dependent. The increase in water vapour decreased the measurable corrosion attack, and, in addition decreased sulphation was observed. Results from the current investigation and from previously reported findings suggest that an increase in water vapour will cause competitive adsorption on active sites.

\textbf{Keywords:} High temperature corrosion, KCl, sulphation, H\textsubscript{2}O vapour, austenitic stainless steel.

\textsuperscript{vi} Paper published in Energy & Fuels.
1. Introduction

One of the major operational challenges experienced in power plants firing biomass is the severe corrosion of superheater tubes [8, 94, 186, 256]. The release of K, Cl, S and other organically/inorganically associated species into the vapour phase during combustion of biomass leads to subsequent condensation of deposits on superheater tubes [21]. The corrosion rate caused by KCl containing deposits accelerates with increasing steam temperatures, and therefore reduces the efficiency of biomass-fired plants relative to those fired with fossil fuels. As a consequence, the outlet steam temperature of biomass fired plants (in Denmark) is limited to about 540 °C.

KCl induced corrosion of high temperature materials has been the subject of a number of investigations [112, 137, 138, 141, 164, 191, 193, 207] to clarify the mechanism of attack in order to pave the way for the development of advanced high temperature resistant materials. Laboratory investigations have shown that the alkali earth metal plays a role in the initial corrosion process [135, 137, 191, 192, 257, 258]. Such studies indicate that a protective Cr2O3 layer cannot be formed on high Cr-alloyed steels due to the formation of K2CrO4 which leads to the formation of a Fe-rich porous oxide. Chlorine transport through the scale was suggested to proceed according to an electrochemical –“Wagner type” redox mechanism involving Cl reduction and metal oxidation [125, 135]. However, other studies with SO2 in the gas reported that corrosion is accelerated by Cl generation from the sulphation of the alkali chloride present in the deposit [111, 112, 259]. In such studies, it was suggested that the HCl released from sulphation of the deposits is able to dissociate according to the Deacon reaction [156] into Cl species which are transported through cracks and pores to the corrosion front. A cyclic attack involving the chlorination, oxidation and re-chlorination by the released chlorine was proposed to be responsible for the increased corrosion attack [111, 112, 259].

Other studies [114, 126, 127, 193, 230, 232, 260] suggest that SO2 in the flue gas can affect the corrosion process in a couple of ways:
(a) fast conversion of the corrosive chloride (KCl) to the less corrosive sulphate (K2SO4) [230, 232]. In this process, SO2 is also converted to SO3,
(b) formation of surface sulphates which prevent the vaporisation of CrO3(OH)2 and thus, slow down the corrosion process [126, 230], and;
(c) the ability of surface sulphates to inhibit surface reactions involved in corrosion [126].

It has to be noted however, that most of such studies have been carried out either with a very low surface coverage of the deposits on the samples, or with very high concentrations of SO2 which may affect the sulphation and, hence, the corrosion process. In fact, it was stated [232] that a high concentration of SO2 may induce preferential sulphation at the gas-deposit interface resulting in HCl generation away from the metal surface.
Effects of H$_2$O vapour on high temperature corrosion of materials have been widely investigated in the absence of deposits (relevant to steamside oxidation of superheater tubes) [41,52,53,61–63,124,229,261–263]. Generally the corrosion results in an outward growing magnetite layer and an inward growing Fe-Cr spinel phase. Likewise in the presence of synthetic deposits in simplified atmospheres (relevant to fireside corrosion during biomass-firing), the effect of H$_2$O vapour has frequently been studied [115,118,124,129,137,264,265]. Results from such investigations revealed that H$_2$O can exert either an accelerating [129,137,264,265] or inhibiting [115,118,124] effect on the corrosion of the investigated samples. Hence, a need for further understanding of its effect on the corrosion process is important. Even more indispensable is the need to investigate the effect of H$_2$O vapour under realistic laboratory-scale conditions related to biomass-firing and its possible influence on the sulphation of the deposits.

This paper focuses on laboratory-scaled investigations of high temperature corrosion of an austenitic stainless steel (TP 347H FG) under conditions mimicking biomass-firing in thermal power plants. The effect of the amount of H$_2$O vapour in the flue gas stream was investigated to gain better understanding of its influence on both the deposit sulphation and the corrosion mechanism. Results are compared to those from an exposure at 168 h [208] to reveal the influence of exposure time.

2. Experimental procedures

2.1 Sample preparation

Fine grained (FG) TP 347H austenitic stainless steel (chemical composition given in Table 1) was used for the present investigation. Arc shaped samples with a surface area of 1.2 cm$^2$ of concave curvature were cut from a virgin steel tube utilised as superheater tubes in the plants. The samples were ultrasonically degreased in acetone and subsequently dried with ethanol. Afterwards, the concave surfaces of some of the clean samples were coated with a slurry of the synthetic deposit prepared by mixing 32 – 63 μm sized KCl particles in a solution of 2-propanol. Each sample was coated with a 1 mm thick deposit. Using deposit slurries for laboratory investigation of high temperature corrosion forms part of the EU guidelines for effective simulation of such processes [142,194].

Table 1. Chemical composition (in wt %) of the as-received steel (TP 347H FG)

<table>
<thead>
<tr>
<th>Si</th>
<th>Cr</th>
<th>Mn</th>
<th>Ni</th>
<th>Fe</th>
<th>Nb</th>
</tr>
</thead>
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<tr>
<td>0.4</td>
<td>18.1</td>
<td>2.0</td>
<td>10.3</td>
<td>68.7</td>
<td>0.5</td>
</tr>
</tbody>
</table>
2.2 High temperature corrosion exposures

High temperature exposure of both deposit-coated and deposit-free samples was carried out in a series of experiments summarized in Table 2, under controlled atmospheres mimicking biomass firing conditions. To achieve this, a high temperature corrosion test-rig, schematically shown in Figure 1, was used. The corrosion test-rig consists of a gas mixing compartment, an electrically heated furnace and a flue gas cleaning system. Mass flow controllers are used to carefully regulate the concentration of each gas component.

Table 2. Exposure conditions at a temperature of 560°C. For comparison, conditions for the 168 h exposure at a similar temperature [208] (reference condition for the present work) is also presented

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Time (h)</th>
<th>HCl (ppmv)/dry</th>
<th>SO₂ (ppmv)/dry</th>
<th>CO₂ (vol %)/dry</th>
<th>O₂ (vol %)/dry</th>
<th>N₂ (vol %)/dry</th>
<th>H₂O (vol %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Condition 1</td>
<td>72</td>
<td>400</td>
<td>60</td>
<td>12</td>
<td>6</td>
<td>82</td>
<td>3</td>
</tr>
<tr>
<td>Condition 2</td>
<td>72</td>
<td>400</td>
<td>60</td>
<td>12</td>
<td>6</td>
<td>82</td>
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<td>60</td>
<td>12</td>
<td>6</td>
<td>82</td>
<td>3</td>
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</tbody>
</table>

Figure 1. Schematic representation of the high-temperature corrosion test-rig.
The furnace contains five quartz reactors in which the samples were placed. In reactors containing more than one sample, a minimum separation distance of 50 mm was maintained between the samples to avoid shielding effects. In order to incorporate the desired H₂O vapour concentration, the gas mixture of CO₂, O₂ and N₂ (carrier gas) was passed through a thermally controlled H₂O bath. The desired H₂O vapour concentration was obtained by setting the temperature of the bath such that the ratio of vapour pressure of H₂O at such temperatures to that at 100 °C gave the desired concentration. The H₂O loaded gas mixture was finally mixed with the HCl and SO₂ gas streams and then fed into the reactors in a preheated channel to avoid condensation. At the exit of each reactor, ball flowmeters are connected in order to maintain a uniform gas flow in each reactor. All exposures were carried out isothermally at 560 °C. After each exposure, the samples are allowed to cool down under a flow of humid N₂. A minimum of 6 samples were exposed at each experimental condition shown in Table 2.

The experiments reported here focus on the effect of parameters relevant for high temperature corrosion in biomass plants. However in the real plant, there are many fluctuating parameters, such as gas and metal temperatures, thermal gradient, flue gas composition, dynamic flow within the boiler which can make it difficult to understand the specific roles of the different corrosive components. Also, it is a simplification of the corrosion process to have isothermal exposures using only a KCl deposit. However, this is undertaken to obtain specific mechanistic data.

2.3 Characterization of exposed samples

The corrosion products formed on the samples were characterized by means of microscopic, spectroscopic and diffraction techniques. Characterization involved both examination of the cross sections, and plan-view investigations coupled with mechanical removal of the corrosion products (in the case of deposit-coated samples).

To facilitate cross-sectional investigations on exposed deposit-coated samples, a two-stage process for metallographic embedding was employed. First, the samples were mounted in the as-exposed condition under vacuum using an epoxy based resin. This preserved the as-exposed morphology of the corrosion products. Subsequently, mounted samples were sectioned under dry conditions to assess the cross-section of the samples. A second stage mounting under vacuum using an epoxy based resin was carried out with the exposed cross-section facing downwards in the mount. The mounted samples were then prepared according to standard metallographic techniques down to 1μm diamond suspension. During the metallographic preparation process, the samples did not come in contact with water; instead, absolute ethanol (99.9 %, VWR Chemicals) was used as a lubricant to prevent dissolution of the water-soluble corrosion products (such as metal chlorides).
For deposit-free samples, a direct mounting under vacuum in epoxy was carried out. The mounted samples were also prepared according to the water-free techniques utilized for the deposit-coated samples.

Plan-view investigations of the deposit-coated samples started directly on the exposed deposit surface and continued with subsequent characterization of the revealed interfaces after stepwise mechanical removal of the corrosion products. Owing to the thin corrosion products observed on deposit-free samples, only direct plan-view surface investigations on the as-exposed samples were carried out.

Both plan-view and cross section analysis was carried out with scanning electron microscopy (SEM). This microscopic analysis of the morphology of the corrosion scale and the microstructure of the steel beneath the affected surface was combined with chemical element analysis applying energy dispersive spectroscopy (EDS) in the SEM. The prepared cross-sections were coated with carbon prior to SEM analysis.

For all SEM (Inspect S, FEI) investigations, an acceleration voltage of 15 keV and a beam spot size of 5 were used. Micrographs were obtained using the backscatter electron (BSE) detector in order to reveal information from the compositional contrast of the corrosion products. For some plan-view investigations, BSE images were supplemented by secondary electron (SE) imaging.

Quantitative elemental compositions of the corrosion products were revealed with an EDS (Oxford instruments) system attached to the SEM. An acceleration voltage of 15 keV was also utilized for EDS measurements. Due to the heterogeneous surface morphology of the corrosion products, EDS results are shown only for values above 1 wt % to minimize possible errors. Also, due to possible contamination from the metallographic preparation and mechanical removal steps using SiC grinding paper, Si was intentionally not analysed.

Crystalline corrosion products were identified by qualitative phase analysis using X-ray diffraction (XRD). The diffractometer (Bruker AXS, D8 Discover) was operated with Cr-Kα radiation. An asymmetric beam path (grazing incidence geometry) with a fixed incidence angle of $\gamma = 2^\circ$ was employed for XRD. These diffraction measurements were further combined with stepwise removal of corrosion products, where each removal was larger than the maximum X-ray penetration depth during grazing incidence measurements. Due to the geometry of the samples, measurements were carried out with a point focused incidence beam using a polycap optics system.
3. Results

3.1 Reference exposure (straw-firing flue gas, 3 vol % H₂O, 168 h)

A similar exposure of the same alloy (TP 347H FG) coated with the same deposit (KCl) at the same temperature (560°C) for 168 h to straw-firing flue gas composition containing 3 vol % H₂O has been previously reported [208]. For comparison, selected results of this previous study are summarized in Figure S1 (see supporting information) as they form the basis for discussion of results from the present samples. These results originate from the examination of more than 10 samples and are representative of the corrosion morphology. As observed from the various micrographs, the morphology of the corrosion products is not uniform. However, a general observation is the occurrence of three layers of corrosion products (Figure S1, a-d in the supporting information). Layer 1 and layer 2 are similar in all samples, while layer 3 exhibits some variation. Detailed characterization revealed that layer 1 consists of K₂SO₄-KCl-FeₓOᵧ, while layer 2 consists of mainly MₓOᵧ; M = {Fe, Cr} [208]. A sponge like Ni-S-rich microstructure dominated in layer 3 (Figure S1 a). In addition to Ni and S, Cr and Fe could be identified within layer 3 on some locations (Figure S1 b-d). However, such regions did not exhibit a clear porous structure but rather a continuous layer or pit like morphology. Irrespective of the morphology of layer 3, the presence of a Ni-rich band at the interface between the corrosion product and the bulk of the alloy was always observed from EDS mapping across the cross section. Preferential attack along grain boundaries is often observed below layer 3 of the corrosion product. Detailed microstructure characterization of the corrosion products resulting from exposure under this condition is contained in Okoro et. al. 2014 [208].

3.2 Exposure under straw-firing flue gas with 3 vol. % H₂O (condition 1, 72 h)

The exposure of deposit-coated samples to flue gas containing 3 vol % H₂O for 72 h (condition 1 in Table 2) resulted in the formation of the corrosion products shown in Figure 2a – d, illustrating their non-uniform nature. Consistently, however, the corrosion products observed below the initial deposit consist of three layers marked as 1, 2, and 3 in the micrographs.

The corresponding elemental composition of the corrosion products revealed by EDS mapping are presented in the Figures 3a – c. Layer 1 appears similar to that observed after the reference exposure (cf. Figure S1 in supporting information). This layer consistently contains Fe, K, S and O regardless of the overall morphology of the corrosion product. Similarly, layer 2 also consistently is comprised of Fe, Cr and O. However, the Cr maps show that Cr is enriched in the lower parts of layer 2. The morphology of layer 3 is rather non-uniform. Observations from this layer are summarized as follows:
- Double layered regions (Figure 2a) with a very porous upper layer, and a relatively continuous layer below. Such regions are comprised of Fe, Cr, Ni, O and S (Figures 2a and 3a). A number of pores can be identified also in the lower layer (Figures 2b and 3b).

- Fe, Cr, Ni, O and S containing pits (Figures 2c and 3c).

- Regions with a dual-layered morphology similar to (i), but with selective attack along grain boundaries extending into the bulk of the alloy (Figure 2d). The EDS line scans (not shown here) along such grain boundaries reveal Fe and Cr depletion, with a corresponding enrichment of Ni, S and O.

Figure 2. Selected cross sections of corrosion product resulting from exposure to condition 1 (flue gas with 3 vol % H₂O) (1: layer-1, 2: layer-2, 3: layer-3). Micrographs in a) to d) refer to different locations on the exposed samples.
Figure 3. EDS maps showing elemental composition of the corrosion products resulting from exposure under condition 1 (flue gas with 3 vol % H₂O). Maps in a) to c) refer to different locations on the exposed samples, cf. Fig. 2.

More detailed results on the morphology and composition of the corrosion products are obtained from plan-view characterization, combined with mechanical removal of the corrosion product layers. In Figures 4a and b, plan-view microstructures of the deposit observed from the flue gas/deposit and deposit/corrosion product interfaces are shown respectively.
At the flue gas/ deposit interface, large facetted particle agglomerates consisting exclusively of K, S and O are detected (Table S1, supporting information). The size of these particle agglomerates decreases with distance from the flue gas/ deposit interface into the bulk of the deposit (see arrows (i) and (ii) in Figure 4a). Deeper in the deposit, these features agglomerate around the initial deposit particles. Similarly, examination of the deposit particles from the deposit/corrosion product interface (Figure 4b) also revealed accumulation of these K, S and O rich features around the KCl deposit particles but to a reduced extent. This observation supports the identification of Cl from the deposit particles in the EDS analysis shown in Table S1 (supporting information). After partial removal of the surface deposit, the Fe, K, S and O containing layer shown in Figure 2 (layer 1) is seen to accumulate around the KCl deposit particles (Figure 5 and location 1 and 2 in Table S2, supporting information). EDS analysis on positions where the initial KCl particles have been removed (location 3 in Table S2) reveal high concentration of Fe (61.4 wt %), in addition to Cr and Mn. Previously identified elements (K, S and O) from the maps in Figure 3 were also revealed by plan-view EDS analysis.

Figure 6 shows secondary electron (SE) plan-view micrographs of corrosion products obtained after removal of the M$_2$O$_y$-K-S-O deposit-coated layer shown in Figure 5 (M = {Fe, Cr, Mn}). EDS analysis (location 1 in Table S3, supporting information) revealed that this layer consists mainly of M$_2$O$_y$; where M = {Fe, Cr, Mn}. 

**Figure 4.** Plan view microstructure of the synthetic deposit at the flue gas/deposit (a) and deposit/corrosion product (b) interfaces after exposure to condition 1 (flue gas with 3 vol % H$_2$O). For elemental composition of locations 1 and 2, see Table S1 in the supporting information.
Figure 5. Selected plan view micrographs of the corrosion product showing the observed microstructure after partial removal of the initial KCl deposit, i.e. beneath surfaces shown in Fig. 4, on a sample exposed to condition 1. For elemental composition of locations 1-3, see Table S2 in the supporting information.

Figure 6. Selected plan view microstructures (SE images) of the corrosion product observed directly below the KCl-K_2SO_4 rich layer in Figure 5, after further removal of the corrosion product resulting from exposure to condition 1. For elemental composition of locations 1 and 2, see Table S3 in the supporting information.

The Fe-rich layer (Figure 6a) is observed to contain isolated nodular as well as blade-like structures. After removal of the Fe-rich layer, the revealed corrosion product layer in Figure 6b is Cr-rich (location 2 in Table S3). These results agree with that revealed by EDS mapping on the cross-section of the corrosion product (cf. Figure 3), i.e. outer Fe-rich oxide and inner Cr rich oxide.
Plan-view BSE images of regions where the internal attack occurred are shown in Figure 7 and supplemented by EDS results in Table S4 (supporting information). More than 20 wt % of each of the alloying elements Fe, Cr and Ni were present in the internally attacked zones. The analysis reveals that Cr and Ni are enriched in these regions compared to the bulk alloy and that Fe is depleted. In addition, small amounts of chlorine and large amounts of oxygen were also identified. Also at these positions, attack along grain boundaries was observed (Figure 7b).

Figure 7. BSE plan view microstructure of regions of internal attack (close to the corrosion front) due to exposure to condition 1. For average elemental composition of location 1, see Table S4 in the supporting information.

Results from grazing incidence XRD (GI-XRD) measurements after the stepwise removal of the corrosion products are shown in Figure 8. The rough morphology of the corrosion product (cf. Figure 5) resulted in a high signal to noise ratio in the diffractograms. Nonetheless, both KCl (JCPDS card 41-1476) and K$_2$SO$_4$ (JCPDS card 05-613) could be identified in the diffractogram obtained from the sulphated deposit layer (cf. Figure 5). On the Fe-rich layer shown in Figure 6a, Fe$_2$O$_3$ (JCPDS card 33-664) was the predominant crystalline phase identified. Apart from the austenite phase (γ-Fe, JCPDS card 33-397), no other phase could be detected in the diffractogram recorded at the regions of internal attack (cf. Figure 7).
Figure 8. Grazing incidence XRD diffractograms showing the predominant crystalline corrosion product phases (after exposure to condition 1) on the different layers of corrosion product shown in Figures 5, 6 and 7. The peak at ~ 69° is due to stress-induced austenite to martensitic transformation during mechanical removal.

The corrosion products resulting from exposure under the same flue gas condition, but on deposit-free samples are shown in Figure 9. The plan-view investigation indicates that the corrosion product includes regions with thicker, coarse and blade-like features with increased concentration of Fe and Mn (Figure 9a, location 1 in Table 3) compared to regions with relatively finer morphological features and greater Cr and Ni concentration (Figure 9b, location 2 in Table 3). Examination of the cross section (not shown here) showed a thinner layer of corrosion product relative to the deposit coated samples. The elemental composition revealed by EDS mapping (Figure 9c) showed that the corrosion product consists of Fe, Cr and O. However, only O, Cr and Ni maps are shown here in order to show the differences between the thick and thinner corrosion product regions. Discrete enrichment of Ni was also observed by EDS mapping on the cross sections at the interface between the corrosion product and the bulk of the alloy. The predominant crystalline phase identified by GI-XRD (Figure 10) on the exposed samples was Fe₂O₃ (JCPDS card 33-664), in addition to peaks from the bulk sample (γ-Fe, JCPDS card 33-397).
Figure 9. Plan-view (a), (b) and EDS maps (c) of resulting corrosion products on deposit-free samples after exposure to condition 1 (without KCl deposit, straw-firing flue gas with 3 vol% H₂O). For elemental composition of locations 1 and 2, see Table 3.

Table 3. Elemental composition of selected locations of the corrosion product in Figure 9

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<thead>
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<th>location</th>
<th>elemental composition (wt %)</th>
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<td>2</td>
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3.3 Exposure under straw-firing flue gas with 13 vol % H₂O (condition 2, 72 h)

Exposure with increased H₂O vapour content in the flue gas resulted in the formation of corrosion products presented in Figure 11, indicating the heterogeneity of the corrosion products, similar to observations for the previous exposure (cf. Figure S1 in supporting information and Figure 2). Again, three corrosion product layers can be identified as indicated in the micrographs.

Similar to the corrosion products observed in condition 1, layer 1 also consists of Fe, K, S and O (see Figure 12a-c). Fe, Cr and O are the major elements of layer 2. Cr is observed to be enriched at the lower sections of layer 2 (Figure 12a, b). However on some locations across the cross section, Cr enrichment forms a significant part of layer 3 (Figure 12c). On other locations, the Cr enriched sections extend into internal attack (grain boundary attack) towards the alloy bulk (Figure 12a, b).

Layer 3 is sometimes observed as a continuous layer (see Figure 12c), consisting mainly of Cr-rich oxide whereas in the other maps (Figure 12a), the Cr rich oxide is in localised areas. On some locations on the exposed samples (Figures 11b and 12b), layer 3 is lacking, except for local enrichment of Ni. On locations where layer 3 is observed, the elemental composition consists of Cr, Ni, S, O and Fe. A general feature
observed in layer 3 is the enrichment of Ni as marked with the arrows in Figure 12. Ni enriched regions in the grain interior are observed adjacent to grain boundary attack where Cr rich oxide penetrates into the alloy.

**Figure 11.** Selected cross sections of the resulting corrosion product after exposure to condition 2 (flue gas with 13 vol% H₂O) (1: layer-1, 2: layer-2, 3: layer-3). Micrographs a)-d) originate from different regions along the sample surface.
Figure 12. EDS maps showing elemental composition of corrosion products (shown in Figure 11 (a-c)) resulting from exposure to condition 2 (flue gas with 13 vol % H₂O).

EDS line scans (not shown here) reveal a difference in the elemental composition of the attacked grain boundaries as the bulk of the alloy is approached. Grain boundaries extending directly from layer 3 are observed to be depleted in Fe and Ni, and relatively enriched in Cr, O and S. In contrast, the attacked
grain boundaries closer to the bulk of the alloy are depleted in Fe, Cr and O. Instead, only an enrichment of Ni and S is observed on such grain boundaries.

In Figures 13 and 14, plan-view micrographs of the corrosion products obtained from stepwise scale removal are presented. Similar to the observation in previous exposure conditions (cf. Figure 4 and the reference exposure [208]), extensive agglomerations are observed around the original deposit particles. These agglomerates fully cover the deposit particles at the flue gas/deposit interface (Figure 13a); hence only K, S and O were identified by EDS. In contrast, partial coverage of the deposit particles is observed at the deposit/corrosion product layer interface (Figure 13b); consequently in addition to K, S and O, Cl is also identified there.

Figure 13. Plan-view microstructure of the synthetic deposit observed from (a) the flue gas/deposit and (b) deposit/corrosion product interfaces after exposure to condition 2 (flue gas with 13 vol % H2O).

Beneath the deposit particles, the corrosion product layer appears as shown in Figure 14a. This layer also contains partly sulphated particles of the deposit similar to that for the exposure with 3 vol. % H2O in the flue gas (condition 1). Potassium, S, O, Fe, Mn and Ni make up the elemental composition of the continuous regions of this corrosion product layer. On some regions (location 2 in Table 4), it was observed that the initial deposit particles are covered by such continuous regions. In Figure 14b the microstructure of the underside of layer 2 and topside of layer 3 are shown. The underside of layer-2 consists predominantly of Cr, Fe and O as previously detected in Figure 12. A correlation is observed between the micrographs in Figure 14b and c. The cross linked features in Figure 14b clearly matches the distribution of the attacked grain boundaries in Figure 14c. A severe case involving selective attack of a complete grain is shown in the insert in Figure 14b. Elemental analysis shows that the corrosion product resulting from such selective attack consists of Cr, Fe, Ni, and O, with minor concentrations (<
2 wt %) of S and Cl. EDS maps (in Figure S2, supporting information) show that Fe and Cr are essentially depleted on the attacked grain boundaries. Instead, a pronounced enrichment of Ni, S, K, Cl and O is observed.

Figure 14. Plan-view microstructures of the corrosion product after exposure to condition 2 (flue gas with 13 vol % H₂O) and stepwise layer removal; (a): observed below the initial deposit, (b): observed from the interface between the corrosion product scale and the alloy bulk, (c), (d): selective attack along grain boundaries as the alloy bulk is approached.
Table 4. Elemental composition of selected areas in Figure 14

<table>
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<tr>
<th>location</th>
<th>elemental composition (wt %)</th>
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<tbody>
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<td>31.4</td>
</tr>
<tr>
<td>4</td>
<td>26.3</td>
</tr>
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</table>

The identified crystalline phases of the corrosion product are shown in the diffractograms presented in Figure 15. From the GI-XRD measurements on layer 1 of the corrosion product (cf. Figures 11 and 14a), the phases KCl, K₂SO₄ and Fe₂O₃ could be identified according to the JCPDS cards 41-1476, 05-613 and 33-664 respectively. On the revealed surface of the selective attacked layer (layer 3, Figure 14c); both K₂SO₄ and Fe₂O₃ were identified. In addition, peaks from the alloy bulk (γ-Fe, JCPDS card 33-397) are detected. With increasing depths, the γ-Fe phase becomes the predominant phase.

![Figure 15. GI-XRD diffractograms showing the predominant crystalline corrosion product phases on the different layers of corrosion product obtained after exposure to condition 2 (flue gas with 13 vol % H₂O) and subsequent stepwise layer removal.](image-url)
Corrosion of deposit-free samples exposed to condition 2 resulted in the corrosion products shown in Figure 16. The corrosion product is only very thin and, apparently, it cracked during metallographic preparation of the cross section, hence hindered thorough EDS analysis.

Figure 16. Plan-view and EDS maps of deposit-free sample exposed to condition 2 (flue gas with 13 vol % H2O). The elemental composition of locations 1 and 2 are given in the supporting information Table S5.

However, the EDS maps on the corrosion product cross section (not shown here) indicate that the corrosion product consists of Fe, Cr and O. Sulphur was identified on local positions at the lower region of the corrosion product. It is observed from plan-view investigation (Figure 16) that the interior of the alloy grains is affected by corrosion, whereas regions surrounding the grain boundaries are less attacked. EDS analysis on the different regions show a difference in the concentration of Cr, Fe, Ni and O (see Table S5, supporting information). Near the grain boundaries, there is an increased concentration of the alloying elements (Cr and Ni). The only crystalline phases identified were Fe2O3 (JCPDS card 33-664) and γ-Fe (JCPDS card 33-397), see Figure 17. The γ-Fe phase originates from the underlying alloy bulk because of the thin nature of corrosion product layer on the deposit-free sample.
Figure 17. GI-XRD diffractogram showing the predominant crystalline corrosion product phase(s) on the deposit-free sample exposed to condition 2.

3.4 Thickness of corrosion product layers

The thicknesses of the different corrosion product layers on the various samples after exposure to the different conditions was measured on more than 20 positions for each sample. Measurement of layer 3 involved both regions where internal / grain boundary attack have occurred. The box charts in Figure 18 shows the statistical distribution of the corrosion product thicknesses. The mean of the measured thickness are represented by the dots inside each box. The standard deviation from the mean is denoted by the two horizontal edges of the box. The ‘error’ bars above and below the box depict the maximum and minimum measured thicknesses, while the position of 50 % of the measured values is shown by the horizontal line inside each box.

The thickness of corrosion product layers after exposure to the reference condition [208] is observed to exhibit the highest degree of variation. However, for layer 1 (Figure 18a), the mean thickness obtained after exposure to condition 1 and the reference conditions was relatively similar (31.1 ± 8.5 μm and 36.3 ± 12.6 μm, respectively), despite the difference in exposure time. A similar trend is observed for layer 2 of corrosion product (Figure 18b): 20.7 ± 5.9 μm and 19.2 ± 10.0 μm for condition 1 and the reference exposure, respectively.
Figure 18. Thicknesses of the resulting corrosion products after exposure to the different conditions. The maximum and minimum thicknesses are represented by the marks above and below each box. Round dots in each box represent the mean thickness. The standard deviation from the mean is represented by the horizontal edges of the box. Location of 50% of the distribution is depicted by the horizontal bar in each box. At least, 20 positions on the exposed samples were measured to obtain the thickness plot.

Exposure to condition 2 (with 13 vol% H2O in the flue gas) showed relatively lower values of the mean thickness (11.3 ± 4.2 μm and 10.3 ± 5.3 μm for layer 1 and layer 2, respectively). It is observed that the thickness of the internal/grain boundary attack regions depended neither on the exposure time, nor the amount of H2O vapour in the flue gas (cf. Figure 18c). The average thickness values of these regions from the reference exposure, condition 1 and condition 2 were; 10.6 ± 4.9 μm, 10.2 ± 3.6 μm and 9.7 ± 3.2 μm, respectively.

In Figure 19, a schematic summary of the corrosion products after exposure of deposit coated samples to the different conditions is presented.
Figure 19. Schematic representation of the resulting corrosion products on deposit coated samples from the exposures under the reference condition (a), condition 1 (b) and condition 2 (c).

4. Discussion

4.1 Effect of the exposure time

High temperature corrosion of superheater materials under biomass-firing conditions is complex. This can be attributed to the interplay between the various corrosive species present. However, the long-term (168 hours) exposure of the investigated material (TP 347H FG) under laboratory conditions simulating biomass-firing indicated that the prominent corrosion mechanisms involve chlorination-oxidation and sulphidation [208]. Under such conditions (which serve as the reference condition in the current study), sulphation of the initial deposit, direct reaction of the deposit with the preformed oxide on the alloy as well as direct attack of the flue gas on the alloy, were suggested as possible pathways to initiate the corrosion attack. Thorough comparison of the morphology of corrosion products formed after both 168 h (reference, Figure S1 in supporting information) and 72 h (condition 1, Figure 2) of exposure to such conditions showed the formation of three layers of corrosion products. The only pronounced difference between the two exposure times is the clear establishment of the Ni-rich porous region in layer 3 as a result of the extended exposure time of 168 h. Such difference suggests that the action of Cl species in selectively extracting ‘less noble’ alloying elements (Fe and Cr [208]) is time dependent and therefore a propagating step and not an initiation step. As clearly observed from the EDS maps of the corrosion products after 72 h of exposure (Figure 3), layer 3 has not fully developed into a Ni-rich porous layer. Instead, Cr is observed in addition to Ni where such porous regions have started to form. The time dependent evolution of the Ni rich porous layer due to selective attack by Cl is supported by the clear
development of this layer after a longer (field) exposure (3462 h) of the investigated material in a straw fired plant [104].

The exposure time marginally influences the thickness of the corrosion products layers (for the flue gas containing 3 vol % H₂O) as the average measured thicknesses of the three layers are in close agreement (Figure 18). However, the maximum thickness of the corrosion product layers is observed to clearly increase with time. The observed thickness of corrosion product after 72 h of exposure is in agreement with that observed in a similar study[112]. Based on the slow increase in corrosion product thickness recorded for the investigated material even after 150 days of exposure to similar conditions [111], the similarity in average thickness of corrosion products after 72 and 168 h is confirmed. This observation has two implications:

- The resulting corrosion products after a given time impose some degree of resistance to transport of species to/from the corrosion front.

- The catastrophic corrosive species (KCl) become consumed in the corrosion process after a given period. Subsequently, the flue gas components and the less corrosive corrosion product (for example, potassium sulphate) will result in attack leading to a relatively slow increase in the thickness of corrosion products. This is one of the constraints of such a laboratory set-up because in the real plant; the deposit is constantly being replenished.

### 4.2 Effect of H₂O vapour concentration in the flue gas

Although from a generalized perceptive, three layers of corrosion products were observed regardless of the concentration of H₂O vapour in the flue gas, the morphology, thickness and distribution of the corrosion products varied significantly as a function of H₂O vapour concentration (see Figures 2, 3, 11 and 12). The synergistic/antagonistic behaviour of H₂O vapour on high temperature oxidation has been effectively reviewed in the literature [41,63]. It has been suggested that H₂O vapour can influence the corrosion process via several mechanisms, for example:

(a) Formation of volatile metal-oxyhydroxide species consequently leading to the formation of less protective Fe-rich oxides [52,53,229,257,261,266].

(b) Enhanced growth of the oxide scale due to faster transport of H⁺/OH⁻ in the scale [61,263].

(c) Assisting the internal oxidation of Cr and as a result aiding the outward growth of Fe-rich oxide [61,62].

(d) Competitive H₂O/O₂ adsorption at the scale-gas and scale-metal interfaces [41,61,267].
A general consequence of the above mechanisms is an increase in the growth of an external Fe-rich corrosion product. Since the concentration of other gas species (SO$_2$, CO$_2$, O$_2$ and HCl) in the flue gas were kept constant in the different exposures, H$_2$O vapour is observed to influence high temperature corrosion of deposit-free samples in the present investigation. A similar effect of H$_2$O in dominating the oxide formation mechanism was reported for studies under oxyfuel gaseous conditions [50]. Plan-view investigations on samples exposed to a flue gas containing 13 vol % H$_2$O (Figure 16) show that regions at the grain boundaries are attacked to a lesser extent relative to the alloy grain interior. This observation hence supports the fact that the continuous supply of Cr from faster transport paths (grain boundaries) is able to sustain the formation of a more protective oxide. Insufficient supply of Cr from the bulk alloy to the interior of grains in the subsurface caused the formation of thicker Fe-rich corrosion products as the outer oxide probably according to mechanism (a) above. The corrosion products on deposit-free samples exposed to a flue gas with 3 vol % H$_2$O content did not display a similar trend. In fact very little sign of grain boundary protectiveness is observed on the regions with fine morphological features (see Figure 9). Under such conditions, $\frac{p_{H_2O}}{p_{O_2}} < 1$ holds and, hence, H$_2$O vapour would have a reduced effect on corrosion. However, either Cl or SO$_2$ from the flue gas could have caused an accelerated attack to justify the thick and coarse corrosion product morphology observed on some regions of the exposed samples (Figure 9a). Considering that HCl dissociates into Cl$_2$ according reaction (1), it is expected that in order to sustain equilibrium, an increase in $p_{H_2O}$ will cause a decrease in $p_{Cl_2}$. An opposite effect will be observed at low $p_{H_2O}$ which may explain the resulting thick and coarse corrosion products on some regions of the exposed sample due to enhanced attack by Cl$_2$.

\[
2\text{HCl}(g) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{Cl}_2(g) + \text{H}_2\text{O}(g) \quad (1)
\]

In the present investigation of the effect of H$_2$O vapour in the presence of a KCl deposit, a decrease in the corrosion product thickness is observed with increasing H$_2$O vapour concentration. Additionally, no clear increase of the corrosion product porosity/densification can be observed after exposure to conditions 1 and 2 (see Figures 2 and 11). Justifiably the above listed mechanisms (a – d) cannot explain the H$_2$O vapour effect observed on deposit coated samples since they were solely developed based on a gas-metal interaction. However, it has been suggested that in the presence of solid corrosive species (KCl, NaCl) [129,140,264,265], the synergistic corrosion accelerating effect of H$_2$O vapour originates from the higher thermodynamic favourability of reaction (2) compared to reaction (3).

\[
x\text{NCl}(s) + M_x\text{O}_y + H_2\text{O} \rightleftharpoons N_xM_x\text{O}_y \left( y+1 \right) + x\text{HCl} \quad (2)
\]

\[
x\text{NCl}(s) + M_x\text{O}_y + \frac{1}{x} \text{O}_2 \rightleftharpoons N_xM_x\text{O}_y \left( y+\frac{2}{x} \right) + \text{Cl}_x \quad (3)
\]
(N = \{K, Na\}, M = \{Fe, Cr\}, and x, y are integers).

The HCl released from reaction (2) is able to chlorinate the alloying elements resulting in the formation of volatile metal chlorides (reaction 4). Oxidation of these species yields a porous oxide and also the regeneration of HCl (reaction 5) which partly reinitiates the chlorination reaction in a cyclic manner.

\[
M + xHCl \rightleftharpoons MCl_x + \frac{x}{2}H_2 \quad (4)
\]

\[
MCl_x + yH_2O \rightleftharpoons M_yO_x + (2y)HCl \quad (5)
\]

The present results reveal that H_2O vapour does not increase corrosion attack on the investigated alloy under the present conditions. Similar investigations of high temperature corrosion of austenitic steel AISI 304 L [63], alloy 625 [118], ferritic 10CrMo910 steel [118] and FeCrAl alloy [124] show a decrease in corrosion with an increase in H_2O vapour concentration. The densification of the resulting corrosion product or ability of the HCl from reaction (2) to exit from the corrosion system has been suggested to compensate for the observed trend. However, in the present investigation where the sulphation of the deposit particles also contributes to an increase in the corrosive species (HCl, K_2SO_4), it is meaningful to consider the possible effect of H_2O vapour on the flue gas-deposit interactions.

With the presence of SO_2 in the flue gas, sulphation of the initial deposit (KCl particles) is expected to proceed in a mechanism similar to the Hargreaves process [268] (reaction 6) in which HCl is released in the flue gas.

\[
2KCl(s) + SO_2(g) + \frac{1}{2}O_2(g) + H_2O \rightleftharpoons K_2SO_4(s) + 2HCl(g) \quad (6)
\]

Comparison of the cross-sections in Figure 2 for condition 1, and Figure 11 for condition 2 reveal a decrease in thickness of layer 1 when specimens are exposed to the 13 vol % H_2O containing flue gas. The degree of K_2SO_4 accumulation around the deposit particles is also observed to be significantly reduced with 13 vol % (Figure 13), instead of 3 vol % (Figure 4) H_2O. These observations suggest that more of the KCl deposit is sulphated (and therefore more HCl is generated) in the flue gas with lower concentration of H_2O vapour. A corresponding small increase in thickness of the metal oxide containing layer of the corrosion product - layer 2 (Figure 18) also suggests that a significant proportion of the released HCl from the sulphation process (reaction 5) has contributed to corrosion. The generated HCl can dissociate into Cl_2 (reaction 1) which can migrate to the corrosion front and induce chlorination of thermodynamically favourable alloying elements (reaction 7) [76,131,139,269]. Similarly, electrochemical migration of adsorbed Cl ions to the corrosion front [75,124,125] will give rise to
chlorination of the most favourable alloying element. The resultant volatile metal chlorides are transported away from the corrosion front and subsequently oxidized to release Cl (reaction 9), which partly migrates back to the corrosion front and continues the process in a cyclic mechanism (the so-called chlorine cycle). The selective depletion of Fe and Cr are explained by the thermodynamically favoured chlorination of these elements relative to Ni [76,139,156,208], hence suggesting a Cl assisted type of corrosion attack.

\[ M(s) + xCl \rightleftharpoons MCl_x(s) \]  
\[ MCl_x(s) \rightleftharpoons MCl_x(g) \]  
\[ yMCl_x(g) + \frac{z}{2}O_2(g) \rightleftharpoons M\gamma_0\zeta(s) + yCl_x(g) \]  

Owing to the porous morphology of the oxides converted from metal chlorides, it is reasonable that enhanced migration of corrosive species occurs. This explains the accumulation of S at the corrosion front after exposure of the deposit-coated samples to the different conditions (see Figures 3 and 12). It is suggested that sulphidation may proceed due to enhanced transportation of SO2 across the porous oxide formed as a result of the cyclic Cl attack.

With respect to the kinetics of reaction 6, reported results on the effect of H2O vapour concentration are somewhat inconclusive. While model predictions and some experimental results suggest an insignificant effect of H2O concentration on the heterogeneous sulphation of alkali chlorides (KCl/NaCl) [196,197,246,270,271], thorough analysis of some experimental results reported in literature reveal an interesting trend. At constant SO2 and O2 concentrations, a potential maximum in the reaction kinetics is observed in the sulphation of NaCl (at 600 °C) [271] when the H2O vapour concentration approaches 10 vol%. Above this concentration, a decrease in conversion rate is observed. The rate determining steps in the heterogeneous sulphation of deposit particles will involve adsorption of SO2, O2 and H2O on the surface of the deposit [196,271,272]. Hence the present authors suggest that a competitive adsorption on active sites of the deposit particle may influence the kinetics of the process, and by extension, the rate with which HCl is released. A similar mechanism based on preferential adsorption of H2O in CO2 containing gases has been used to explain reduced carburisation [54]. Even though H2O facilitates the formation of the intermediate specie (H2SO4) in the sulphation process via a proton transfer to SO2 [272], it is possible that above a certain concentration, the adsorbed H2O species exert an inhibiting influence instead. Alternatively, it is probable that with increased active site coverage by adsorbed H2O species, the available sites for adsorption of other species such as SO2 become restricted (steric hindrance) and accordingly a decrease in sulphation rate is observed. Although the limits of experimental error in previous experimental investigations [197,271] is unknown, results indicate that such phenomena will
likely occur above a critical H$_2$O vapour concentration around 10 vol %. Indeed proper studies in this regard are needed to clarify the effect of H$_2$O vapour on the sulphation kinetics of alkali chlorides. Nonetheless, the observed trend with an increase in flue gas H$_2$O content in the present investigation can be explained by the above suggestions.

5. Conclusions

Laboratory-scale high temperature exposures have been carried out with a view to investigate the effect of exposure time and H$_2$O vapour content on the corrosion of TP 347H FG under conditions mimicking biomass firing. Comprehensive characterization of the resulting corrosion products using SEM, EDS and XRD was achieved by both cross-sectional and plan-view investigations after mechanical removal of the corrosion product layers.

Corrosion products generally contain three layers irrespective of the exposure time or condition. However, it is shown that the development of the Ni-rich porous layer due to selective attack by Cl is observed with longer exposure times.

With respect to the influence of H$_2$O vapour, an antagonistic effect was observed on the corrosion process upon an increase in the amount of H$_2$O vapour in the flue gas. The observed corrosion morphologies on samples coated with a KCl deposit could not be explained based on classical H$_2$O vapour corrosion accelerating mechanisms. Such accelerating mechanism was only observed on deposit-free samples exposed to flue gas with 13 vol % H$_2$O vapour.

Based on previous experimental results in literature and results from the current investigation, it is suggested that above a critical H$_2$O vapour concentration, competition for active adsorption sites will lead to a decrease in the sulphation of the initial deposits as well as HCl generation, and consequently a lower extent of corrosion.

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References
References cited in this paper are collected in the general reference list of the thesis.
**Supporting Information**

**Table S1.** Elemental composition of selected locations of the corrosion product in Figure 4

<table>
<thead>
<tr>
<th>Location</th>
<th>elemental composition (wt %)</th>
<th>O</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
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<tbody>
<tr>
<td>1</td>
<td>37.3</td>
<td>18.9</td>
<td>-</td>
<td>43.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>18.9</td>
<td>6.8</td>
<td>29.7</td>
<td>44.1</td>
<td></td>
</tr>
</tbody>
</table>

*due to the morphology of the measured locations, values < 1 wt % (denoted by '-') are not presented. The same holds for the subsequent tables.

**Table S2.** Elemental composition of selected locations of the corrosion product shown in Figure 5

<table>
<thead>
<tr>
<th>Location</th>
<th>elemental composition (wt %)</th>
<th>O</th>
<th>S</th>
<th>Cl</th>
<th>K</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>22.2</td>
<td>8.6</td>
<td>23.6</td>
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<td>-</td>
<td>-</td>
<td>2.8</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>33.8</td>
<td>16.0</td>
<td>2.5</td>
<td>39.0</td>
<td>1.1</td>
<td>-</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>19.0</td>
<td>2.2</td>
<td>-</td>
<td>6.1</td>
<td>8.2</td>
<td>2.3</td>
<td>61.4</td>
<td></td>
</tr>
</tbody>
</table>

**Table S3.** Elemental composition of selected locations of the corrosion product in Figure 6

<table>
<thead>
<tr>
<th>Location</th>
<th>elemental composition (wt %)</th>
<th>O</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.4</td>
<td>4.3</td>
<td>1.7</td>
<td>67.4</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>27.1</td>
<td>38.3</td>
<td>2.1</td>
<td>25.3</td>
<td>4.7</td>
<td></td>
</tr>
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</table>

**Table S4.** Elemental composition of internally attacked regions shown in Figure 7

<table>
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<tr>
<th>Location</th>
<th>elemental composition (wt %)</th>
<th>O</th>
<th>Cl</th>
<th>Cr</th>
<th>Fe</th>
<th>Ni</th>
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<tbody>
<tr>
<td>1</td>
<td>19.2</td>
<td>1.8</td>
<td>22.9</td>
<td>30.2</td>
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</tbody>
</table>

**Table S5.** Elemental composition of selected areas in Figure 16

<table>
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<th>Location</th>
<th>elemental composition (wt %)</th>
<th>O</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Ni</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>32.1</td>
<td>4.2</td>
<td>1.6</td>
<td>61.1</td>
<td>-</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>15.3</td>
<td>16.3</td>
<td>1.7</td>
<td>56.8</td>
<td>8.7</td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. Selected BSE micrographs showing cross sections of corrosion products after exposure to the reference condition (straw-firing with 3 vol % H₂O, 168 h) \textsuperscript{a}.

Figure S2. EDS elemental maps showing the elemental composition of the selectively attacked regions shown in Figure 14(c).

Reference
5.4 – Time and temperature effects on alkali chloride induced high temperature corrosion of superheaters\textsuperscript{vii}

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Abstract

The high content of alkali chloride present in deposits during biomass firing in power plants chiefly contributes to corrosion of the superheaters. In order to understand how time and temperature influences such corrosion, laboratory scale studies under different time and temperature conditions were carried out using KCl coated samples of the austenitic stainless steel (TP347H). To understand the influence of time, isothermal exposures at 560 °C (from 83.5 – 672 hours), and at 600 °C (from 83.5-168 h) were conducted under a gas mixture comprising of O\textsubscript{2}, H\textsubscript{2}O, CO\textsubscript{2}, HCl and SO\textsubscript{2}. In addition, exposures were conducted under thermal cycling conditions between 560 °C and 600 °C to gain insights on the influence of temperature. The microstructure and elemental composition of the corrosion products resulting from the exposures were studied with Scanning Electron Microscopy (EDS) and Energy Dispersive X-ray Spectroscopy (EDS), respectively. The results show that corrosion attack progressed with time such that the thickness of the consistently identified three regions of corrosion products increased with time, therefore suggesting that the corrosion products does not impose any significant influence on the transport of intermediate species during the corrosion process. Also, exposures under thermal cycling conditions revealed that an increased corrosion attack would always occur once the superheater experiences a higher temperature, because, a memory effect from prior exposure to a higher temperature, propagates more corrosion attack during subsequent exposure to a lower temperature.

Keywords: Biomass firing, Alkali chloride, High temperature corrosion, Thermal cycling.

\textsuperscript{vii} Manuscript in preparation
1. Introduction

Owing to the depletion of global resources, the rising demand for energy and climate considerations, the need for renewable energy resources cannot be overemphasized. In line with this, the Danish energy sector aims to be powered by 100% renewable energy by 2050, and to be coal-free by 2030 [273,274]. Consequently, most coal-fired boilers are being modified for biomass use [8,31]. However, during biomass firing in power plants, corrosion of superheater tubes has been identified as a serious challenge that limits operation at high steam temperatures, thereby minimizing efficiency [31]. This challenge originates from the high content of alkali chlorides in the deposits that form when biomass is fired in power plants [24,27]. The mechanisms behind the fast corrosion of superheaters are still not completely understood due to the influence of a number of parameters such as deposit composition, temperature and gas chemistry. Nonetheless, Cl from the deposit has been recognized to be chiefly responsible for the fast corrosion of superheaters through the mechanism referred to as active oxidation [101,131,138,152,156,186].

Previous laboratory scale investigations have shown that under a gaseous atmosphere mimicking biomass firing, conversion of the original KCl particles in the deposit to \( K_2SO_4 \) occurs according to reaction (1) [111,112,127,275]. The resulting \( K_2SO_4 \) is less corrosive than KCl [119] hence, technologies facilitating sulphation of KCl to \( K_2SO_4 \) in the gas phase, are employed to minimize the fast corrosion of superheater tubes [96,167].

\[
2KCl(s) + SO_2(g) + \frac{1}{2}O_2(g) + H_2O \rightleftharpoons K_2SO_4(s) + 2HCl(g) \quad (1)
\]

However, sulphation of condensed KCl particles on the surface of the superheater tube can have serious implications for the corrosion attack, because, the released HCl (see reaction 1) close to the metal surface may serve as a source of chlorine to propagate corrosion. Despite this, the present understanding on how corrosion attack progresses with time under such conditions is inconsistent. On one hand, laboratory-scale studies with very low deposit coverage (0.01 mg/mm\(^2\)) at 600 °C[127], have revealed that conversion of KCl to the less corrosive \( K_2SO_4 \), is complete after 1 h of exposure, and accordingly, corrosion attack should reduce significantly afterwards. However, using a high deposit coverage (0.75 mg/mm\(^2\)), laboratory-scale investigations at 560 °C [112], under the same gas atmosphere as will be employed in the present study, have shown that conversion of KCl to \( K_2SO_4 \) was below 10% after 72 h. Consequently, the present work aims to provide an improved insight on the progression of corrosion attack with time under laboratory conditions simulating in-deposit sulphation of KCl to \( K_2SO_4 \) for durations up to 672 h.

From full scale investigations in biomass fired power plants, it has been observed that slight temperature increases above the typical steam temperature of 540 °C (which approximately corresponds to a surface metal temperature of 560°C) result in significantly increased corrosion rates [31]. However, as the steam temperature in actual superheaters can vary a lot due to fluctuating operating conditions, studies under
controlled conditions are important to obtain proper understanding of the influence of temperature on corrosion of superheaters during biomass firing. From isothermal laboratory scale studies involving exposure of KCl coated 304-type austenitic stainless steel to an oxidizing atmosphere (5% O₂ + 40% H₂O) between 400-600 °C [137], it has been suggested that the temperature dependence of the reaction between deposits and the initial oxide on superheater surfaces (i.e. reaction 2), as well as the ability of the ensuing oxide to offer protection, govern the alkali chloride induced corrosion under different temperature conditions.

\[
(\text{Cr}_x\text{Fe}_{1-x})_2\text{O}_3(s) + 4x\text{KCl}(s) + 1.5x\text{O}_2(s) + 2x\text{H}_2\text{O}(g) \\
\rightleftharpoons (1 - x)\text{Fe}_2\text{O}_3(s) + 2x\text{K}_2\text{CrO}_4(s) + 4x\text{HCl}(g)
\]

(2)

However, recent studies [213,276] have suggested that the corrosion process during biomass firing can involve other mechanisms such as sulphation and chlorination, thus, the influence of temperature on the corrosion mechanism may not only be limited to its suggested effect based on reaction 2 [137]. Accordingly, the present paper, by means of dedicated corrosion exposures under well-defined conditions mimicking biomass firing, also aims to provide insights on the effect of temperature on superheater corrosion. In addition to isothermal exposures at different temperatures, the influence of thermal variations on corrosion was also investigated, with the example of thermal cycling between 560 °C and 600 °C. The temperature variations have been applied by cycling from low to high temperature as well as vice versa from high to low temperature under otherwise the same exposure conditions that mimicked biomass firing.

2. Experimental

2.1 Sample preparation and high temperature corrosion exposures

The austenitic stainless steel TP 347H FG (fine grained), being a typical superheater material in thermal power plants, was used for the investigations. The chemical composition of the steel has been determined to be: 18.1 wt% Cr, 10.3 wt% Ni, 2.0 wt% Mn, 0.5 wt% Nb, 0.4 wt% Si and Fe as balance. The C-content of the steel amounts to 0.057 wt% [149]. The investigated samples were concave shaped with width of 10 mm, height of 7.4 mm and arc length of 14.6 mm, and were cut from the as received tube. The samples were cleaned ultrasonically using acetone and ethanol. Afterwards, they were coated with a deposit slurry that was obtained by mixing KCl and 2-proponol. After evaporation of the solvent, a deposit thickness of about 1mm, which corresponds to a deposit coverage of about 1 mg/mm² was realized on the surface of the samples.

The deposit coated samples were exposed in a corrosion test rig that comprised of a gas mixing panel, a furnace and a gas cleaning unit. A detailed description of this setup is given elsewhere [244]. The corrosion exposures were carried out under a gas atmosphere comprising of 60 ppmv SO₂, 400 ppmv HCl, 6 vol% O₂, 12 vol% CO₂ and 82 vol % N₂ (on dry basis). This corresponds to the gas composition measured during straw firing in a power plant, with the concentration of HCl representing a worst case
scenario [111]. With the exception of SO₂ and HCl, the gas mixture was bubbled through a water bath to incorporate 3 vol% of H₂O into it.

Corrosion exposures were conducted under the time and temperature conditions summarized in Table 1. Experiments T1-T6 were carried out isothermally with the intention to understand the progression of corrosion with time, while experiments T7 and T8 which were structured to reveal the influence of temperature, involved thermal cycling as illustrated in Figure 1. After each experiment, samples were cooled inside the furnace under a flow of the gas mixture.

**Table 1.** Summary of the experimental conditions investigated. All investigations involved exposure of KCl-coated TP 347H FG samples to the oxidizing-chlorinating-sulphidizing gas atmosphere.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T1</td>
<td></td>
<td>83.5</td>
</tr>
<tr>
<td>T2</td>
<td>560</td>
<td>168</td>
</tr>
<tr>
<td>T3</td>
<td>336</td>
<td></td>
</tr>
<tr>
<td>T4</td>
<td>672</td>
<td></td>
</tr>
<tr>
<td>T5</td>
<td>600</td>
<td>83.5</td>
</tr>
<tr>
<td>T6</td>
<td>600</td>
<td>168</td>
</tr>
<tr>
<td>T7</td>
<td>560 → 600</td>
<td>168 (83.5+83.5)</td>
</tr>
<tr>
<td>T8</td>
<td>600 → 560</td>
<td>168 (83.5+83.5)</td>
</tr>
</tbody>
</table>

**Figure 1.** Schematic illustration of the thermal cycling process in experiments T7 and T8.
2.2 Characterization of corrosion products

The corrosion products resulting from the various high temperature exposures in Table 1 were characterized by investigating cross sections of the exposed samples using scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). The sample cross sections were accessed following a two-stage mounting process according to a previously described procedure [244]. Absolute ethanol (VWR Chemicals, 99.9 %) was utilised as lubricant during metallographic preparation due to the solubility of some corrosion products in water.

An Inspect S (FEI) was utilized for SEM characterization of the corrosion products. The microscope was operated with an acceleration voltage of 15 keV and imaging was carried out with a backscatter electron detector. EDS analysis was carried out using an Oxford silicon drift detector attached to the SEM, and was also conducted with an acceleration voltage of 15 keV.

3. Results and discussions

3.1 The influence of time

Figure 2 shows the typical morphology of corrosion products observed after isothermal exposures at 560 °C for different durations ranging from 83.5 h (Figure 2a) to 672 h (Figure 2d). As have been previously shown in another study [244], the morphology and composition of the corrosion products under the investigated conditions can be inhomogeneous, hence, Figure 2e is employed to schematically illustrate the representative morphology of the non-compact layers of corrosion products which generally appeared as three regions. The topmost region of corrosion products is designated as region 1 and from the observed contrast in Figure 2, it is probable that the region consists of two phases. Region 2 which contains several voids and porosities, is located below region 1, and is often separated from region 3 by a crack. Judging by infiltration of these cracks by the embedding matrix, it is likely that they have originated during sample handling prior to the mounting process.

Region 3 was typically the most porous region of the corrosion products and also encompasses the location where grain boundary attack occurred. In addition to the obvious crack between regions 2 and 3, various cracks are observed within the corrosion products and they may have originated from sample handling or preparation. As observed from the micrographs in Figure 2, the existence of the three regions of corrosion products was not altered as a function of time, rather their thicknesses varied (Figure 3).
Figure 2. Morphology of corrosion products after isothermal exposure at 560 °C for different durations. (a) 83.3 h, experiment T1, (b) 168 h, experiment T2, (c) 336 h, experiment T3, and (d) 672 h, experiment T4. The schematic in (e) provides a representation of the typical regions of corrosion products.
Figure 3. The mean thicknesses of the different regions of corrosion products as a function of exposure time at 560 °C (experiments T1-T4). The shaded areas outline the corresponding standard deviation.

The plots in Figure 3 showing the thickness of the different regions were obtained from over 50 measurements using the commercial software ImageJ. Since the investigated alloy was the same in all the experiments, the observed variation in thickness of the various regions of the corrosion products is utilized to assess the degree of corrosion attack. The plots clearly show that the average thicknesses of the three regions of corrosion product increased with time while the large standard deviations reiterates the non-uniform thickness of the different regions as was previously suggested from Figure 2.

Figure 4 shows the representative elemental composition of the three regions of corrosion products on the example of a sample that was isothermally exposed at 560 °C for 672 h. As observed from the
elemental maps, region 1 is enriched in K, S, Mn, Fe and O with the darker features being particularly rich in K and S. Region 2 is Fe, Cr, and O rich with remarkable Cr enrichment in the lower parts. In region 3, strong enrichment of Ni is evident. In addition, enrichment of Cl is observed here, however, it is important to note that signals from the epoxy resin infiltrated into this porous region, may have contributed to this. The composition of regions 1 and 2 are moderately constant for the varying morphologies of corrosion products observed. However, in region 3, the composition occasionally deviates from being exclusively Ni-rich to include S, O and other alloying elements such as Fe or Cr. As such variation was observed even on samples isothermally exposed for 672 h, the earlier suggestion that establishment of a Ni-rich porous layer at the corrosion front is time dependent [244] cannot be confirmed in the present work.

The composition of the corrosion products and their distribution in the different regions are a consequence of the Cl catalyzed mechanism of corrosion under biomass firing conditions in which chloride species in the gas or from reaction 1, induce chlorination of alloying elements at the corrosion front [101,112,156]. The tendency of Cl to selectively chlorinate Mn, Fe and Cr in austenitic stainless steels results in the observed enrichment of Ni at the corrosion front (Figure 4) and is due to the relatively low driving force for the chlorination of Ni compared to the other alloying elements [76,134,277,278]. Consequently, porous Fe-Cr-Mn rich oxides are identified in region 2 due to conversion of chlorides of these elements to their oxides. It is also noteworthy that as part of this corrosion mechanism, KCl deposited on the surface of the samples, reacts with SO2 in the gas mixture resulting in formation of K2SO4 (i.e., in-deposit sulphation in accordance with reaction 1), and accordingly, corroborates the presence of K and S in region 1 of the corrosion products (Figure 4). Although the exact degree of KCl conversion to K2SO4 cannot be precisely followed with the characterization techniques applied in the present study, the observed increase in thickness of region 1 (Figure 3) gives an indication that the sulphation process (i.e., reaction 1) is still ongoing even after 672 h. Moreover, the concurrent increase in thicknesses of regions 2 and 3 suggests that the sulphate layer in region 1 did not effectively hinder the transport of corrosive species to and from the corrosion front, thereby essentially suggesting that, as long as the sulphation of the deposit is incomplete, the Cl-catalyzed corrosion mechanism will progress with time under a static (non-replenished) deposit, as applied in the present study.

Because of the non-compact nature of the corrosion products (Figure 2), it is very likely that corrosion attack under the investigated condition will not be limited by solid-state diffusion, but possibly, by gas phase transport of species through the porous corrosion products. The possibility that corrosion is limited by gas phase transport is supported by the steady increase in thickness of the different regions of the corrosion products (Figure 3), as opposed to a parabolic kinetics which should ensue assuming solid-state diffusion was the limiting mode of transport during the corrosion process [33,279].
Figure 4. EDS maps showing the typical composition of the different regions of corrosion products after 672 h of isothermal exposure at 560 °C.

The influence of time on the corrosion process was also investigated at 600 °C. In Figure 5, the typical morphology of corrosion products observed after corrosion exposures at 600 °C for 83.5 h (Figure 5a) and 168 h (Figure 5b) are shown. Just as was observed for isothermal exposures at 560 °C (cf. Figure 2), the corrosion products after exposures at 600 °C can also be generally categorized into three typical regions, with the usual local variations in region 3. The typical enrichment of Ni in region 3 also occurred during corrosion exposures at 600 °C but in addition, attack along grain boundaries was pronounced (Figure 5c). From Figure 6, it is observed that similar to the corrosion attack at 560 °C (cf. Figure 3), the extent of corrosion at 600 °C increases with time. However, contrary to the observation at 560 °C, a clear increase in the mean thickness of the different regions is observed after 168 h indicating that temperature significantly influences the corrosion mechanism. This is further addressed in section 3.2.
Figure 5. Microstructure of corrosion products after isothermal exposures at 600 °C for (a) 83.5 h, experiment T5 and (b) 168 h, experiment T6. (c) EDS maps of the selected area in (a).

Figure 6. The mean thicknesses of the different regions of corrosion products after isothermal exposure at 600 °C for different times (experiments T5 and T6). The shaded areas outline the corresponding standard deviation.
3.2 The influence of temperature

By comparing Figures 3 and 6, the degree of corrosion attack during isothermal exposure at 600 °C is observed to be higher than at 560 °C after exposure to otherwise same conditions (i.e. deposit, gas atmosphere and time). Interestingly, it is also observed that after 168 h at 600 °C, the resulting thickness of region 3 (which provides an indication of the internal attack on the sample [213]), surpasses that developed after 672 h at 560 °C. The pronounced depth of grain boundary attack in Figure 5 is also in agreement with this.

To obtain more insight on how temperature influences corrosion, exposures under thermal cycling conditions between 560 °C and 600 °C were conducted (experiments T7 and T8). The morphology of corrosion products originating from thermal cycling from a low to high temperature (experiment T7), and vice versa (from a high to low temperature, experiment T8) is shown in Figure 7.

![Figure 7](image)

**Figure 7.** Morphology of corrosion products resulting from thermal cycling exposures: (a) transition from 560 °C to 600 °C (experiments T7) and (b) transition from 600 °C to 560 °C (experiment T8).
Similar with isothermal exposures (Figures 2 and 5), the corrosion products resulting after exposure to conditions involving thermal variations, also existed in the form of three regions (Figure 7a and b). However, the order of thermal cycling is observed to influence the predominant morphology of corrosion products, particularly that of regions 2 and 3, albeit the local variation in morphology and elemental composition of region 3. The morphology of regions 2 and 3 after thermal cycling from 600 °C to 560 °C (experiment T8, Figure 7b) are similar to those observed after isothermal exposures at 600 °C (experiment T6, Figure 5b). Despite the difference in morphology, results from EDS mapping (not shown here) disclosed that the composition of the three regions of corrosion products were, in generic terms, similar to those observed after isothermal exposures. Thus in both thermal cycling scenarios, region 1 was K, S, Mn, Fe and O rich, region 2 was Fe, Cr, and O rich, while region 3 was enriched in Ni, in addition to Fe, Cr, S and O. On this basis, it is probable that the order of thermal cycling only influences the degree of corrosion, and not necessarily the previously described Cl-catalyzed mechanism through which corrosion attack occurs.

Figure 8 reveals how thermal cycling influences the degree of corrosion attack, by means of comparison of the mean thicknesses of the three regions of corrosion products, based on a minimum of 50 measurements. Compared with the pronounced increase in corrosion attack after 168 h of isothermal exposure at 600 °C, relative to 560 °C, thermal cycling during corrosion exposure had a relatively lower effect on the degree of attack. Notwithstanding, for the exposures that involved thermal cycling, it is observed from Figure 8 that an initially higher temperature in the course of corrosion (i.e. 600 °C, experiment T8), results in at least a 10 μm increase in thickness of each of the corrosion product regions, compared with corrosion exposure that started with a lower temperature (560 °C, experiment T7). Interestingly, considering the total exposure period of 168 h, Figure 8 also reveals that even with an initial or final exposure a 600 °C during thermal cycling, the extent of corrosion attack is significantly higher than that after isothermal exposure at 560 °C.

On the basis of these observations, it is probable that a superheater will always suffer more corrosion attack once it encounters a temperature above its typical operating temperature. More so, the sequence in which the material experiences a higher temperature during operation will influence the degree of corrosion attack such that prior experiencing of higher temperatures can propagate faster corrosion even during subsequent operation at lower temperatures.
The observed influence of temperature on the extent of corrosion attack could relate to its effect on both the kinetics and thermodynamics of some underlying processes involved in corrosion during biomass firing. As stated in section 1.0, the breakdown of native oxides due to their reaction with alkali chloride deposits, which is expected to be of relevance during the initiation stages of corrosion attack, can be influenced by temperature. Using as an example, the reaction between KCl and the Fe-Cr rich oxide that is known to form on austenitic stainless steels during the initial stages of corrosion [52,137] (reaction 2), thermodynamic calculations show that the Gibbs free energy becomes less positive as temperature increases [184]. However, it is important to note that the Gibbs free energy change for such reaction becomes more negative with KCl vapour [184]. Thus, it is expected that increased generation of KCl vapour due to temperature increase will enhance breakdown of native oxides on the sample surface, thereby providing access for transport of corrosive species. More so, based on literature, sulphation of KCl is expected to occur under biomass firing conditions, and this process can be enhanced when KCl is in the vapour phase [197]. Consequently, a higher partial pressure of HCl can be realized with temperature increase, as has been reported in reference [246] for the sulphation of condensed KCl. Accordingly, it is likely that when temperature was increased in the present investigation, more chlorine was generated from dissociation of the resulting HCl [156,280], to sustain corrosion attack. Although the resulting HCl may leave the system via the flowing gas stream during the corrosion exposure, the

Figure 8. The mean thicknesses of the different regions of corrosion products after 168 h of exposure under isothermal (560 °C or 600 °C), and thermal cycling (between 560 °C to 600 °C) conditions.
observation of lesser corrosion attack on samples that were isothermally exposed at 560 °C, compared to samples that were cycled from 600 °C to 560 °C (Figure 8), strongly suggests that the enhanced generation of HCl at a higher temperature does result in formation of chlorine that incites more chlorination at the corrosion front. Based on the cyclic nature of the Cl-catalyzed corrosion mechanism [134,156,244], it is probable that part of the generated chlorine remained in the system to propagate corrosion during subsequent exposure at a lower temperature, thereby explaining the observed trend in thickness of corrosion products on isothermally exposed samples at 560 °C, compared to samples exposed under thermal cycling conditions (Figure 8).

It is important to also note that within the temperature range investigated in the present study (560 °C-600 °C), Cr diffusion for oxide formation is mainly along the alloy grain boundaries [281]. In addition, the reaction of the major alloying elements (Fe, Cr, Ni) in the investigated alloy, with chlorine is thermodynamically feasible within this temperature range [184], with the chlorination of Cr being particularly more favourable compared to Fe and Ni. Consequently, the expected promotion of Cr diffusion along the grain boundaries due to temperature increase, will not lead to formation of a protective Cr₂O₃ under the investigated biomass firing conditions. Instead, its preference for chlorination facilitates corrosion attack along grain boundaries as was observed in Figures 5 and 7.

One of the important factors controlling the nature of corrosion under chlorine-containing atmospheres, is the stability of the metal chlorides resulting from the chlorination process. Increase in temperature provokes an increase in evaporation of metal chlorides, due to an increase in their vapour pressures [134]. Thus, with increasing temperatures, there is greater tendency for the metal chlorides formed at the corrosion front to evaporate, consequently leading to faster removal rates. Indeed, kinetic consideration of the high temperature reaction of metals under chlorinating atmospheres suggests an Arrhenius law controlled rate limiting step, which gives rise to exponential removal rates of the resulting reaction products upon temperature increase [282]. In line with the suggestion that the predominant transport of species during corrosion under the investigated condition is probably via the gas phase, temperature provoked exponential removal rates is expected to contribute to the observed influence of temperature on the degree of corrosion attack.

Although lattice diffusion of species through the corrosion products may not be the dominant transport mode during corrosion under biomass firing conditions, it is worthy to note that above 570 °C, the non-stoichiometric Fe-oxide phase (wüstite) becomes stable [184]. As the transport of species through wüstite can be promoted by its non-stoichiometric nature [283,284], the probable formation of this phase during exposures at 600 °C may also have contributed to the observed temperature influenced increase in corrosion attack.

4. Conclusions

The influence of time and temperature on the KCl induced corrosion of austenitic stainless steel, TP 347H FG under a gas mixture of 60 ppmv SO₂, 400 ppmv HCl, 6 vol% O₂, 12 vol% CO₂, 3 vol% H₂O
and N₂ as balance, has been investigated. Corrosion of the alloy results in attack of Mn, Cr and Fe through a Cl-catalyzed mechanism.

Under isothermal conditions, corrosion attack increases with time. In particular, the thickness of the sulphate layer resulting from sulphation of KCl increases with time, suggesting that the reaction was uncompleted even after 672 h. The thickness of the Fe-Cr-rich oxides concurrently increased with time suggesting that the sulphate layer on top of it does not effectively prevent transport of corrosive species.

Temperature increase from 560 °C to 600 °C significantly increases the degree of corrosion attack. Chlorination of alloying elements is enhanced with temperature increase due to increased vapour pressure of KCl and the corresponding enhanced sulphation to generate HCl. The vapour pressure of metal chlorides also increases with temperature leading to their faster removal from the corrosion front. Thus, operation of biomass fired power plants at high steam temperatures will result in increased corrosion attack on the superheaters.

Temperature enhanced diffusion of Cr is not advantages under biomass firing conditions because of the favourable chlorination of Cr. Increased preferential attack along grain boundaries therefore occurs when temperature is increased.

The order of thermal cycling influences the degree of corrosion attack such that initial exposure at a higher temperature will result in more corrosion attack probably because the high partial pressure of chlorine generated at high temperatures sustains corrosion attack during subsequent exposure at a lower temperature. Thus, a single increase of the service temperature as part of typical temperature fluctuations has a dramatic effect.

Acknowledgements

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References

All references cited in this manuscript are collected in the general reference list of the thesis.
Chapter 6 – The corrosion performance of modified surfaces and alternative superheater materials
6.1 – Influence of preoxidation on the high temperature corrosion of a FeCrAl alloy under conditions relevant to biomass firing

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Abstract

Preoxidation of a commercial FeCrAl alloy (Kanthal APM) was evaluated as a surface modification approach to reduce alkali chloride induced corrosion during biomass firing in power plants. Samples of the alloy preoxidized at 900 °C in O₂ or O₂ + 10 vol % H₂O, and at 1100 °C in O₂, were coated with KCl and exposed at 560 °C to a gas mixture comprising of 12 vol % CO₂, 6 vol % O₂, 3 vol % H₂O, 400 ppmv HCl and 60 ppmv SO₂. The oxide formed at 1100 °C showed no reactivity with the corrosive species. In contrast, all samples preoxidized at 900 °C suffered severe attack, resulting in formation of Fe, Cr and Al containing corrosion products in a heterogeneous morphology, similar to non-preoxidized samples. The observed differences with respect to the degree of corrosion attack on the preoxidized samples are discussed in terms of the composition and thickness of the different types of Al₂O₃ layers obtained by the preoxidation treatment.

Keywords: FeCrAl alloy, Preoxidation, High temperature corrosion, KCl, Chlorination, Sulphation.

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1. Introduction

Combustion of biomass for power production results in the deposition of corrosive K, Cl and S rich species on the superheater tubes [8,25]. These species aggravate fast corrosion of the superheaters at higher temperatures [104]. To avoid catastrophic corrosion of the superheaters, the present biomass fired boilers operate at or below a safe steam temperature limit (~540 °C). Operating at such low steam temperatures limits the efficiency of biomass fired boilers and as an alternative to lowering the operation temperature, new material solutions are needed to provide corrosion resistance at higher temperatures under biomass firing conditions.

Mechanistic understanding of high temperature corrosion under biomass firing conditions is necessary to find alternative superheater materials. From previous studies [101,111,131,138,164], it has been recognized that high Cr alloyed steels, that conventionally form a protective surface layer under oxidizing conditions, fail in alkali chloride containing environments because of: i) reactivity between alkali chloride and chromia, which consumes Cr from the alloy and consequently provokes the formation of a less protective Fe-rich oxide that is permeable to Cl species [138,164] and ii) selective attack of Cr and Cr-rich precipitates (possibly carbides) causing the development of a porous Cr depleted zone in the alloy [101]. In view of these observations, a viable approach would involve the initial formation of a protective oxide layer, which does not react with the corrosive species (KCl, HCl, SO2, etc.) encountered in biomass fired power plants.

The potential of preoxidation for protecting superheaters from corrosion has received considerable attention under sulphidizing environments [285–288]. However, under biomass firing conditions, i.e. involving oxidizing, chlorinating and sulphidizing species, investigations with focus on the influence of preoxidation are few. Investigations [130,228] involving only gaseous corrosive species (O2, HCl and SO2) have highlighted some positive effects of preoxidation on reducing corrosion of the investigated metals and alloys. Similarly, exposures involving solid deposits of KCl have recorded beneficial effects of preoxidation [147,231,289]. In particular, it is important to note that the preoxidation of Al-containing alloys seems promising because the stable oxide (α-Al2O3) is slow growing and permits lower ionic transport relative to Cr2O3 [147]. Moreover, chemical reactions between Al2O3 and KCl have been reported to be less likely compared with the reactivity between Cr2O3 and KCl [290]. However, assuming that the alloy contains enough Al, which can diffuse towards the surface to form a layer of Al2O3, it is also important to note that the protective nature of the oxide layer for subsequent exposure to biomass firing conditions will depend on the preoxidation environment and the temperature, because both parameters affect the evolution and stability of different Al2O3 polymorphs [41,51,55,291–294].

To explore the potential of Al2O3 to protect Al-containing alloys from corrosion, the present work investigates both the formation of Al2O3 and its effect on the high temperature corrosion of a commercial FeCrAl alloy (Kanthal APM) under laboratory conditions mimicking biomass firing.
2. Experimental

2.1 Material

A tube of the commercial FeCrAl alloy (Kanthal APM) with the composition given in Table 1 was employed for the experiments. Rings of 4 mm thickness were cut from the tube using a precision cut-off machine (Struers, Accutom-50). These rings were further sectioned into pieces to obtain arc-shaped specimens with external arc length of 21.4 mm which were ultrasonically degreased and dried in acetone and ethanol. For preoxidation as well as corrosion exposure, the samples were used in the as-cut condition without further surface preparation since it has been reported [295] that the nature of sample preparation influences the rate of oxidation.

Table 1. Chemical composition (in wt %) of Kanthal APM measured by energy dispersive X-ray spectroscopy.

<table>
<thead>
<tr>
<th></th>
<th>Cr</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>22.7</td>
<td>6.0</td>
<td>0.4</td>
<td>Bal</td>
</tr>
</tbody>
</table>

2.2 Preoxidation and high temperature corrosion exposure

Preoxidation was carried out in a horizontal tube furnace applying different conditions to investigate the effect of both the preoxidation atmosphere (O₂ with or without H₂O) and temperature (900 °C and 1100 °C). The following conditions were used:

i) O₂ at 900 °C,

ii) O₂ + 10 vol% H₂O at 900 °C

iii) O₂ at 1100 °C.

Samples for each preoxidation experiment were isothermally treated for the period of 168 h and cooled to room temperature in the furnace under a flow of the applied gas.

For evaluating the effect of the preoxidation on corrosion resistance, the preoxidized samples as well as non-preoxidized samples (as reference) were subjected to an atmosphere containing 12 vol% CO₂, 6 vol% O₂, 400 ppmv HCl and 60 ppmv SO₂ at a temperature of 560°C for the period of 168 hours. Before the high temperature corrosion exposure, samples were coated with a deposit consisting of KCl, which together with the applied gas atmosphere resembles conditions in the power plant. The deposit was obtained by mixing 32-63 μm sized KCl particles (Sigma ≥ 99%) with iso-propanol. After drying the slurry, it left an approximately 1 mm thick KCl deposit on the surface of the samples. The samples were exposed in a corrosion test rig which consists of a gas mixing unit, a horizontal furnace and a gas cleaning unit. Details of the experimental setup are given elsewhere [244]. The gas mixture was passed through a
water bath, to add 3 vol% H2O, before feeding into the furnace through preheated gas lines using N2 as a carrier gas. A minimum of 3 samples, in a given condition, were exposed to check reproducibility of the results. After each exposure, samples were cooled inside the furnace under a flow of the applied gas mixture.

2.3 Characterization of preoxidized surfaces and corrosion products

Microstructure characterization of samples after preoxidation was carried out on sample cross sections, and supplemented by plan view investigations. Non-preoxidized and preoxidized samples were mounted in an epoxy resin followed by standard metallographic preparation of the sample cross sections down to 1 μm diamond suspension polishing.

The cross sections of preoxidized samples were coated with carbon prior to investigations with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), to avoid charging of the embedded samples in the SEM. The thickness of the oxide layers was measured from SEM images of the cross sections with the help of an image analysis software (ImageJ). In addition, plan view investigations applying SEM and EDS were carried out on the preoxidized samples and further supplemented with X-ray diffraction (XRD) analysis for identification of phases in the oxide layers.

Corrosion products were characterized by both cross-section and plan view investigations. As described previously [244], the metallographic preparation of sample cross sections after corrosion exposure occurred with special care to preserve the corrosion product. Plan view investigations started on the topside and underside of the deposit which had sintered during exposure and could easily be removed to reveal the as-corroded surface, and subsequently involved successive mechanical removal of the corrosion product layers with a scalpel or SiC paper. The revealed interfaces were characterized by the complementary use of SEM, EDS and XRD. The methodology of comprehensive plan view and cross section analysis has been previously reported [208].

The SEM (FEI Inspect S or Quanta ESEM FEG with EDS system from Oxford Instruments) was operated for both imaging and chemical analysis with an acceleration voltage of 15 keV (unless stated otherwise). Both secondary electrons (SE) and backscattered electrons (BSE) were used for imaging. For qualitative phase analysis by XRD, a Bruker AXS D8 Discover diffractometer equipped with Cr-Kα radiation was used. All XRD measurements were carried out in grazing incidence mode (GI-XRD) with a counting time of 10 s per step size of 0.03°. A fixed incidence angle (γ) of 2° was used for oxide phase identification after preoxidation, which corresponds to a uniform X-ray penetration depth of about 1μm. XRD investigations on samples after corrosion exposures employed γ=5°, thus, covering slightly larger depths, which combined with subsequent mechanical removal, prevents averaging over the expected differences in chemical and phase composition below the surface.
For microstructure analysis of the FeCrAl bulk alloy before and after preoxidation as well as after corrosion exposure, polished cross-sections were etched with glyceregia and investigated using reflected light optical microscopy (LOM).

3. Results

3.1 Preoxidation under different gas atmospheres (O₂, O₂ + 10 vol% H₂O) and temperatures (900°C, 1100°C)

The microstructure of the oxide formed after preoxidation in O₂ at 900 °C is shown in Figure 1, from which features exhibiting globular (insert in Figure 1a) and platelet (Figure 1b) morphologies can be seen. Figure 1c showing the cross section of the sample reveals a thin oxide of about 0.5 μm thickness (Figure 2), which predominantly contains Al and O (Figure 1d).

![Figure 1](image)

**Figure 1.** Oxide morphology resulting from preoxidation in O₂ at 900 °C. (a, b) SE micrographs (acceleration voltage, 10 keV) showing plan view morphology of the sample surface, (c) BSE micrograph showing a cross section of the sample. The EDS maps in (d) reveal that the oxide is Al rich.

Changing the gas atmosphere by adding 10 vol% H₂O during preoxidation (O₂ + 10 vol% H₂O) at 900°C, does not considerably affect the morphology and composition of the oxide (Figure 3), but results in local thickness variations with a slightly higher thickness (about 0.7 μm on average) of the preoxidized layer.
(Figure 2). The corresponding oxide surface and cross section as shown in Figure 3, reveal similar morphology (platelets and globular features, Figure 3b, c) and composition (Al enriched surface) as the oxide obtained after preoxidation at 900°C in O₂ (cf. Figure 1). In contrast to preoxidation in O₂, local enrichment of Cr was observed within the oxide adjacent the oxide/alloy interface where thicker oxides formed (Figure 3e).

![Graph showing oxide thickness](image)

**Figure 2.** Thickness of oxide layers after preoxidation under different gas atmospheres and temperatures. A minimum of 50 measurements were employed to obtain the statistical distribution of the oxide layer thickness. The round dots represent the mean thickness, while the vertical extensions depict the maximum and minimum oxide thickness. The box edges represent the standard deviation of the mean, and the horizontal bar inside each box depicts the position of 50% of the distribution.

Compared to the minor effect of the gas atmosphere during pre-oxidation at 900°C as described above, an increase of the temperature to 1100°C was found to strongly affect the thickness of the oxide. After preoxidation in O₂ at 1100 °C, thickness measurements as well as microscopic cross section analysis with EDS measurements (Figure 4) reveal an about 4.3 μm thick oxide layer (Figure 2), which fully covers the surface. In addition, the platelet features observed on samples preoxidized at 900°C (Figures 1b and 3b) were absent on samples preoxidized at 1100°C. Instead, the oxide contained features with a globular morphology (Figure 4b).
Figure 3. Oxide morphology resulting from preoxidation in O$_2$ + 10 vol % H$_2$O at 900 °C. (a-c) SE micrographs (acceleration voltage, 10 keV) showing plan view morphology of the oxide. (d, e) BSE micrographs and EDS maps showing the cross-section and elemental composition of different regions of the oxide.
Figure 4. Oxide morphology resulting from preoxidation in O$_2$ at 1100 °C. (a, b) SE micrographs (acceleration voltage, 10 keV) of the oxide in plan view of the sample surface. (c) BSE micrograph showing the cross-section and (d) elemental composition of the oxide.

The diffraction patterns obtained from grazing incidence X-ray diffraction measurements on samples subjected to the different preoxidation treatments are shown in Figure 5. For the samples that were preoxidized at 900°C, phase analysis confirmed the presence of the thermodynamically stable phase α-Al$_2$O$_3$ [Joint Committee on Powder Diffraction Standards (JCPDS) card: 46-1212] with a rhombohedral crystal lattice. Also Cr$_2$O$_3$ [JCPDS card: 38-1479] was detected on these samples independent of the applied gas atmosphere at 900°C. However, as α-Al$_2$O$_3$ and Cr$_2$O$_3$ are of the same crystal lattice, the formation of a solid solution of these oxides is possible [296–298] and the simultaneous presence of Cr-Al-oxide ((Al$_{0.948}$Cr$_{0.052}$)$_2$O$_3$, [JCPDS card: 71-0958]) is suggested from the observed asymmetry of measured oxide peaks.
Figure 5. (a) XRD diffraction patterns measured for samples from the various preoxidation treatments. (b, c) Magnified regions of the diffraction patterns showing asymmetric peak profiles due to overlapping peaks from different phases in the preoxidation layers. Identified oxide phases are marked.

A metastable Al$_2$O$_3$ [JCPDS card: 46-1131] with a tetragonal lattice, possibly δ-Al$_2$O$_3$ [299], was also present in the oxides formed at 900 °C and overlap of its peaks with those of Cr$_2$O$_3$, (Al$_{0.948}$Cr$_{0.052}$)$_2$O$_3$
and α-Al₂O₃ also contributes to the observed asymmetric profile of some α-Al₂O₃ peaks as exemplified in Figure 5b. On the other hand, the oxide obtained after preoxidation in O₂ at 1100 °C consists mainly of α-Al₂O₃. However, at higher diffraction angles, peaks corresponding to the α-Al₂O₃ phase also exhibit an asymmetric profile (Figure 5c), which indicates the simultaneous presence of a solid solution (Al₀.₉₄₈Cr₀.₀₅₂)₂O₃. As a result of the thin nature of these oxides, reflections from the bulk alloy (α-Fe [JCPDS card: 85-1410]) were also recorded in all the diffraction patterns.

3.2 Characterization of corrosion products

3.2.1 Corrosion of non-preoxidized samples

Figure 6 shows the cross section of the heterogeneous corrosion product resulting from severe attack after corrosion exposure of a non-preoxidized Kanthal APM sample. From the BSE micrograph in Figure 6a, it appears that the corrosion product has grown outwards and inwards, i.e. above and below the original sample surface. The corrosion attack progressed towards the bulk alloy by grain boundary attack.

![Figure 6](image_url)

**Figure 6.** Corrosion of a non-preoxidized sample. (a) BSE micrograph. (b, c) Magnified images emphasizing the microstructure of the corresponding areas in (a).
Figure 7. EDS map showing the elemental distribution in corrosion products resulting from corrosion exposure of non-preoxidized sample.

EDS maps in Figure 7 showing the elemental distribution within these corrosion products reveal that those formed above the original surface consist of a mixture of oxides of the alloying elements (Al, Cr and Fe) with K (from the applied deposit) and S (from the gas atmosphere). This is supported by the contrast differences observed by microscopy (Figure 6b), which relate to the formation of oxides and sulphate (dark regions) in the micrograph. The corrosion product formed below the original surface also consists of a mixture of different phases (Figure 6c) which is revealed by EDS mapping (Figure 7) to be an oxide mixture containing Al, Cr and Fe. The maps also show that Al and Cr oxides are present in the regions where grain boundary attack occurred. Slight local enrichment of S and Cl is observed at the corrosion front.

Results from plan view characterization (Figure 8 and 9) provide more information on the morphology of the corrosion products. At the gas/deposit and deposit/corrosion product interfaces, the typical microstructures of the deposit after exposure are shown in Figures 8a and b, respectively. A distinctive observation is the accumulation of K, S and O rich features, indicating the formation of K₂SO₄, around KCl deposit particles. The size of these K₂SO₄ accumulations is largest at the gas/deposit interface, partly obscuring identification of the KCl deposit particles, but is much smaller just below the surface (Figure 8a). Consistently, the smaller size of these K, S and O rich accumulations also is observed at the deposit/corrosion product interface (Figure 8b) where, consequently, EDS analysis also shows the presence of Cl due to contribution from the deposit particles.
Figure 8. BSE micrographs showing the plan view microstructure of deposits at the (a) gas/deposit and (b) deposit/corrosion product interfaces after exposure of a non-preoxidized sample. Inserted EDS results are given in wt %.

The plan view morphology of corrosion products after removal of the deposit is shown in Figure 9a, from which Fe-Cr containing oxides with platelet morphologies are evident. With successive mechanical removal of the outer corrosion products, regions of grain boundary attack were revealed. Figure 9b shows a typical plan view microstructure of such regions. In agreement with observations on sample cross sections (Figure 7), the accompanying EDS maps (Figure 9c) reveal that Al, Cr and O were present in the attacked grain boundaries. Local Cl accumulation is also identified around the regions of grain boundary attack.

Figure 10 shows the crystalline phases at different depths within the corrosion product as detected with XRD. At the deposit/gas interface, the presence of K$_2$SO$_4$ [JCPDS card: 70-1488] in the initial KCl deposit [JCPDS card: 41-1476] is revealed. This is in agreement with the observation of K, S and O rich features in Figure 8a. At the surface of the corrosion product, after deposit removal, Fe$_2$O$_3$ [JCPDS card: 33-0664] and FeCr$_2$O$_4$ [JCPDS card: 34-140] were identified. No additional phase is observed with further removal of the corrosion products, until the bulk alloy was approached. Instead, the peak intensities for Fe$_2$O$_3$ and FeCr$_2$O$_4$ decreased, while those from the bulk alloy (α-Fe [JCPDS card: 85-1410]) increased.
Figure 9. Selected results from plan view ‘top-down’ characterization of corrosion products on a non-preoxidized sample after corrosion exposure. (a) SE micrograph showing heterogeneous Fe-rich oxide after removal of the deposit (i.e. at the corrosion product/deposit interface). (b) BSE micrograph and (c) EDS maps showing the microstructure and elemental composition of grain boundary attacked regions at the corrosion product/bulk alloy interface. Inserted EDS results in (a) are given in wt %.
3.2.2 Corrosion of samples preoxidized at 900 °C

Figures 11-14 show the microstructure and chemical composition of the corrosion products formed after corrosion exposure of samples preoxidized at 900 °C in different atmospheres. Samples preoxidized in O₂ at 900 °C suffered corrosion attack (Figure 11a) but to a lesser degree, compared to the non-preoxidized samples. With a composition similar to the non-preoxidized sample (cf. Figure 7), the outer corrosion products consist of an oxide mix containing Al, Cr and Fe (Figure 11b). K and S are also present in the upper regions of the outward grown part of the corrosion product and in addition, plan view investigations (not shown here) revealed accumulation of K₂SO₄ particles around the deposits. The inward grown corrosion product consists predominantly of Fe oxide with Al and Cr enrichment closer to the corrosion front. Corrosion attack along the alloy grain boundaries resulted in an enrichment of Al, Cr and O. In addition, the EDS maps in Figure 11b reveal the presence of S and Cl in the attacked grain boundaries.
Figure 11. Corrosion of a preoxidized sample (in O\textsubscript{2} at 900 °C) (a) BSE micrograph. (b) EDS map of corrosion products.

Complementary information on the morphology and composition of these corrosion products is revealed by plan view investigations as shown in Figure 12. Interestingly, the presence of an Al-rich layer was still identifiable on some regions beneath the deposit after its removal (Figure 12a). However, it is also observed that Fe-Cr containing oxides with platelet morphologies similar to the non-preoxidized samples (cf. Figure 9a) have formed beneath the initial Al-rich oxide as a result of the corrosion attack. In addition, the corrosion products after removal of the deposit consisted of Cl-rich protrusions (Figure 12b) which appear to grow out from the bulk alloy. The regions of grain boundary attack, as revealed by successive mechanical removal of external layers (Figure 12c), show the presence of Al, Cr, S, Cl and O in the attacked grain boundaries, which confirms the observations on cross sections (cf. Figure 11b). The crystalline phases identified on the revealed interfaces were the same as those identified on the non-preoxidized sample (cf. Figure 10).
Figure 12. Selected results from plan view ‘top-down’ characterization of corrosion products on a preoxidized sample (in O$_2$ at 900 °C). (a) SE micrograph showing the heterogeneous Fe-rich oxide at the corrosion product/deposit interface. The initial oxide layer is evident on some regions. (b) Cl-rich protrusions (BSE micrograph) at the corrosion product/deposit interface. (c) BSE micrograph and EDS maps showing the microstructure and elemental composition of grain boundary attacked regions at the corrosion product/bulk alloy interface. Inserted EDS results in (a) and (b) are given in wt %.
For the samples which were preoxidized in O$_2$ + 10 vol% H$_2$O at 900 °C, Figure 13a shows that some regions (less than 15% of the investigated cross sections) did not suffer significant corrosion attack after corrosion exposure. EDS maps in Figure 14a clearly show the presence of an Al rich layer in such regions, in addition to K, Cl, S and O. In contrast to these regions of considerable reduced attack, severe corrosion attack (Figure 13b) which preferentially progressed towards the bulk alloy through the grain boundaries also occurred for samples preoxidized in O$_2$ + 10 vol% H$_2$O at 900 °C. Such attack was observed on more than 80% of the sample cross section. In such regions where severe corrosion attack occurred, EDS maps
Figure 14b reveal that the corrosion products were similar in composition, to that observed after corrosion of the sample preoxidized in O$_2$ at 900 °C (cf. Figure 11b).

![Figure 14](image.png)

**Figure 14.** EDS maps showing the elemental composition of corrosion products on (a) ‘non-attacked’ and (b) severely attacked regions of a preoxidized sample (in O$_2$ + 10 vol % H$_2$O at 900 °C) after corrosion exposure.

Although the general morphology and composition of the corrosion products on non-preoxidized samples and samples preoxidized at 900 °C (in O$_2$ and in O$_2$ + 10 vol% H$_2$O) were similar, the extent of corrosion damage differed. Based on the mean thickness of over 50 measurements on the sample cross sections (Table 2), it was observed that samples preoxidized at 900 °C (in O$_2$ and in O$_2$ + 10 vol% H$_2$O) sustained less corrosion attack relative to the non-preoxidized samples.
Table 2. Mean thickness of the outward and inward growing layers of the corrosion products on non-preoxidized samples and samples preoxidized at 900 °C, after corrosion exposures.

<table>
<thead>
<tr>
<th>Sample condition</th>
<th>Thickness of corrosion products (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Outward growing</td>
</tr>
<tr>
<td>Non-preoxidized</td>
<td>197 ± 47</td>
</tr>
<tr>
<td>Preoxidized at 900 °C in O₂</td>
<td>67 ± 31</td>
</tr>
<tr>
<td>Preoxidized at 900 °C in O₂ + 10</td>
<td>133 ± 51</td>
</tr>
</tbody>
</table>

3.2.3 Corrosion of samples preoxidized at 1100 °C

The formed α-Al₂O₃–rich layer due to preoxidation in O₂ at 1100 °C was still visible on the sample after corrosion (Figures 15 and 16) and obviously has protected the surface from severe corrosion attack as shown in Figure 15a. The localized regions (less than 40% of the sample) where corrosion attack occurred (Figure 15b) were close to the sample edges. The corrosion product, as shown in Figure 15b, laterally progressed underneath the preoxidation layer from the attack initiated close to the edges of the sample. From Figure 16, it is observed that the corrosion attack resulted in the formation of K₂SO₄ containing Fe and Al₂O₃-rich oxide above the α-Al₂O₃–rich layer, and an Al, Cr and Fe containing oxide below. In the attacked grain boundaries, an enrichment of Al, Cr, S and Cl is observed.

Comparison of results after exposure of samples preoxidized in O₂ at 1100 °C (Figure 15), with the exposure of samples preoxidized at 900 °C (Figures 11, 12 and 13) indicate that the resistance of the oxide layers to corrosion attack has been influenced by the preoxidation temperature. To check whether this effect is related to changes in the bulk microstructure due to the different preoxidation temperatures, the thermal stability of the sample bulk alloy at both 900 °C and 1100 °C was investigated with reflected light optical microscopy (not shown here) and confirmed that the bulk microstructure remained stable. Thus, the observed differences in the final corrosion attack of the various samples are solely related to the nature of the surface layers obtained by preoxidation (see section 4.3), and not induced by changes of the bulk microstructure, which could have implied different diffusion conditions during exposure.
Figure 15. BSE micrographs showing microstructure of a sample preoxidized in O$_2$ at 1100 °C, after exposure. (a) Non-attacked regions are representative for most of the preoxidized sample, and (b) corrosion attack are close to positions at the sample edges.

Figure 16. Elemental composition of the corrosion products on local attacked regions of a sample preoxidized in O$_2$ at 1100 °C, after corrosion exposure. Presence of Cl in the epoxy is responsible for its identification in the upper parts of the Cl map.
4. Discussion

4.1 The influence of preoxidation conditions

The 6 wt% of Al in the investigated alloy is above the minimum Al concentration suggested for the formation of Al-rich oxide layers on FeCrAl alloys [300] and, indeed, the formation of an Al-rich oxide layer was evident after the different preoxidation treatments (Figures 1, 3 and 4). It is well documented [41,51,291,292,294,300–307] that formation of any of the Al$_2$O$_3$ polymorphs ($\alpha$-, $\gamma$-, $\delta$-, $\theta$-phase) is influenced by variables such as H$_2$O in the environment, temperature and time. Earlier studies [293,294,299] have reported that $\alpha$-Al$_2$O$_3$ formation is favoured at temperatures above 1050 °C, while at lower temperatures metastable polymorphs ($\delta$-, $\gamma$-, $\theta$-Al$_2$O$_3$) predominate. However, in agreement with previous investigations on FeCrAl alloys (Kanthal AF and Kanthal APMT) [51,291,292,305,307], XRD (Figure 5) indicated the formation of $\alpha$-Al$_2$O$_3$ after preoxidation of Kanthal APM already at 900 °C. Nonetheless, for preoxidation at 900°C, additional reflections from Cr$_2$O$_3$ and the tetragonal (metastable) Al$_2$O$_3$ were also recorded (Figures 5b), thus indicating that the oxide formed at 900 °C did not only consist of $\alpha$-Al$_2$O$_3$. Cr$_2$O$_3$ can be formed during the initial stages of oxidation of Cr-containing alloys [51,291,305], and is known to facilitate the nucleation of $\alpha$-Al$_2$O$_3$ as well as the transformation of metastable Al$_2$O$_3$ polymorphs to the stable $\alpha$-Al$_2$O$_3$ [293,308].

As previously mentioned in section 3.1, the isomorphous lattices of $\alpha$-Al$_2$O$_3$ and Cr$_2$O$_3$ can allow the formation of a solid solution of the oxides. Furthermore, the incorporation of the larger Cr$^{3+}$ into the $\alpha$-Al$_2$O$_3$ lattice will cause an increase in its lattice cell parameter, in accordance with Vegard’s law, and therefore the $\alpha$-Al$_2$O$_3$ peak positions will shift to lower diffraction angles if an $\alpha$-Al$_2$O$_3$ layer contains some amount of Cr [296–298]. For molar fractions of Cr$_2$O$_3$ higher than 0.5, separate reflections from Cr$_2$O$_3$ will also be recorded in the diffraction pattern [296]. On the example of the 116 reflection of $\alpha$-Al$_2$O$_3$ at $2\theta = 91.3^\circ$ (Figure 5b), the high amount of Cr in the oxides formed at 900 °C is probably responsible for the separate 116 reflection of Cr$_2$O$_3$ at a lower $2\theta$ value of 86.4$^\circ$. The asymmetric profile of the $\alpha$-Al$_2$O$_3$ 116 peak is rather attributed to the overlapping 211 reflection of Cr$_2$O$_3$, as well as reflections from the metastable $\delta$-Al$_2$O$_3$. On the basis of these observations, it is suggested that the oxides formed at 900 °C contain a Cr-rich solid solution of the stable $\alpha$-Al$_2$O$_3$ and Cr$_2$O$_3$, as well as the metastable $\delta$-Al$_2$O$_3$. The possible presence of metastable Al$_2$O$_3$ in these oxides is also supported by the platelet features observed by SEM (Figures 1b and 3b), which is the typical morphology reported for metastable polymorphs of Al$_2$O$_3$ [302,309,310]. In contrast, the oxide formed at 1100 °C did not contain such platelet features, but rather exhibited globular morphologies, hence suggesting the absence of metastable Al$_2$O$_3$ in such oxides. In addition, XRD results (Figure 5a, c) suggest that these oxides are not Cr-rich. On the example of the 300 reflection of $\alpha$-Al$_2$O$_3$ at $2\theta = 112.9^\circ$ (Figure 5c), a high amount of Cr in the oxide should have caused separate 300 reflections from Cr$_2$O$_3$ at $2\theta = 106.2^\circ$. Instead, a Cr-deficient solid solution of Al-Cr-oxide, i.e. (Al$_{0.948}$Cr$_{0.052}$)$_2$O$_3$, was present in the oxide and overlap between its peaks and $\alpha$-Al$_2$O$_3$ peaks is responsible for the asymmetric profile of the $\alpha$-Al$_2$O$_3$ peak shown.
in Figure 5c. The low content of Cr in this oxide could be due to volatilization of Cr from the oxide, which should be significant around 1100 °C [39,311].

It has been suggested that the ability of H₂O to cause hydroxylation of metastable Al₂O₃ surfaces stabilizes these polymorphs against α-Al₂O₃ [291]. However, on the basis of XRD and microstructural characterization (Figures 1, 3 and 5), results from the present investigation do not suggest any strong effect of H₂O on delaying the transformation of metastable alumina polymorphs to stable α-Al₂O₃. On the other hand, the preoxidation temperature is observed to influence the thickness and composition of the resulting oxide layer such that a thicker oxide comprising mainly of α-Al₂O₃ formed after preoxidation at 1100 °C (Figures 2 and 5).

4.2 Corrosion of non-preoxidized samples

The porous and heterogeneous morphology of corrosion products on non-preoxidized samples of Kanthal APM (Figure 6) suggest that corrosion possibly involved vapour phase transport of species rather than transportation through the oxide lattice. It is known that HCl in the inlet gas mixture, in addition to that formed from conversion of the deposits to K₂SO₄ [111,112,246], is able to induce chlorination of alloying elements, causing formation of non-stable metal chlorides. Thermodynamic calculations [184,235], in line with previous investigations [156] show that chlorination of the major alloying elements in Kanthal APM (Fe, Cr and Al) is favourable at 560 °C. The high vapour partial pressures of the metal chlorides generated from the chlorination process [76,208,228] is suggested to have provoked vapour phase transport of these species away from the corrosion front. This is supported by the heterogeneous and porous morphology of the corrosion products (Figures 6 and 9a). Although the investigated alloy contains about 6 wt % Al, which under oxidizing atmospheres should form a protective layer of Al₂O₃ [300], the nature of corrosion attack under biomass firing conditions prevented this. Al oxides can result from conversion of their chlorides to oxides (Figure 7), however AlCl₃ is so volatile that it evaporates from the alloy before being oxidised and therefore does not form a compact uniform layer but instead a porous heterogeneous oxide in the corrosion products above the original metal surface.

The preferential nature of corrosion attack along the alloy grain boundaries (Figures 6 and 9b) may have been caused by faster transportation through such pathways. However, as bulk microstructural characterization of the investigated alloy showed the presence of Cr-rich precipitates, possibly Cr-carbides (micrographs not shown here), the preferential attack of such precipitates, owing to the sensitivity of Cl towards Cr-carbides [104,144,156,160], may have caused attack to progress along the grain boundaries.

Since the oxide formed from conversion of the metal chlorides is not protective, both atomic and molecular transport of sulphur towards the corrosion front is possible during corrosion. The relatively low oxygen partial pressure at such positions may allow for sulphidation attack in addition to chlorination. This probably accounts for S accumulation in the internally formed corrosion products (Figure 7).
4.3 Corrosion of preoxidized samples

From assessment of the corrosion products on samples preoxidized at 900 °C in O₂ or in O₂ + 10 vol% H₂O, and at 1100 °C in O₂ (cf. Figures 11, 12, 13, and 15), it is evident that the samples preoxidized at 1100 °C resisted corrosion attack to a larger degree than those preoxidized at 900 °C. As was suggested in section 3.2.3, the stable bulk microstructure of the samples after the different heat treatments suggests that the difference in corrosion performance is related to the nature of the oxides obtained after the different preoxidation treatments. Specifically, the observed differences in thickness and composition of the oxides as a function of the preoxidation conditions are suggested as the main influence on the corrosion performance.

As shown in Figure 2, the type of preoxidation treatment resulted in different thickness of the oxide layers. The larger oxide thickness of samples preoxidized at 1100 °C exhibited resistance to corrosion because it physically prevented diffusion of the corrosive species through the oxide, compared to samples preoxidized at 900 °C. However, the thick oxide regions on samples preoxidized at 900 °C in O₂ + 10 vol% H₂O (Figure 4e) did not offer protection against corrosion, so this consideration may not fully explain the observed trend in corrosion attack. According to results in reference [130], the oxide composition as well as its compactness, is more important than the oxide thickness with respect to the resistance of pure metals (Fe, Cr and Ni) towards corrosion attack in Cl-containing environments. In line with this, the relatively low attack observed on samples preoxidized at 1100 °C may not solely relate to the thicker oxide, but may also originate from the observed difference in composition of this oxide, compared to the oxide obtained at 900 °C.

In literature, it is noted that the initiation steps of corrosion under biomass firing conditions involves direct reaction between the corrosive species and the material (or oxide) [119,138,312]. In this respect, the reaction between Cr₂O₃-rich oxides and KCl depletes an alloy of Cr and causes the formation of a less protective Cr-depleted oxide. Considering such reaction as a criteria for initialization of corrosion attack under the conditions investigated in this study, the severe corrosion attack suffered by samples that were preoxidized at 900 °C (Figures 11-14) may result from reaction between KCl and Cr₂O₃ identified in these oxides (Figure 5). Subsequently, the less protective oxide may have allowed further ingress of corrosive species which propagated the corrosion attack. On the contrary, because the samples preoxidized at 1100 °C contained a very low amount of Cr in solid solution with α-Al₂O₃ (Figure 5c), they did not suffer severe corrosion attack. Indeed, microstructural investigations (Figures 15 and 16) show that the α-Al₂O₃ rich oxide was not attacked after the 1 week corrosion exposure. Thus both the increased thickness of this oxide and the very low content of Cr₂O₃ eliminated initiation sites for corrosion attack.

Considering also the direct reaction between KCl and different polymorphs of Al₂O₃, thermodynamic calculations with FactSage [184,235] show that both the thermodynamically stable α-Al₂O₃, and the metastable δ-Al₂O₃ polymorph will withstand corrosion attack due to the positive Gibbs free energy.
change ($\Delta G^0$) of their reactions with solid KCl at 560 °C (Table 3). However, according to data in literature [119], KCl is expected to have a vapour pressure of more than $10^{-6}$ atm at 560 °C, implying that gradual volatilization of the KCl deposits occurs. Interestingly, thermodynamic calculations in Table 3 suggest a slightly higher driving force (a negative $\Delta G^0$) for reaction between the metastable $\delta$-polymorph of $\text{Al}_2\text{O}_3$ and the deposit when it is in the gas phase, in contrast to the reaction with stable $\alpha$-$\text{Al}_2\text{O}_3$ (a positive $\Delta G^0$).

Table 3. Gibbs free energy changes for the reactions of different alumina polymorphs with KCl (s, g). Calculations were performed with FactSage [184,235].

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta G^0$ at 560 °C (kJmol$^{-1}$ HCl)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2} \text{Al}_2\text{O}_3$ (s) + KCl(s) + $\frac{1}{2}$ H$_2$O ⇌ KAlO$_2$(s) + HCl(g)</td>
<td>$\alpha$ 101.11 96.92</td>
</tr>
<tr>
<td>$\frac{1}{2} \text{Al}_2\text{O}_3$ (s) + KCl(g) + $\frac{1}{2}$ H$_2$O ⇌ KAlO$_2$(s) + HCl(g)</td>
<td>$\delta$ 4.15 -0.04</td>
</tr>
</tbody>
</table>

Thus, assuming that the initiation of corrosion attack was influenced by the thermodynamic favourability of reactions between KCl (g) and the preoxidized surfaces, the severe corrosion attack suffered by samples that were preoxidized at 900 °C (Figures 11-14), which contained the metastable $\delta$-$\text{Al}_2\text{O}_3$ polymorph, corroborates the fact that the resistance of the oxide to corrosion attack is influenced by its composition.

In the event of breakdown of the preoxidized layer, it was not possible to form a new protective oxide layer during exposure (Figures 11-14) since the exposure temperature (560 °C) is too low to support protective $\text{Al}_2\text{O}_3$ formation. Therefore the corrosion process almost proceeds in a manner similar to the non-preoxidized samples such that the alloying elements are chlorinated and redeposited as porous oxides. Moreover, as was observed for the non-preoxidized samples, the transport of S-species leading to sulphidation (Figures 11b and 12c) also becomes possible by virtue of the porous morphology of the corrosion products, as well as the low oxygen partial pressure induced by the presence of Cr- and Al-rich oxides close to the corrosion front [313]. Previous investigations [285–287,314] have also suggested that sulphidation of preoxidized samples only occurs if sulphur transport is facilitated by fissures or pores in the oxide. However, comparison of the corrosion products from such studies with the present results clearly suggests that the attack by Cl-containing species is more aggressive.

5. Conclusions

The phase composition and thickness of $\text{Al}_2\text{O}_3$ formed from preoxidation of Kanthal APM varies with temperature and preoxidation environment. At the lower preoxidation temperature of 900 °C, a Cr-rich
solid solution of Al-Cr-oxide was detected. Also, a metastable Al₂O₃, possibly δ-Al₂O₃, was identified in the oxides formed at this temperature. On the contrary, preoxidation at 1100 °C in O₂ leads to formation of a layer consisting mainly of the thermodynamically stable α-Al₂O₃.

The corrosion attack on preoxidized Kanthal APM under conditions relevant to biomass firing is sensitive to the composition and thickness of the preoxidation layers. Thinner preoxidation layers formed in both O₂ and O₂ + 10 vol % H₂O atmospheres at 900 °C containing a solid solution of Al with high amounts of Cr in the oxide as well as a metastable δ-Al₂O₃, suffer corrosion attack. Oxide layers formed at 1100 °C in O₂, containing mainly α-Al₂O₃ are resistant to corrosion attack. In this regard, the preoxidation temperature, is more important than the preoxidation atmosphere with respect to corrosion resistance.

Corrosion attack does not occur on mechanically stable α-Al₂O₃ after 1 week exposure to conditions simulating biomass firing.

In the absence of a protective layer on Kanthal APM, the alloy suffers severe corrosion attack under biomass firing conditions. Protective Al-oxides cannot form under such conditions, instead porous, heterogeneous and non-protective corrosion products form due to volatile species involved in the corrosion attack.

Acknowledgements

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All references cited in this manuscript are collected in the general reference list of the thesis.
6.2 – The influence of mechanical and chemical integrity of a preoxidized $\alpha$-Al$_2$O$_3$ layer on the corrosion resistance of Kanthal APM under laboratory conditions simulating biomass firing$^\text{ix}$

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Abstract

The corrosion resistance of a commercial FeCrAl alloy (Kanthal APM) after formation of a preoxidation layer of $\alpha$-Al$_2$O$_3$ was investigated, under conditions related to biomass firing. Careful microstructural characterization revealed that severe corrosion attack, as well as internal formation of nitrides beneath the preoxidation layer occurred. However, the $\alpha$-Al$_2$O$_3$ layer itself showed good chemical integrity and did not suffer corrosion attack. The local but severe corrosion, as well as internal nitridation, are discussed in relation to the observed adhesion and local cracking of the otherwise protective $\alpha$-Al$_2$O$_3$ layer.

Keywords: High temperature corrosion, Chlorination, Preoxidation, Alumina, FeCrAl alloy.

$^\text{ix}$ Manuscript planned for submission as a letter (short communication)
High corrosion rate of superheaters is among the challenges facing biomass fired power plants. The formation of protective oxides is not possible under biomass firing conditions due to reactions between deposits (KCl), flue gas species (HCl, SO₂) and the surfaces of superheaters. In particular, Cr₂O₃ forming alloys fail under biomass firing conditions because of the reaction between KCl and Cr₂O₃ [138,149,164], which cause the chromia layer to be not protective in these cases. In contrast, such reaction with α-Al₂O₃ is not thermodynamically favoured [184], hence, Al₂O₃-forming alloys are promising alternative materials for use in biomass fired power plants. However, it is important to note that the typical metal temperatures of superheater tubes in such plants are too low to facilitate formation of the corrosion resistant α-Al₂O₃ polymorph, and, therefore, an additional pre-treatment dedicated to its formation is necessary. Studies on the corrosion performance of α-Al₂O₃ layers obtained by preoxidation to atmospheres relevant to biomass firing are few [147,231,315] and have revealed that under KCl deposits, corrosion attack on a preoxidized Kanthal APMT is initiated at flaws containing transient Fe-rich oxides [315].

Protection offered by the preoxidation layer may not only depend on its chemical reactivity with the corrosives species, and can also include mechanical integrity. For α-Al₂O₃ layers, the tendency of local mechanical failure at sample edges is high due to thermal and growth induced stresses [294]. However, the implications of this on the possibility of α-Al₂O₃ layers to offer corrosion resistance under alkali chloride and sulphur containing environments, relevant for biomass firing, is not well investigated.

The aim of this work is to investigate the mechanical and chemical integrity of a preoxidized α-Al₂O₃ layer formed on Kanthal APMT when exposed to laboratory conditions simulating biomass firing. The chemical composition of the investigated alloy (Kanthal APM) as determined with energy dispersive X-ray spectroscopy (Oxford instruments) is as follows: 22.7 wt% Cr, 6.0 wt% Al, 0.4 wt% Si with Fe as balance. Arc shaped samples cut from the tube were sequentially degreased and dried in acetone and ethanol before preoxidation for 168 h in O₂ at 1100 °C. After cooling under O₂ to room temperature, the resulting 4 μm thick oxide layer was identified with grazing incidence x-ray diffraction as α-Al₂O₃. However, characterization with Scanning Electron Microscopy (SEM, Quanta ESEM FEG, FEI) showed spallation at regions close to the edge of the sample (Figure 1) suggesting that the oxide layer possessed poor mechanical properties.
The preoxidized samples were coated with a deposit slurry comprising of a KCl mixture with isopropanol before isothermal exposure at 560 °C for 168 h to a gas mixture comprising of: 400 ppmv HCl, 60 ppmv SO$_2$, 12 vol % CO$_2$ and 6 vol % O$_2$ (on a dry basis). 3 vol % of H$_2$O was added to the dry gas mixture and N$_2$ was used as a carrier gas. This was carried out in a special corrosion test rig described elsewhere [208] to simulate the conditions during straw firing in power plants [111]. To the authors’ knowledge, this is the first investigation assessing the corrosion performance of $\alpha$-Al$_2$O$_3$ layer under such complex conditions. After exposure, samples were allowed to cool in the furnace under a flow of the applied gas mixture before subsequent mounting in epoxy to enable analysis on cross sections. Details of metallographic sample preparation are given elsewhere [208]. Using an acceleration voltage of 15 keV, the cross sections were analysed by SEM and Energy Dispersive X-ray Spectroscopy (EDS, Oxford instruments).

As suggested by thermodynamic calculations with FactSage [184], Figure 2 shows that the $\alpha$-Al$_2$O$_3$ layer remains unaffected by the corrosive species. Such protective behaviour with morphology as in Figure 2 was observed on more than 60% of the specimen surface. However, major corrosion
Figure 3. Severe corrosion of the preoxidized sample after corrosion exposure (a) Overview of the sample microstructure from the sample edge towards the centre (right to left in the micrograph), (b) severe corrosion attack at the sample edge, (c) formation of Fe/Cr/Al-rich oxide below the preoxidized α-Al₂O₃ layer, (d) local internal precipitation of nitrides below the preoxidized α-Al₂O₃ layer.
attack occurs close to the sample edge (Figure 3a, b) corresponding to the regions where mechanical integrity was lost prior to exposure (cf. Figure 1). Starting from the unprotected sample edges, corrosion attack laterally progressed underneath the α-Al₂O₃ layer which remained chemically stable (Figure 3c). This is in agreement with a previous investigation [315], and highlights that corrosion attack only occur when the mechanical integrity of the α-Al₂O₃ layer is lost. From EDS analysis (Figure 4a), the porous corrosion products are observed to consist of Fe, Cr and Al together with K, O and S in the outer parts. This observation indicates that KCl in the deposit reacts with SO₂ to form K₂SO₄ and HCl, which, in addition to that in the gas mixture, dissociated to produce chlorine through the Deacon process [156].
Chlorine reacts with the alloying elements Fe, Cr and Al to form their metal chlorides which have appreciable vapour pressures to provoke evaporation from the corrosion front. Their subsequent conversion to oxides results in the porous Fe-Cr-Al-rich oxide mixed with K₂SO₄. As the formation of metal chlorides is accompanied by a volume change, they result in delamination of the α-Al₂O₃ layer from the metal surface (Figure 3a), thereby compromising the mechanical integrity of the α-Al₂O₃ layer in the form of delamination from the alloy.

Close to areas where the preoxidized layer was not fully delaminated, the formation of precipitates in the near surface region of the bulk alloy is observed (Figure 3d) and these are probably nitrides (see Figure 4b). Such precipitates are disadvantageous as they will consume Al in the alloy necessary for protective oxide formation, if the right conditions are fulfilled. Formation of these precipitates cannot be explained by diffusion through the α-Al₂O₃ layer because they are absent on places where the layer was adherent (cf. Figure 2). It has been argued that porous oxides resulting from KCl-induced corrosion provide pathways for nitrogen transport [315], thus in this respect, nitridation would be a consequence of poor chemical integrity of the oxide layer. However, this consideration does not hold for the present investigation because nitrides were absent at the oxide/alloy interface where severe corrosion attack occurred (Figure 3b and 3c).

Detailed examination of the sample was carried out to clarify the dependence of nitridation on mechanical integrity of the oxide layer. Figure 5, which supports Figure 3d, shows that nitrides form underneath the α-Al₂O₃ layer only at locations where no severe corrosion attack occurred, but where the α-Al₂O₃ layer was delaminated, thus, at locations with poor mechanical integrity. Literature [316] suggests that nitrogen permeation (from the gas mixture) through cracked layers will cause internal nitridation at the oxide/metal interface, and as the nitrides closest to the surface will convert to oxides (Al₂O₃), more nitrides would form at the corrosion front. In the present study, nitride precipitation was only present near positions where the α-Al₂O₃ layer was partly delaminated (Figure 5). The precipitates are absent underneath the positions where either the α-Al₂O₃ layer was fully delaminated (Figure 5a) or adherent (Figures 2, 5b and c). Accordingly, it is suggested that the low oxygen partial pressure at the crevice between delaminated and adherent α-Al₂O₃ layers facilitates nitridation, thus, it is a consequence of poor mechanical integrity of the oxide layer.
Figure 5. Microstructure of corrosion products on a location close to the centre of the sample. (a) An overview of typical delaminated region with fractures in the preoxidized $\alpha$-$\text{Al}_2\text{O}_3$ layer, (b, c), close up views of the interface between the delaminated and adherent preoxidized $\alpha$-$\text{Al}_2\text{O}_3$ layer with internal nitride precipitation in these regions.
In mixed corrosive atmospheres, one of the potential conditions for nitride formation below an oxide layer would be that the oxygen partial pressure established by the equilibrium between the metal and oxide is low enough to facilitate formation of the nitride \[316,317\]. Observations in Figures 3d, 5b and c suggest that this condition is only fulfilled at the crevice between delaminated and adherent \(\alpha\)-Al\(_2\)O\(_3\) layers.

In conclusion, the loss of protection offered by a preoxidation layer of \(\alpha\)-Al\(_2\)O\(_3\) on Kanthal APM when coated with KCl and exposed isothermally at 560 °C to a gas mixture of HCl: 400 ppmv, SO\(_2\): 60 ppmv, CO\(_2\): 12 vol \%, O\(_2\): 6 vol \%, H\(_2\)O: 3 vol \% and N\(_2\) as balance, results from its poor mechanical integrity which is extreme at sample edges. Severe active corrosion of Fe, Cr and Al in the alloy, as well as internal nitridation occurs following mechanical damage. The instantaneous nature of the chlorine catalyzed corrosion attack \[131\] is a possible reason for the absence of internal nitridation on severely attacked regions of the alloy. However, in the absence of such severe corrosion, internal nitridation is favoured at the crevice between delaminated and adherent \(\alpha\)-Al\(_2\)O\(_3\) layers. In both degradation cases, the \(\alpha\)-Al\(_2\)O\(_3\) layer is chemically inert, thus degradation is primarily induced by poor mechanical integrity of the layer.

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The references cited in this manuscript are collected in the general reference list of the thesis.
6.3 – Influence of preoxidation on high temperature corrosion of a Cr-Ti-Al containing Ni-based alloy under conditions relevant to biomass firing

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Abstract

Development of corrosion resistant materials in biomass fired power plants demands specific attention since the condensation of deposits rich in KCl on heat exchange surfaces induces severe corrosion attack, which is different from corrosion in traditional coal fired plants. As a result, the ability of preoxidized layers formed on a commercial Cr-Ti-Al-containing Ni-based alloy (Nimonic 80A) to withstand biomass-induced corrosion is investigated. Preoxidation treatments at 900 °C in O₂ and O₂ + 10 vol % H₂O, respectively, were conducted before samples were exposed to deposit and gas conditions that mimicked biomass firing. Complementary characterization methods were employed to study the preoxidized samples and corrosion exposed samples. The oxides obtained by the preoxidation treatments protected the alloy during corrosion exposure at 560 °C for a period of 168 h. In contrast, non-preoxidized samples suffered corrosion attack and formed porous non-protective oxides containing the alloying elements, Ni, Cr, Ti and Al. The influence of the preoxidation layers on the corrosion mechanism is discussed.

Keywords: High temperature corrosion, Biomass firing, Preoxidation, KCl deposit, Chlorination, TiO₂.

*Manuscript planned for submission*
1. Introduction

High temperature corrosion of heat exchanger components is a serious problem for biomass fired power plants [31] due to the formation of corrosive KCl rich deposits on the heat exchanger surfaces (such as superheaters) [165,205]. This arises mainly from the high content of organically bound K and Cl in biomass, which during combustion, become devolatilized and condense as deposits rich in K and Cl [8,12]. To handle the corrosion problem in biomass fired plants, the maximum operation steam temperature is limited to low values (usually below 540 °C), thereby limiting the electrical efficiency of biomass fired power plants to about 30%. Identification of materials with improved corrosion resistance for use as superheaters in biomass fired power plants is therefore of utmost importance [138].

Recent investigations have shown that without any dedicated surface modification, chromia and alumina forming alloys do not give adequate protection in the presence of alkali chlorides (see for example [118,122,124,138,149,191,264]). One of the principal factors responsible for this is the thermodynamic favourability of the reaction between alloying elements and chlorine, leading to formation of volatile metal chlorides which then are oxidized to form non-protective oxides [200]. Consequently, the protecting ability of coatings containing possible protective elements have been investigated under conditions related to biomass firing [145,150,155,163,318,319]. However, the inter-diffusion of alloying elements as well as the possibility of corrosive species to diffuse through the coating splat boundaries [155] are vital factors to be considered if coatings are to be applied for protection of superheaters against alkali chloride induced corrosion in biomass fired power plants.

Surface modification employing the materials own alloying elements for the formation of protective oxides prior to corrosion exposure (i.e. preoxidation), provides an avenue for rendering protection to materials under aggressive conditions. This approach has been widely investigated under sulphidation conditions [285,286,288,314,320], and in a few cases, under conditions related to biomass firing [130,147,228,289,321]. With respect to investigations under conditions related to biomass firing, the effect of preoxidation for protection against corrosion depends on the composition and crystallography of the preoxidized layer, preoxidation conditions, as well as the corrosive environment [130]. In particular, a positive effect of preoxidation of pure Cr and Ni against HCl attack was reported in [130], while pure Fe preoxidized under similar conditions suffered corrosion. Similarly, the resulting Al₂O₃ from preoxidation of a commercial FeCrAl alloy has been reported to give some degree of protection against KCl induced corrosion attack [147]. Furthermore, an investigation with chromia forming alloys (EN 1.4982, EN 1.4301 and EN 1.4845) revealed a positive effect of preoxidation against attack by HCl at low temperatures (400 °C) [228]. On the other hand, no positive effect was reported for preoxidation of Fe-30Cr alloys in oxygen, when they were subsequently exposed to a gaseous KCl environment [321]. It therefore implies that although Cr-oxide rich preoxidation layers may be resistant to attack by HCl [130,228], they can exhibit poor resistance to KCl-induced attack [321] possibly due to the reaction between KCl and Cr₂O₃ [164].
Investigations of the reactivity of a number of oxides and KCl under oxidizing conditions have indicated that KCl does not react with TiO₂, ZrO₂, Y₂O₃, Ta₂O₅, HfO₂, Al₂O₃, NiO, Fe₂O₃, CeO₂ and Co₃O₄ [290]. These results suggest that alloys with the capability of forming such oxides may experience limited corrosion attack under biomass-firing conditions. Based on this and with the need for further exploration of preoxidation as an avenue for corrosion protection under biomass firing conditions, the present work reports on the influence of preoxidation on the corrosion resistance of a Cr-Al-Ti-containing Ni-based alloy (Nimonic 80A) under laboratory conditions mimicking biomass firing.

2. Experimental procedures

2.1 Sample preparation, preoxidation and high temperature corrosion exposures

The investigated material was a Ni-based alloy (Nimonic 80A). Its chemical composition as determined by Energy Dispersive X-ray Spectroscopy (EDS), is as follows (in wt%): Al-1.3, Ti-2.2, Cr-20.6, with Ni as balance. Using fusion thermal conductivity detection units, LECO CS230 and LECO TN500, the carbon and nitrogen contents of the alloy has been determined and amount to 0.070 wt% C and 0.014 wt% N [122]. Arc shaped samples having external arc length of 23.6 mm were obtained from the tube material with a precision cut-off machine (Struers, Accutom-50). The samples were ultrasonically cleaned and dried in acetone and ethanol, before preoxidation, annealing or exposure to corrosive atmospheres. The various heat treatments are summarized in Table 1.

### Table 1. Summary of the different heat treatment conditions in the present study

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Temperature (°C)</th>
<th>Time (h)</th>
<th>Atmosphere</th>
</tr>
</thead>
<tbody>
<tr>
<td>Preoxidation I</td>
<td>900</td>
<td>168</td>
<td>O₂</td>
</tr>
<tr>
<td>Preoxidation II</td>
<td>900</td>
<td>168</td>
<td>O₂ + 10 vol% H₂O</td>
</tr>
<tr>
<td>Annealing</td>
<td>900</td>
<td>96</td>
<td>Ar</td>
</tr>
<tr>
<td>Corrosion exposures</td>
<td>560</td>
<td>168</td>
<td>KCl deposit + 400 ppmv HCl, 60 ppmv SO₂, 12 vol% CO₂, 6 vol% O₂, 3 vol % H₂O, N₂-balance</td>
</tr>
</tbody>
</table>

(a) with the exception of H₂O, gas compositions are given on a dry basis.

This involved either preoxidation in oxidizing atmospheres to form surface oxides, or annealing in inert atmospheres to investigate possible temperature induced changes of the bulk microstructure, and finally, corrosion exposure of the different samples. All experiments were conducted isothermally and samples were subsequently allowed to cool under their respective gaseous atmospheres applied for the treatment.
The preoxidation and annealing experiments were carried out in horizontal tube furnaces, while corrosion exposure of KCl-coated samples was carried out in a dedicated test rig described elsewhere [244]. A slurry of KCl in isopropanol was used to obtain an about 1mm thick KCl deposit on each sample before its exposure to the corrosive gases. With the applied conditions (deposit and gases), the corrosion exposure mimics the environment experienced by superheaters in biomass fired power plants. At least three samples in either the as-received, preoxidized or annealed condition have been exposed to high temperature corrosion and investigated afterwards.

2.2 Characterization of samples

Light optical microscopy (LOM), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD) were employed for sample characterization. Cross sections of the as-received, preoxidized and annealed samples were mounted in an epoxy resin and prepared down to 1 μm diamond suspension polishing according to standard metallographic procedures. For characterization of the bulk microstructure of the as-received (non-preoxidized), preoxidized and annealed samples, prior to and after corrosion exposures, cross sections of these samples were etched with glyceregia before microstructure analysis using LOM (OLYMPUS GX 41). The cross sections of all samples exposed to the corrosive conditions mimicking biomass firing were carefully prepared under water free conditions. Details of this procedure are described elsewhere [244]. These cross sections were analysed with SEM (Inspect S or Quanta ESEM FEG, FEI) and EDS (Oxford instruments) using an acceleration voltage of 15 keV. SEM investigations were conducted with both backscattered electron (BSE) and secondary electron (SE) detectors to obtain information on variations of both chemical composition and morphology. From the obtained SEM images, the thicknesses of the preoxidation layers and corrosion products were measured using the image analysis software ImageJ. Over 50 measurements were carried out for each set of samples to meet statistical requirements for the thickness distribution.

In addition to the conventional cross sectional mapping by EDS, an elemental re-quantification method (previously described in [322]) was employed to obtain an averaged one-dimensional representation of depth-profiles of relevant chemical elements. This involved subdivision of the mapped regions into strips of meshes in directions parallel to the sample surface, and subsequent re-quantification (from the acquired EDS map data) of the average composition of elements in these meshes using the INCA software (Oxford instruments). Generally, the length of these meshes (in the direction parallel to the surface of the sample) were over 100 μm. However, due to the difference in thickness of the oxides obtained from preoxidation, and the reaction products obtained after corrosion exposures, different mesh thicknesses were employed. For the relatively thick oxides on the preoxidized samples, a mesh thickness was 1.5 μm was utilized for these samples, while a 0.5 μm thick mesh was used to properly capture the chemical variations in corrosion products observed on non-preoxidized samples. The elemental profiles were then obtained by plotting the re-quantified averaged compositions from each strip of mesh, as a function of distance in the direction perpendicular to the oxide (or corrosion product)/metal interface.
Plan view investigations using SEM, EDS and XRD were also carried out in order to supplement the analysis of the cross sections. For corrosion exposed samples, plan view investigation involved careful successive removal of the corrosion products, starting from the deposit/gas interface, and characterization of the exposed interfaces (for details, see [208]). In all the plan view investigations, a diffractometer ( Bruker AXS, D8 Discover) equipped with Cr-Kα radiation was applied for XRD measurements. To limit the X-ray penetration depth, measurements were carried out in grazing incidence geometry (GI-XRD) using a fixed incidence angle (γ = 2° for analysis of preoxidation layers, and 5° for corrosion product analysis). A counting time of 10 sec per 0.03° detector step was employed for all XRD measurements.

3 Results

3.1 Morphology and composition of preoxidation layers

Results of microscopy and chemical analysis of the oxide surfaces after preoxidation of Nimonic 80A at 900 °C in O₂ (preoxidation I), and in O₂ + 10 vol% H₂O (preoxidation II), are shown in Figures 1 and 2, respectively. After preoxidation in either atmosphere (H₂O or H₂O+O₂), both preoxidation layers were similarly enriched in Cr and Ti, with local Ti rich agglomerates (cf. Figures 1a and 2a). The preformed oxide in both atmospheres consisted of: i) an outer layer, containing some voids as well as discrete features with a lower atomic weight, and, ii) an internal oxidation zone, which contained features with an acicular microstructure (Figures 1b and 2b). Oxidation along alloy grain boundaries was commonly observed within the internal oxidation zone. Figures 1b and 2b also show that the alloy contains Ti-N rich and Cr-rich precipitates. While the Ti-N precipitates were present in the as-received alloy, the Cr-rich precipitates only became apparent after the preoxidation treatment (see section 3.2.3). Within the inner oxidation zone, both types of precipitates were absent.

The EDS maps in Figures 1c and 2c clearly reveal a similar composition for the layers resulting from preoxidation I and II, thus, the result of preoxidation does not depend on the applied atmosphere. The outer layer comprises of Ti and Cr rich oxide, with Ti being enriched in the outermost regions of the oxide and also as discrete precipitates in the outer layer. The acicular features in the internal oxidation zone are identified as Ti and Al-rich oxides. Oxides along alloy grain boundaries are enriched in Ti, Al and, on some regions, in Cr. On the example of a sample from preoxidation I, the elemental profiles in Figure 3 reveal quantitatively that Ti and Cr are enriched in the outer layer while Cr is depleted in the internal oxidation zone within which enrichment of Al and Ti is evident.
Figure 1. Microstructure of the oxide resulting from preoxidation in O₂. (a) SE micrograph showing the plan view morphology of the oxide. (b) BSE micrographs showing the cross section of the sample after preoxidation. (c) EDS maps showing the elemental distribution within the oxide. The inserted EDS results in (a) are given in wt%.
Figure 2. Microstructure of the oxide resulting from preoxidation in O\textsubscript{2} + 10 vol\% H\textsubscript{2}O. (a) SE micrographs showing the plan view morphology of the oxide. (b) BSE micrographs showing the cross section of the sample after preoxidation. (c) EDS maps revealing the elemental composition of the oxide.

In line with EDS results (Figures 1c, 2c and 3), phase analysis by means of XRD (Figure 4) revealed that the oxides formed after preoxidation I and II have similar phase composition. The presence of TiO\textsubscript{2} (Rutile, according to Joint Committee on Powder Diffraction Standards, JCPDS card: 21-1276) is clearly detected, with an additional oxide either consisting of Cr\textsubscript{2}O\textsubscript{3} (JCPDS card: 38-1479) and/or a solid solution of Ti in Cr-oxide (Cr\textsubscript{0.88}Ti\textsubscript{0.12})\textsubscript{2}O\textsubscript{3} (JCPDS card: 82-0211).
Figure 3. Elemental profiles showing variation in the average elemental composition obtained from re-quantification of EDS maps covering the preoxidation layer and the bulk alloy on samples preoxidized in O₂ (preoxidation I). Note the difference in the horizontal scales.

Figure 4. XRD patterns showing the crystalline phases present in the oxidized layers under different conditions of preoxidation.
Table 2. Average thickness of the outer layer (OL) and inner oxidation zone (IOZ) resulting from the different preoxidation treatments.

<table>
<thead>
<tr>
<th>Preoxidation treatment</th>
<th>Average thickness (μm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>OL</td>
<td>IOZ</td>
</tr>
<tr>
<td>Preoxidation I</td>
<td>9 ± 2</td>
<td>14 ± 8</td>
</tr>
<tr>
<td>Preoxidation II</td>
<td>7 ± 1</td>
<td>11 ± 6</td>
</tr>
</tbody>
</table>

With over 50 measurements on the sample cross section, the statistical distribution of the thickness of the outer layer and internal oxidation zone, as summarized in Table 2, indicate similar thicknesses for the respective layers after sample treatment under the different preoxidation conditions.

3.2 Results from corrosion exposures

3.2.1 Corrosion attack on non-preoxidized samples

Figure 5 presents the microstructure and elemental composition of the corrosion products observed after exposure of non-preoxidized samples to the simulated biomass firing conditions. The micrograph in Figure 5a reveals that the corrosion product consisted of a highly porous oxide located above the bulk alloy. In addition, localized pores/voids are observed at the corrosion front. It is observed that Cr-rich precipitates are detected in the bulk of the non-preoxidized sample after the corrosion exposure (Figure 5a). The elemental maps in Figure 5b show that the upper layer of the corrosion product above the porous oxide consists mainly of K, S and O. Its morphology suggests that this layer has been molten during exposure. Additionally, Cr and Ni rich precipitates are present in this layer. The porous oxide is revealed to consist of Ni, Cr, Ti, Al and O (Figure 5b). In particular, Ti and Al are enriched in the lower regions of the porous oxide, i.e. closer to the bulk alloy. The elemental profiles generated from the elemental re-quantification method (Figure 5c) started from the interface between the molten K,S,O rich layer and porous oxide and progressed into the bulk alloy, and reveal that Cr, Ti and Al are enriched in the innermost region of the porous oxide. In between the porous oxide region and the bulk alloy, these elements are depleted resulting in the observed enrichment of Ni.

Results from plan view investigations coupled with mechanical removal of the deposit layer, show that large K, S and O rich agglomerates formed on the original KCl deposit particles, both at the deposit/gas (Figure 6a) and deposit/corrosion product (Figure 6b) interfaces. The observation of such features at the latter interface is in agreement with the K, S and O rich layer above the porous oxide observed on the sample cross section (cf. Figure 5). In addition, minor amounts of Cr and Ni were also identified together with the K, S and O rich features at the deposit/alloy interface (Figure 6b).
Figure 5. Microstructure of the corrosion product resulting from corrosion exposure of a non-preoxidized sample. (a) BSE micrographs showing the cross section of the corrosion product. (b) EDS maps revealing the elemental composition of the corrosion product. The re-quantified elemental profiles in (c) show the variation in average elemental composition starting from the porous oxide rich part of the corrosion product towards the bulk alloy.

Phase analysis by XRD (not shown here) revealed that the crystalline phases at these interfaces include both the deposit, i.e. the original KCl (JCPDS card: 41-1476), and its transformation to K$_2$SO$_4$ (JCPDS card: 70-1488), thus accounting for the K, S and O rich layer. Compared to plan view investigations, KCl was not detected in prepared cross-sections and this could indicate that the compound was removed during preparation, even though absolute alcohol was used as lubricant instead of water during preparation. The plan view microstructure of the Ni, Cr, Ti, Al and O rich porous layer of the corrosion
product located below the K$_2$SO$_4$-rich layer is shown in Figure 6c. The very porous nature of this layer is also evident from the micrograph in Figure 6d which shows plan view microstructure of some needle-like porous Ni-rich regions of the corrosion product.

![Figure 6](image_url)

**Figure 6.** BSE micrographs showing the plan view microstructure of the corrosion product resulting from corrosion exposure of a non-preoxidized sample. (a) The deposit appearance from the gas/deposit and (b) deposit/oxide interfaces. (c and d) The plan view microstructure of the porous corrosion product layer observed after removal of the deposit and the K$_2$SO$_4$-rich layer. Elemental compositions are given in wt %.

### 3.2.2 Corrosion of preoxidized samples

No significant change in the morphology of the oxides obtained from the different preoxidation treatments (I and II) could be observed after their exposure to conditions simulating biomass firing.
Figures 7 and 8 present the microstructure and elemental composition of preoxidized samples, illustrated with the example of a sample preoxidized in O\textsubscript{2} (preoxidation I).

**Figure 7.** Microstructure of a sample preoxidized in O\textsubscript{2} after its exposure to corrosion conditions mimicking biomass firing.

**Figure 8.** EDS maps showing elemental composition on the cross section of the sample preoxidized in O\textsubscript{2} after its exposure to corrosion conditions mimicking biomass firing.
Apart from the presence of K and S on the surface (Figure 8), the elemental composition of the oxide remained unchanged after the corrosion exposure. The presence of the Ti and Cr rich outer layer as well as the Ti and Al rich oxide within an internal oxidation zone, was still evident after the corrosion exposure.

Furthermore, comparison of the element depth-profiles across the preoxidized samples before (cf. Figure 3) and after the corrosion exposure (Figure 9) reveals no qualitative difference in elemental composition of the preoxidation layer. Based on the statistical representation of the thickness of the different oxide layers, as shown in Figure 10, it is also observed that both the average thicknesses of the outer oxide and the internal oxidation zone of the preoxidized samples were not affected by the corrosion exposure.

**Figure 9.** Elemental profiles showing variation in average elemental composition, starting from the outermost region of the preoxidation layer towards the bulk alloy, on a sample preoxidized in O$_2$ after their exposure to corrosion conditions mimicking biomass firing. The spikes in Ti concentration within the bulk alloy (at 42 μm and 60 μm) are due to the presence of Ti-rich precipitates. Note that K and S observed above the outermost region of the preoxidation layer are not shown in the plot.
To further understand the resistance of the preoxidized samples to corrosion attack observed on cross sections (Figure 7), plan view characterization including stepwise removal of the deposit, was additionally conducted. As shown in Figures 11a and b, K, S, O rich features accumulated around the KCl deposit particles, both at the deposit/gas (Figure 11a) and at the deposit/alloy interfaces (Figure 11b), similar to observations on non-preoxidized samples (cf. Figures 6a and b). However, the size and degree of coverage of the deposit particles by these features is less, compared to the deposits on the non-preoxidized samples (cf. Figure 6). As a result, substantial amounts of Cl (>20 wt %) were detected by EDS analysis on these features. In line with EDS results in Figure 11a and b, both KCl (JCPDS card: 41-1476), and K₂SO₄ (JCPDS card: 70-1488) were identified by XRD at the gas/deposit and deposit/alloy interfaces (diffractograms not shown here). No porous oxide was observed after removal of the deposits on preoxidized samples. Instead, fragments of K and Cl rich features (possibly deposit particles) on a sulphate layer were present above the preoxidation layer (Figure 11c). Upon successive mechanical removal of the sulphate rich layer in Figure 11c, only the Cr and Ti rich outer layer of the initially formed oxide (Figure 11d) and Ti and Al enriched features in the inner oxidation zone (Figure 11e) were observed.
Figure 11. BSE micrographs showing the plan view microstructure of the corrosion product resulting from corrosion exposure of preoxidized samples. (a) The deposit appearance from the gas/deposit and (b) deposit/oxide interfaces. (c) Plan view microstructure of the corrosion product directly below the deposit. The micrographs in (d) and (e) show the microstructure of the Cr-Ti rich oxide and the internal oxidation zone respectively, following successive mechanical removal of the preceding layers. Elemental compositions are given in wt %.
3.2.3 Changes in bulk microstructure and corrosion of annealed samples

The bulk microstructure of the non-preoxidized and preoxidized samples was investigated with LOM following etching of cross sections with glyceregia. As shown in Figure 12a, only Ti-rich precipitates are present in the as-received state of the alloy. Although SEM analysis revealed the presence of Cr-rich after corrosion exposure of non-preoxidized samples (Figure 5a), LOM investigations (Figure 12b) show that at 560 °C these precipitates are not so pronounced compared to their distribution after the preoxidation treatment at 900 °C (Figure 12c). Evidently, preoxidation treatment at 900 °C promoted the formation of Cr-rich precipitates and, in addition, modified the bulk microstructure of the alloy with respect to its grain size. This may have consequences for the diffusion of alloying elements during the subsequent corrosion exposure, such that the observed resistance of the preoxidized samples to corrosion may be either due to the modified microstructure of the bulk alloy, or an effect of the preoxidation layer. To isolate these effects, prior annealing of non-preoxidized samples under inert atmospheres (argon, Ar), at 900 °C for 96 h was conducted to provoke a bulk microstructure (Figure 12d), similar to that after the preoxidation treatments. The annealed samples were finally subjected to corrosion exposure under conditions mimicking biomass firing.

![Figure 12](image_url)

**Figure 12.** Optical micrographs showing the bulk microstructure of (a) the investigated alloy in the as-received condition, (b) a non-preoxidized sample after corrosion exposure (560 °C, 168 h), (c) a sample preoxidized in O₂ at 900 °C, 168 h and (d) a sample annealed in Ar at 900 °C, 96 h. Dotted arrows indicate the location of Ti-rich precipitates while solid arrows mark Cr-rich precipitates in the alloy.
Figure 13 show that the annealed samples suffered similar corrosion attack as the non-preoxidized samples (cf. Figure 5 and Figure 13). The outer part of the corrosion product on the annealed samples consisted of a K, S and O rich heterogeneous layer with Cr and Ni rich particles. Below this, there was a continuous, but porous layer in which Ni is essentially enriched in the outer regions (Figure 13b), while Cr, Ti and Al are enriched in the inner regions (closer to the bulk alloy). This observed similarity between the corrosion attack on the annealed and non-preoxidized samples strongly indicates that the resistance of the preoxidized samples to corrosion attack is due to the presence of the preoxidation layer and not due to the change in bulk microstructure of the alloy induced by the heat treatments.

Figure 13. Microstructure of the corrosion product resulting from corrosion exposure of a sample initially annealed in Ar at 900 °C. (a) BSE micrographs showing cross sections of the corrosion product. (b) EDS maps showing the elemental composition of the region highlighted in (a).

4 Discussion

The preoxidation treatment of Nimonic 80A resulted in an outer layer of oxide, identified by XRD (Figure 4) and SEM-EDS to contain both TiO₂ and Cr₂O₃. In addition, an inner oxidation zone, in which Al, Ti and Cr were oxidized (Figures 1c and 2c), developed above the bulk alloy. The observed
microstructure and oxide composition after preoxidation are typical for Ni-Cr-Al alloys [323,324], because the high content of Cr in the alloy (20.6 wt %) can facilitate the growth of an external Cr$_2$O$_3$ layer after development of the transient Ni-Cr-Al-rich oxide [324]. In contrast, the low concentration of Al (1.3 wt %) in the alloy cannot facilitate the formation of a continuous Al$_2$O$_3$ layer, hence, Al becomes internally oxidized both as discrete particles (the acicular features in Figures 1b and 2b) and along the grain boundaries of the alloy. In addition, the low oxygen partial pressure ($p_{O_2}$) in equilibrium with Al$_2$O$_3$ will support internal oxidation of Al, and by a similar consideration, the internal oxidation of Ti, below the Cr$_2$O$_3$ rich layer [37,325]. However, because of the faster diffusion of Ti through Cr$_2$O$_3$, it is observed that TiO$_2$ was also formed at the outermost part of the outer layer. A similar enrichment of TiO$_2$ above a Cr$_2$O$_3$ layer has been observed after the oxidation of Ni-Cr-Al alloys [325,326].

By comparison of Figures 5, 8 and 13, it is evident that preoxidation has a positive effect with respect to reducing the corrosion attack on Nimonic 80A, under laboratory conditions mimicking biomass firing. The fact that no significant attack occurred on the preoxidation layer containing a Cr/Ti-oxide is intriguing because previous work has suggested that KCl can destroy Cr-rich oxides according to reaction 1 [138,164,321]. With appreciable amount of KCl vapour (> 10$^{-6}$ atm) [119] being generated at 560 °C, this reaction is highly favourable with a Gibbs free energy change ($\Delta G^0$) of -60.3 kJmol$^{-1}$(HCl) at 560 °C [184,235].

\[
\frac{1}{4}Cr_2O_3(s) + KCl(s, g) + \frac{3}{8}O_2(g) + \frac{1}{2}H_2O(g) \rightleftharpoons \frac{1}{2}K_2CrO_4(s) + HCl(g) \tag{1}
\]

However, for the similar reaction involving TiO$_2$ (rutile), thermodynamic calculations with FactSage [184,235] reveal that at 560 °C, reaction 2 is accompanied with a positive Gibbs free energy change ($\Delta G^0$) of 123.7 kJmol$^{-1}$ (solid KCl) and 26.8 kJmol$^{-1}$ (gaseous KCl), making such a reaction to be thermodynamically unfavoured.

\[
\frac{1}{2}TiO_2(s) + KCl(s, g) + \frac{1}{2}H_2O(g) \rightleftharpoons \frac{1}{2}K_2TiO_3(s) + HCl(g) \tag{2}
\]

Hence, it appears that the thin TiO$_2$ enriched layer in the outermost part of the outer oxide layer (Figures 1c and 2c) rendered protection against corrosion attack. Although this is in agreement with a previous study [290] in which no reactivity was observed for a mixture of TiO$_2$ and KCl exposed at 650 °C for 15 h to an atmosphere containing 5% O$_2$ + 15% H$_2$O, corrosion exposures for longer durations will be necessary to evaluate the long term durability of the resistance offered by the TiO$_2$ enriched layer.

The severe corrosion attack observed on non-preoxidized samples (Figures 5 and 13) can be explained by the absence of a protective oxide on the samples, prior to the corrosion exposures. The tendency of reaction (1) to occur during the transient stages of the exposures, due to the absence of a protective Ti-rich surface oxide may have resulted in formation of non-protective oxides that allowed ingress of Cl-containing species. It has to be noted that HCl can be released from reaction (1), and from the reaction.
between KCl and SO$_2$ in the gas phase (reaction 3) [208,246,327], forming K$_2$SO$_4$ which was identified on samples after the corrosion exposures (Figures 5b, 6a, b, 8 and 11a, b). Upon dissociation of HCl via the Deacon process [131,156,280], Cl$_2$ is generated and can propagate the corrosion attack through chlorination of the alloying elements at the corrosion front, where the oxygen partial pressure is relatively low. Although the HCl originally present in the gas mixture also has the tendency of inducing chlorination attack by itself, previous studies [213,234] has shown that this has a lower influence on the degree of corrosion attack, compared to corrosion attack in the presence of KCl deposits.

\[
2\text{KCl}(s) + \text{SO}_2(g) + \text{H}_2\text{O}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g) \tag{3}
\]

Results from plan view characterization (Figures 6 and 11) also reveal that the preoxidation layer has an effect on the sulphation process (i.e., reaction 3) as less accumulation of K$_2$SO$_4$ around the KCl deposit particles was observed on preoxidized samples (Figure 11a and b), compared to non-preoxidized samples (Figure 6a and b). At low temperatures (such as in the present study), it has to be noted that a vital intermediate step in reaction (3) involves the oxidation of SO$_2$ to SO$_3$, which is often catalyzed by oxides [197,327,328]. This is substantiated by the fact that KCl is converted to sulphate at the deposit/flue gas interface (as would be expected due to high SO$_2$ content in the flue gas) and at the oxide/deposit interface, but remains unconverted within the bulk of the deposit [208,244]. Based on previous studies, Fe$_2$O$_3$, Cr$_2$O$_3$, V$_2$O$_5$, CaO and CuO exhibit better catalytic activity than oxides of Ti, Si, Th, U, Ce, W, Sn, As and Mo [329–332]. Thus, the TiO$_2$ in the outer layer of the preoxidized samples may have hindered the oxidation of SO$_2$ to SO$_3$ during the corrosion exposure, and thus, the sulphation process (Figure 6) thereby reducing HCl formation which propagates the corrosion attack. Thus in addition to the unfavourable reaction between TiO$_2$ and KCl deposits (reaction 2), the presence of TiO$_2$ in the preoxidation layer may have contributed to the observed resistance to corrosion attack, because of its negative influence on the generation of HCl close to the alloy surface. This dual effect against corrosion under biomass firing conditions suggests promising potentials for surface modification approaches that can promote the formation of TiO$_2$ surface layers, for applications in biomass fired power plants. Corrosion exposures for longer durations will be required to clarify this.

From Figures 5b and 13b, it is evident that the total chlorine partial pressure ($p_{\text{Cl}_2}$) resulting from dissociation of the HCl in the gas mixture, in addition to that from reactions (1) and (3), was sufficient to cause chlorination of the alloying elements, Ni, Cr, Ti and Al in the non-preoxidized samples. According to thermodynamic calculations with FactSage [184,235], metal chlorides resulting from chlorination of Ti and Al will require a lower $p_{\text{O}_2}$ for conversion to their oxides, and this correlates with the presence of Ti and Al rich oxides, closer to the corrosion front as observed in Figures 5b and c, as well as in Figure 13b. In contrast, Ni and Cr-rich oxide precipitates (whose corresponding metal chlorides require relatively higher $p_{\text{O}_2}$ conditions for conversion to oxides), were mostly observed in the outermost regions of the corrosion product and in some cases, in a mixture with the K, S, O rich layer above the porous oxide (Figures 5a and 13a). It is important to note that even though the low $p_{\text{O}_2}$ condition required
for conversion of Ti and Al chlorides appears to have caused formation of their oxides above the alloy bulk (Figures 5b and c), the porous and heterogeneous morphology of the entire corrosion product suggests that such oxides will not give adequate protection against further corrosion attack in a manner similar to the previously reported halogen effect [333].

5. Conclusions

The influence of preoxidation of Nimonic 80A on its high temperature corrosion performance under laboratory conditions mimicking biomass firing at 560 °C was investigated. From the observed results, the following conclusions are made.

Without preoxidation, Nimonic 80A suffers corrosion resulting in the formation of an inner oxide of Ti and Al and an outer porous oxide containing Ni, Cr, and Al. The outer porous oxide is submerged in a layer of K₂SO₄ ensuing from the reaction of the KCl deposit with SO₂ in the gas mixture.

Preoxidation of Nimonic 80A at 900 °C for 168 h results in an outward growing TiO₂ and Cr₂O₃ containing oxide in which Ti is enriched in the outermost part, and an inner oxidation zone in which Al and Ti are oxidized. The preoxidation atmosphere (with or without water vapour) seem not to affect the composition, morphology and thickness of the pre-oxidized surface layers.

The reaction between KCl and TiO₂ is thermodynamically unfavourable, and in addition to the poor catalytic ability of TiO₂ towards HCl formation from the sulphation reaction, TiO₂ in the outer part of the preoxidation layer protects against corrosion attack on the alloy.

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The references cited in this manuscript are collected in the general reference list of the thesis.
6.4 – Evaluation of surface modification approaches for protection against biomass induced high temperature corrosion

\textsuperscript{xii} Manuscript in preparation
1. Introduction

The need for material solutions to curb the high temperature corrosion of superheater tubes in biomass fired power plants cannot be overemphasized. The current operation of such plants below a safe steam temperature limit of 540 °C leads to low efficiency hence, materials resistant to the KCl induced corrosion in such atmospheres are desired.

The mechanism of corrosion attack in biomass fired power plants operates in a way that most of the conventionally promising alloying elements present in stainless steels may be prone to selective attack from Cl species [30,31,156,200]. The known protective effect of Cr is not attainable under biomass firing conditions because of reactivity between Cr-rich oxides and KCl at high temperatures. This consequently prevents the formation of a protective oxide in high Cr-alloyed steels [149,164].

Investigations have shown that alloying elements such as Ni, Al and Si may provide positive effects towards impeding the KCl induced corrosion attack (see for example, [152,153,170]). As intrinsic alloying elements, promoting the diffusion of such elements to form adherent protective oxide layers will be desirable. However, there are limits to which these elements can be employed as intrinsic alloying elements, due to considerations of cost and mechanical properties of the alloy.

In contrast to surface modification relying on diffusion of intrinsic alloying elements to the alloy surface, another possible way to protect against KCl induced corrosion of superheaters in biomass fired power plants is the deposition of protective layers of suitable elements on the surface of superheaters [106,162,318]. The present work evaluates some of these possibilities, in which Si, Ni and Ni-Al were deposited on the surfaces of commercial superheater materials. In addition, this work evaluates the possibility of hindering the corrosion process based on the strong affinity of nitrogen for alloying elements, which otherwise should have high driving force for chlorination. In this consideration, the gas phase nitriding of a FeCrAl alloy was also explored as a surface modification approach. In general, the emphasis of the study is on the corrosion resistance of the modified surfaces as obtained by standard techniques. The optimization of such surfaces involves development of novel techniques which is beyond the scope of this work.

2. Experimental procedures

2.1 Sample preparation and surface modifications

2.1.1 Low temperature nitriding of FeCrAl alloy

The investigated FeCrAl alloy had the following composition: 72.8 wt% Fe, 22 wt% Cr, 5 wt% Al, 0.1 wt% Y and 0.1 wt% Zr as specified by the supplier (GoodFellow). The samples were of dimensions 23 x 15 x 0.3 mm. Low temperature gaseous nitriding using 2 mL/min flow of NH₃ was carried out at 430 °C for 20 h according to the procedure described in reference [334].
2.1.2 SiOₓ coating on TP 347H FG

For the coating process, samples of about 4mm thickness were cut from a tube of the austenitic stainless steel TP 347H FG. The steel had the following nominal composition: 17.5 wt% Cr, 11.0 wt% Ni, 1.8 wt% Mn, < 1.0 wt% Nb+Ta, 0.4 wt% Si, 0.06 wt% C, ≤ 0.04 wt% P, ≤ 0.0015 wt% S, and Fe being the balance. Prior to coating on the flat side of the samples, degreasing and surface activation were carried out. Hydrogen Silsesquioxane (HSQ) precursor in silanol-based solvent (Dow Corning FOX 25) was deposited on the surface by dip coating at 1 mm/s dipping speed. The solvent was evaporated by heat treatment in an open furnace at 160 ºC for 0.5 h and the remaining HSQ precursor was polymerized to form a SiOₓ-like surface film at 600 ºC in reducing atmosphere (flow of Ar-carrier gas with 10 vol% H₂) for 2 h.

2.1.3 Ni and Ni-Al coatings on Esshete 1250

Arc shaped samples of 10 mm width were cut from a tube of the alloy Esshete 1250 which has the following nominal composition: 15 wt% Cr, 9.5 wt% Ni, 6.3 wt% Mn, 1.0 wt% Nb, 1.0 wt% Mo, 0.5 wt% Si, 0.3 wt% V, 0.1 wt% C, ≤ 0.015 wt% S, ≤ 0.035 wt% P, 0.0005 wt% B and Fe being the balance, as specified by the supplier (SANDVIK). Following degreasing, Ni and Ni-Al coating on the samples were realized by electroplating and subsequent pack aluminizing, respectively, according to details in [335].

2.2 Corrosion exposures

A dedicated high temperature corrosion test rig was employed to conduct corrosion tests under conditions that mimic biomass firing. The description of corrosion test rig is given elsewhere [208]. Exposures under conditions mimicking biomass firing involved coating of samples with synthetic deposit slurry which comprised of 32-63 μm sized KCl particles in isopropanol. The samples were subsequently exposed isothermally at 560 ºC for 168 h, under a gas mixture of 12 vol% H₂O, 6 vol% O₂, 400 ppmv HCl, 60 ppmv SO₂ and N₂ as balance, which was bubbled through a water bath to add 3 vol% H₂O. The different samples with surface modifications as described above were exposed in individual sets of exposures.

2.3 Microstructural and compositional characterization

Scanning electron microscopy (SEM, Inspect S), Energy dispersive X-ray spectroscopy (EDS, Oxford instruments) and X-ray diffraction (XRD, Bruker AXS, D8 Discover) were applied for characterization of the modified surfaces, as well as the corrosion products after exposure to conditions that mimicked biomass firing.

SEM and EDS were carried out on sample cross sections according to similar procedures and conditions of metallographic (mechanical) sample preparation contained in reference [336] (Chapter 6.1). For the SiOₓ coating on TP 347H FG, the cross section was prepared by focused ion beam milling to avoid mechanical destruction of the thin, brittle films. XRD analysis on the nitrided layer was carried out from
the surface in grazing incidence mode according to the description in (Chapter 6.1) [336], but with an incidence angle of 8°.

3. Results and discussions

3.1 Nitrided FeCrAl alloy

3.1.1 Nitride layer

The backscattered electron (BSE) image in Figure 1 shows the microstructure of the FeCrAl alloy after nitriding at 430 °C for 20 h. A nitride layer of thickness 21 ± 3 μm formed at the surface, as a result of nitrogen diffusion from the gas into the alloy [337,338]. Applying XRD (results not shown here), CrN, Fe₂N and Fe₄N could be identified, in addition to the ferrite matrix and expanded austenite. Nitrogen stabilizes the austenite phase, hence, its dissolution in the nitride layer may be responsible for the presence of a nitrogen expanded austenite [337]. Figure 1 also reveals the presence of cracks in the nitrided layer and highlights its brittle nature. The cracks may have resulted from sample preparation, or due to compositional induced stresses as is usually observed with high nitriding potentials [337]. Either way, the brittle nature of the nitride layer will pose strong challenge to its use in real power plants because the resulting cracks can allow ingress of corrosive species that will attack the underlying bulk.

![Figure 1](image-url). Microstructure of the low temperature nitrided FeCrAl alloy (BSE image), after etching with glyceregia. A nitride case is evident on the surface of the alloy.
3.1.2 Corrosion of nitrided FeCrAl alloy

To allow proper evaluation of the influence of the nitriding process, on the corrosion of the FeCrAl, the corrosion of a non-nitrided sample is first presented.

Figure 2 shows that after the corrosion exposure of a non-nitrided FeCrAl alloy, two regions of corrosion products separated by a crack results. It is likely that the crack resulted after the corrosion exposure. The corrosion product in region 1 is voluminous and as shown by the EDS maps in Figure 3, they are rich in Fe, S, K and O. Except for Fe, the composition of corrosion products in region 1 results from the reaction of deposits (KCl) with SO$_2$ in the applied gas mixture during corrosion, to form K$_2$SO$_4$ [246,327]. The dark Cl-rich regions in Figure 3 are not associated with the corrosion products, rather such regions correspond to the epoxy resin in which samples were embedded, to enable characterization.

![Figure 2: Overview of corrosion products after corrosion testing of a non-nitrided FeCrAl alloy. Note that deposit particles that should be located above region 1, have been lost during sample preparation.](image)

Corrosion products in region 2 are separated into two layers which are located above (layer 1) and below (layer 2) the presumed original surface of the alloy (Figure 4). EDS maps in Figure 4 show that corrosion products in layer 1 are enriched in Al, Fe, Cr, with a K-S rich band in the outermost part. Cracks are also evident within layer 2 in region 2 of the corrosion product which is rich in Al, Fe and Cr. However, it appears that Fe is mostly enriched in the outer part of this layer due to the detachment of region 1 from region 2 (Figure 2). From Figure 4, local accumulations of Cl (possibly with Fe) are evident at the corrosion front.
Figure 3. Elemental composition of region 1 of corrosion products on a non-nitrided FeCrAl after corrosion testing.
The microstructure and composition of the corrosion products on the non-nitrided FeCrAl alloy (Figures 2-4) highlights a KCl facilitated corrosion mechanism, which has been reported for a similar FeCrAl alloy (Kanthal APM) [336] (chapter 6.1). The composition of region 1 of the corrosion products suggests that that sulphation of KCl occurred during the corrosion exposure and may have released HCl close to the surface of the alloy [208,246,327]. Literature suggests that Fe-rich oxides facilitates the sulphation reaction [330], and consequently herein, lead to establishment of sufficient chlorine partial pressures that chlorinated alloying elements in the FeCrAl alloy. Corrosion hence occurs through a sequence that involves oxidation of the generated metal chlorides to release chlorine that can continue chlorination if transported back to the corrosion front. The presence of Cl (possibly Fe-chloride) at the corrosion front in Figure 5, strongly infers that corrosion occurred by this well documented chlorine cycle [91,104,131,156,200]. It is also evident from the porous morphology of the corrosion products that they have resulted from conversion of the volatile metal chlorides, to the respective oxides. In particular, the

Figure 4. Microstructure and elemental composition of region 2 of the resulting corrosion products on a non-nitrided FeCrAl alloy after corrosion testing.
high vapour pressure of Fe-chloride [76,156] is responsible for its identification in region 1 of the corrosion product as Fe-oxides (Figure 2 and 3).

Figure 5 shows the microstructure and composition of corrosion products resulting from corrosion exposure of the nitrided FeCrAl alloy. Two characteristic regions separated by the presumed alloy surface, are evident on the sample (region 1 and region 2). Region 1 comprises of a porous Fe-rich oxide above which K-S-O rich features are observed. In region 2, which appears to correspond to the initial nitrided layer, Fe, Cr, Al, O and N are present. There are also indications of local accumulations of S and Cl in region 2.

![Figure 5](image.png)

**Figure 5.** Microstructure an elemental composition of the corrosion products resulting after corrosion exposure of the nitrided FeCrAl. Note that deposit particles located above region 1 were lost during sample preparation.
Comparison of Figures 5 and 4 reveals that the nitrided surface significantly reduced the degree of corrosion attack. As only Fe was observed above the original surface of the nitrided sample (Figure 5), it is possible that nitrides of Cr and Al were more stable than their chlorides under the investigated conditions. Compared to Fe, both Cr and Al have higher chemical affinity for N [339], which may have resulted in selective attack of Fe and its redeposition as a porous oxide above the alloy surface. Although thermodynamic calculations in literature [76,156] suggest a high driving force for the reaction of both Cr and Al with chlorine, observations in the present study suggest that these elements may be stable to chlorine attack when bound to nitrogen. However, additional studies are necessary to validate this suggestion. Moreover, the association of O in the region of the nitrided case, although ambiguous, gives an inkling that Al and Cr may exist as oxides in the nitrided layer. Inward transport of oxygen may have been promoted by the porous morphology generated by attack of Fe by Cl.

### 3.2 SiO\textsubscript{x} coating on TP 347H FG

#### 3.2.1 SiO\textsubscript{x} coating

The micrographs in Figure 6 show the cross-section of alloy TP 347H FG coated with a SiO\textsubscript{x}-like thin film. It has been reported that upon curing of the HSQ-precursor at 600 °C in oxygen deprived atmosphere, dense and pore-free thin films [340,341], with a stoichiometry close to SiO\textsubscript{2} forms [342,343].

![figure 6](image)

**Figure 6.** Secondary electron images showing the cross section of a SiO\textsubscript{x} coated TP 347H FG sample after FIB milling. The overview in (a) shows the variable thickness of the coating on the alloy surface. Pt was deposited to protect the coating during FIB milling.

From Figure 6a, b, the thin film coating labelled ‘2’ is observed to have a non-uniform thickness over the surface. For example a thinner coating thickness can be observed on hills, compared with valleys.
The film appears adherent and no micro-crack formation is observed from the micrographs. Coating defects due to inhomogeneous coverage can however be observed (Figure 6a, centre) and are believed to originate from the rough machined surface of the alloy prior to coating.

### 3.2.2 Corrosion of SiO$_x$ coated TP 347H FG

To evaluate the corrosion protection due to the coating, the corrosion of the uncoated substrate is first presented (Figure 7). These results were the subject of previous investigations (see chapter 4.1)\cite{208,275} but are briefly mentioned here to allow comparison. Figure 7 shows that corrosion of the uncoated alloy results in three layers of corrosion products. Alloying elements such as Fe, Cr and Mn are preferentially attacked leading to the establishment of a porous Ni-rich layer (layer 3) above the corrosion front\cite{208}.

![Figure 7](image)

**Figure 7.** Typical microstructure of the corrosion products on an uncoated TP 347H FG after corrosion exposure.

Compared to Figure 7, the SiO$_x$ coating on the alloy reduced the degree of corrosion attack (see Figures 8 and 9). In fact, on some positions (< 20 %) of the sample (Figure 8), there was no significant oxide formation on the alloy surface and only the formation of K-S-O rich features above the Si-O rich coating can be identified by EDS mapping. The K-S-O rich features above the sample surface are possibly K$_2$SO$_4$, which, as was mentioned in section 3.1.2, results from sulphation of deposits (KCl) during the corrosion exposure\cite{208,246,327}.
The protective effect of Si against KCl induced corrosion is still not fully established in the literature. While studies with Fe-Cr model alloys have suggested that formation of a silica layer provides a barrier to limit diffusion of corrosive species [8,9], a laboratory study on the reactivity between oxides and KCl have revealed that SiO$_2$ may react with KCl under oxidizing conditions [290]. Thermodynamically, the reaction between KCl and SiO$_2$ exhibits a positive Gibbs energy [290], hence, the driving force for such a reaction is low. The observation of non-attacked regions on the coated alloy (Figures 10a and 11) suggests that the Si-based coating exhibits significant resistance to corrosion, probably due to its ability to function as a barrier against diffusion of corrosive species [152,170], or due to the low driving force for its reaction with the deposit as was calculated for SiO$_2$ [290].

Figure 9 shows that corrosion attack occurred on some positions of the coated sample, resulting in formation of Fe and Cr rich oxides above the coating. The composition of the corrosion products is similar to that observed for the uncoated alloy (see chapter 4.1) [208] such that an outer Mn-Fe-K-S-O rich layer, a middle layer of Fe-Cr rich oxide and an inner porous Ni-rich layer forms. The non-uniform coating of the substrate (Figure 6a) may have provided local initiation of the corrosion attack.
The observation of a Si rich layer from the EDS maps questions the claimed potential of Si-rich layers to offer a diffusion barrier against the corrosive species. However, it has to be noted that compared to Mn, Fe and Cr, the chloride of Si has the tendency of being converted to the oxide at relatively lower oxygen partial pressures [156]. This consideration implies that even if Si in the alloy is attacked according to the chlorine cycle [91,104,131,156,200], a Si rich layer is expected to be formed close to the corrosion front. Detailed microstructural and chemical analysis are indeed required to understand if the Si-rich layer resulted from the corrosion process, or if it is a non-protective variant of the original coating.

Figure 9. BSE image and EDS maps of the corrosion products on attacked positions of the SiO$_x$ coated TP 347H FG.

In addition to the non-uniform coating of the substrate, corrosion attack may have been facilitated by mechanical failures in the coating. The micrographs in Figure 8 show that the coating was either cracked or delaminated from the substrate after the corrosion test. While these failures may have been induced by metallographic sample preparation of the exposed samples, they may have serious implications during real applications where mechanical failure may be induced by impaction of deposit particles as well as thermal cycling.
3.3 Ni and Ni-Al coating on Esshete 1250

3.3.1 Coated samples

Figure 10 shows the Ni and Ni-Al coatings realized by electroplating and aluminizing, respectively. The Ni layer obtained by electroplating was of thickness 57 ± 3 μm (Figure 10a) and upon subsequent aluminizing the resulting Ni-Al layer was 58 ± 2 μm thick (Figure 10b). Both coatings were uniformly distributed on the substrate (Esshete 1250), however, some porosities were observed at the Ni-Al/Ni interface (Figure 10b).

![Figure 10](image)

**Figure 10.** BSE images showing the (a), Ni and (b), Ni-Al coatings on Esshete 1250 obtained by electroplating and aluminizing, respectively.

3.3.2 Corrosion of Ni coated Esshete 1250

The micrograph and EDS maps in Figure 11 clearly show that Ni is attacked under the investigated corrosion condition. The corrosion attack resulted in the formation of a porous Ni-rich oxide and Cl species at the oxide/coating interface in addition to Cr-Mn-S rich precipitates close to the Ni/alloy interface. This suggests that in addition to chlorination, sulphidation attack occurred (Figure 13). It is suspected that sulphidation attack is promoted by transport of sulphur through mechanical failures in the Ni coating.
3.3.2 Corrosion of Ni-Al coated Esshete 1250

Figure 12 shows the microstructure and elemental composition of the Ni-Al coated Esshete 1250 after corrosion exposure. Localized corrosion attack which occurred on < 40% of the coated sample, is visible from the micrograph in Figure 12. The corrosion product resulting from such attacks consists of K, S, Cl, Al and O. Depletion of Al is evident in the regions where the coating was locally attacked and this accounts for the Al-rich corrosion products observed above the coating surface. The corresponding identification of K and Cl in the corrosion products suggests that reaction between deposit particles (KCl) and presumably, alumina formed above the coating, occurred locally during the corrosion test. In addition, S identification highlights that deposits may have sulphated above the coating surface, releasing Cl-species that preferentially reacted with Al in the coating. Compared to Al, Ni exhibits resistance to the corrosion attack due to the relatively low driving force for its reaction with chlorine [76]. The results from this exposure are the same with that from an similar exposure, in which 13 vol % H₂O was present in the gas mixture [335].
Figure 12. The microstructure and elemental distribution of the Ni-Al coated Esshete 1250 after corrosion testing.

4. Conclusions

Possibilities of surface modification for protection of superheater corrosion during biomass firing have been investigated with the example of low temperature nitriding of a FeCrAl alloy, SiO\textsubscript{x} coating of an austenitic stainless steel TP 347H FG as well as Ni and Ni-Al coatings on the austenitic stainless steel Esshete 1250. The following conclusions can be drawn from the results.

1. The nitride case on a FeCrAl alloy significantly reduces the degree of corrosion attack relative to the non nitrided alloy. In non nitrided FeCrAl alloy, Fe, Cr and Al are all attacked resulting in non-protective voluminous corrosion products. On the contrary, only Fe is attacked in the nitrided FeCrAl alloy causing the formation of a porous Fe-rich oxide above the alloy surface.

3. SiO\textsubscript{x} coating on TP 347H FG also reduces the degree of corrosion attack relative to the uncoated sample. While localized regions with insignificant corrosion attack are observed, other regions of the coated sample show corrosion products similar to the uncoated alloy such that Mn, Fe and Cr are attacked leaving behind a porous Ni rich layer.
4. Ni coatings suffer corrosion attack by sulphidation and chlorination while Ni-Al coatings sustain local and selective corrosion attack, which results in Al depletion from the coating.

The results indicate the potential of the various surface layers to protect the bulk materials from severe corrosion attack under biomass firing. However, the present study applied those coatings according to well-established surface treatment routines, and did not optimize the coating processes. If such optimization also implies less mechanical failure in terms of crack formation and local delamination of the coating, as observed for the present samples, even more promising results are expected and should be part of future investigations.

5. Acknowledgements

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6. References

All references cited in this manuscript are collated in the final reference list for the thesis.
6.5 – The influence of grain size and manganese as an alloying element on the corrosion of austenitic stainless steels under biomass firing conditions\textsuperscript{xii}

\textsuperscript{xii} Manuscript in preparation
1. Introduction

The mechanism of corrosion attack under biomass firing conditions is attributed to a Cl-propagated process in which alloying elements are chlorinated and their conversion to oxides partly regenerates chlorine that sustains the corrosion attack [91,104,186,200]. Often, this corrosion attack is observed to progress along alloy grain boundaries [94,104,117,121,155].

The grain size of austenitic stainless steels is known to have a strong influence on their oxidation. Alloys with small grain sizes promote formation of protective Cr$_2$O$_3$ (see for example [281]), which is advantageous for steamside oxidation. However, with respect to the fireside corrosion of austenitic stainless steels during biomass firing, information on the effect of grain size is lacking. As diffusion of both corrosive species (chlorine) and alloying elements of the material is favoured along grain boundaries of the alloy, grain size is expected to have an influence also on fireside corrosion.

This study reports on the corrosion performance of a commercial austenitic stainless steel (TP 347H) in its fine grained and coarse grained versions. In addition to the effect of grain size for steel of the same chemical composition, also the effect of chemical changes on the example of the concentration of Mn in steels was investigated. To this end, two fine grained austenitic stainless steels: TP347H with low alloying content of Mn, and Esshete 1250 with high Mn content, has been exposed to corrosion conditions relevant for biomass firing. All three steels are currently used as superheaters in biomass fired power plants.

2. Materials and methods

2.1 Sample preparation and corrosion exposures

Commercial austenitic stainless steels TP 347H (with different grain size) and Esshete 1250 with chemical composition as shown in Table 1 have been investigated.

Arc shaped samples with widths of about 0.1 cm were cut from tubes of the respective alloys. These were cleaned in ethanol and acetone before coating with a synthetic KCl deposit for corrosion exposures as described in chapter 3[208].

High temperature corrosion exposure of the KCl coated samples were carried out in a dedicated corrosion test rig, which is described in detail in [208]. Exposures were conducted isothermally for 168 h at 560 °C under conditions that mimicked biomass (straw) firing. This involved a gas mixture of 60 ppmv SO$_2$, 400 ppmv HCl, 12 vol% CO$_2$, 6 vol% O$_2$ on a dry basis, and 3 vol% H$_2$O. N$_2$ was used as a carrier gas [111].
Table 1. Chemical composition of the investigated steels

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Composition (wt)</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Cr</td>
</tr>
<tr>
<td>TP 347H</td>
<td>Bal.</td>
<td>17.0-20.0</td>
</tr>
<tr>
<td>Esshete 1250</td>
<td>Bal.</td>
<td>14.0-16.0</td>
</tr>
</tbody>
</table>

2.2 Characterization of samples and corrosion products

Cross sections of both as-received samples as well as corrosion exposed samples have been prepared, whereby samples after corrosion exposures have been treated with special care to preserve the corrosion products. These samples were cold mounted in epoxy under vacuum according to the details given in [208] (chapter 3), and metallographic preparation down to 1 μm diamond suspension polishing (as also used for the as-received samples) was carried out under water free conditions using absolute ethanol (99.9%) as lubricant. For investigating the corrosion products on the surface, the cross sections were not etched, but the microstructure of the bulk alloys was revealed by etching with glyceregia.

Microscopic investigations occurred by means of light optical microscopy (OLYMPUS GX 41) and scanning electron microscopy (SEM, FEI-Inspect S) in addition to elemental analysis by energy dispersive spectroscopy (EDS, Oxford instruments). SEM characterization was conducted using a backscattered electron detector. Both SEM and EDS characterization employed an acceleration voltage of 15 keV.

3. Results and discussions

3.1 Bulk microstructure of alloys

The optical micrographs in Figure 1 show the bulk microstructure of the different alloys: the coarse grained TP 347H CG (Figure 1a), the fine grained TP 347H FG (Figure 1b) and Esshete 1250 (Figure 1c).
Figure 1. Light optical micrographs showing the bulk microstructure of the investigated alloys. (a) TP 347H CG, (b) TP 347H FG and (c) Esshete 1250.

3.2 Influence of grain size on corrosion

The comparison of corrosion performance of the coarse and fine grained versions of TP 347H gives an indication of the influence of alloy microstructure on the high temperature corrosion of this stainless steel under biomass firing conditions. The micrographs and EDS maps in Figures 2 and 3 show the microstructure and elemental distribution in the corrosion products after the exposure of coarse and fine grained variants of TP 347H, respectively. Regions were corrosion attack progressed through the alloy grain boundaries are indicated by arrows in the micrographs and no clear effect of the grain size appears to be evident.
Figure 2. Microstructure and composition of the corrosion products after exposure of TP 347H CG to conditions mimicking biomass firing. Note that in the Cl map, intensities above layer 1, and within layers 1 and 2, are likely from the embedding matrix.
Figure 3. Microstructure and composition of the corrosion products after exposure of TP 347H FG to conditions mimicking biomass firing. The Mn map is to be interpreted with care as the X-ray energies of Fe, Cr and Mn are close and may result in overlap. Note that the Si-rich particles above layer 1 are artefacts resulting from sample preparation. Intensities in the Cl maps are mostly from the embedding matrix.
In both alloys (Figures 2 and 3), three layers of corrosion products can be identified with the topmost layer (layer 1) consisting of a mixture of $K_2SO_4$ and Fe-, Mn-oxide. The innermost layer of corrosion products (layer 3) is a porous Ni-rich layer arising from selective attack of Fe, Cr and Mn from the alloy. Accordingly, the middle layer of corrosion product (layer 2) is an oxide of Fe, Cr and Mn. These three layers were present on both alloys, although with local variations which was also common for both alloys.

The distribution of these alloying elements in the corrosion products can be explained by the thermodynamics of chlorination and conversion of metal chlorides to their oxides, according to a Cl-catalyzed corrosion mechanism (the so-called active oxidation) [91, 111, 131, 134, 138]. The relatively higher driving force for chlorination of Fe, Cr and Mn relative to Ni results in selective removal of these alloying elements leaving behind a porous Ni-rich layer. The high vapour pressure of these metal chlorides (Fe, Mn and Cr, compared to Ni) facilitates their evaporation and subsequent conversion to oxides when they encounter regions with sufficient oxygen partial pressures. In this regard, Fe and Mn chlorides require relatively higher oxygen partial pressures than Cr chlorides, to be converted to their corresponding oxides. Thus, Cr is observed from Figures 2 and 3 to be enriched in the lower regions of the oxide layer. For detailed discussion it is referred to reference [208] (chapter 4.1).

The fast diffusion paths provided by grain boundaries should facilitate inward transport of corrosive species (chlorine) to propagate corrosion attack, and in particular intergranular attack, which should be more severe in Figure 3 due to the fine grain structure of the steel. From a general comparison of Figures 2 and 3, it appears that the fine grained microstructure, and thus, the higher fraction of grain boundaries, does not promote more corrosion attack under biomass firing conditions within the investigated time frame.

### 3.3 Mn as an alloying element

As mentioned above, alloying elements such as Fe, Cr and Mn exhibit lower resistance to chlorination attack compared to Ni. This corresponds to the results of the present study based on the comparison of the corrosion performance of the high Mn containing Esshete 1250 (Figure 4) with that of the low Mn-containing TP 347H alloys (Figures 2 and 3). It is observed that the extents of corrosion attack, as well as the elemental distribution in the corrosion product are in general terms, similar. Although with local variations, the three layers of corrosion products on TP 347H samples could be identified on Esshete 1250.
Figure 4. Microstructure and composition of the corrosion products after exposure of Esshete 1250 to conditions mimicking biomass firing. Note that Cl signals from the epoxy resin are responsible for the observed intensities in the Cl map.
However, it is evident that the selective attack of Mn in Esshete 1250 clearly leads to the formation of a Mn rich layer in the topmost region (layer 1) of the corrosion products (Figure 4). Compared to Fe and Cr, a relatively higher partial pressure of oxygen is required for conversion of Mn chlorides to their oxides [156], as a result, Mn is enriched in the outermost part of layer 1 of the corrosion products (Figure 4). These observations suggest that within the investigated time frame, Mn does not render considerable protection towards corrosion attack on austenitic stainless steels under biomass firing conditions.

4. Conclusions

The performance of three austenitic stainless steels under conditions mimicking biomass firing has been evaluated to understand the influence of alloy grain size as well as Mn as an alloying element.

1. The corrosion of both fine grained and coarse grained austenitic stainless steel (TP 347H) is similar, both in terms of the morphology and elemental composition of the different layers of corrosion products.

2. Fe, Cr and Mn are attacked in austenitic stainless steels resulting in a porous Ni-rich layer close to the corrosion front. The alloy grain size exercises no additional influence on the corrosion attack within the investigated time frame. Longer corrosion exposures may be required to clarify this observation.

3. In the time frame of 168 h, Mn does not impose protection against corrosion of austenitic stainless steels under biomass firing conditions.

4. The selective removal of Mn becomes more evident in alloys with high Mn content. For Esshete 1250 with 6.3 wt% Mn, a distinct Mn rich layer forms in the outermost layer of corrosion products due to the high partial pressure of oxygen required for conversion of the chlorinated Mn.

Acknowledgements

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References

All references cited in this manuscript are collated in the final reference list for the thesis.
Chapter 7 – General discussions

This chapter presents a general discussion of the results obtained in this project with the major objective to put them in a broader perspective by relating results presented in the preceding chapters to each other and to data in the literature.

7.1 Methodologies for characterization of corrosion products

The characterization of the complex corrosion products under conditions relevant to biomass firing is rather challenging. The use of advanced characterization techniques is most straightforward for corrosion products from simplified conditions (for example [125]). However, the results in chapter 4 presented appropriate methodologies (i.e. Method I and Method II, as described in chapter 3.2.3) which have been demonstrated to be applicable for thorough characterization of the complex corrosion products formed under biomass firing conditions, both in the laboratory and full scale. While Method I is based on two-dimensional characterization on sample cross sections, Method II is based on plan view characterization coupled with successive mechanical removal of corrosion product layers. In particular the combination of both methods for one and the same sample considerably enhances the information content, as it overcomes limits of the usually applied single methods.

As shown in chapters 4.1, 5.1, 5.2, 5.3, 6.1 and 6.3, Method II which involved plan view characterization with SEM, EDS and AD XRD, is very informative with respect to revealing local features on different layers of corrosion products. The successive mechanical removal of layers using Method II is strongly required for comprehensive characterization of the different layers of the rather thick corrosion product.

Considering the characterization of deposits after corrosion exposures: the conventional analysis of cross section as applied in literature [112] only allows two-dimensional characterization. Information on the morphology of the deposits as well as analysis of its interface with both the gas and corrosion products cannot be easily obtained. Moreover, samples are first embedded in Cl-containing resins which complicate analysis of deposits when they also contain Cl. On the other hand, using Method II, deposits can be simply lifted up after corrosion exposure and comprehensively characterized based on morphology, elemental composition and phase analysis at its interfaces with both the gas and corrosion products.

Unlike Method I, deposit analysis with Method II does not require mechanical surface preparation, and thus, it also has the advantage of revealing the exact morphology of possible reaction products between deposits and corrosion products. With this Method, the earlier suggestion in literature that the sulphation of KCl (reaction 7.1) also involves a melt of KCl [111,112] was confirmed in the present work. As shown in chapter 4.1, partly molten KCl was observed within the K₂SO₄-FeₓOᵧ layer and suggests that the metal chlorides (which were converted to the observed oxides), were responsible for lowering the solidus temperature of the deposit (772 °C [186]) during corrosion exposure.
In the literature, the identification of Cl at the corrosion front helps in clarifying the corrosion mechanism (see for example, [107,199,315]). However, results from this work show that such important features are locally observed (as an example, see Figure 12 in chapter 6.1) and may be absent along a given sample cross section. This therefore suggests that generalization of results from advanced characterization techniques involving relatively small sample sizes (such as in TEM, requiring samples of about 100 nm thickness), have to be done with significant caution.

On the basis of the foregoing considerations, Method II is suggested as an appropriate methodology which can complement Method I, for proper understanding of corrosion mechanisms, even under complex conditions. However, it is essential to note that the mechanical removal of corrosion products makes this method destructive in nature. Also, detailed analysis using this method will be time consuming particularly when very thick corrosion products (such as on plant exposed superheaters) need to be characterized. Another important point to note is that because biomass induced corrosion products are typically heterogeneous and brittle, real depth-resolved analysis using Method II will be challenging owing to difficulty in precise control over the exact amount of corrosion product removed during each step.

When the emphasis is not on detailed understanding of corrosion mechanism, such as ranking the performance of materials performance under a specific corrosive condition, the microstructural and elemental information obtained from SEM and EDS on sample cross sections using Method I is appropriate. In chapter 6.4, it was possible to use Method I to assess the corrosion performance of modified surfaces. Interestingly, this work (chapter 4.2) also demonstrates that depth resolved phase identification can be conducted on sample cross sections by the use of ED XRD in transmission mode. Thus, similar to Method II, Method I can also provide information on microstructure, elemental composition and phase analysis.

Although phase analysis can be carried out using both Methods I and II, proper relation of diffraction results to variations in elemental composition will be difficult with Method II. During successive removal of corrosion products and XRD measurements, slight misalignment of sample height with respect to the X-ray beam is practically inevitable with Method II. As this will cause additional shift in peak positions of a given phase (particularly in grazing incidence geometry), the potential for misinterpretation of diffraction results exists in Method II. However, because ED XRD in Method I involves precise translation of the sample across a gauge volume fixed in space, proper relation of diffraction results to elemental composition of corrosion products is possible. As was demonstrated in chapter 4.2, the variation in energy position of the spinel phase (M$_2$O$_4$, M = Fe, Cr) identified on a plant exposed TP 347H superheater, correspondingly varied with elemental composition across the corrosion product. In chapter 4.2, these variations are interpreted to correspond to the transition between normal and inverse spinel structures across the corrosion product, which would not have been possible to quantify using Method I. On the basis of the example in chapter 4.2, this work shows that the capability of ED XRD for
non-destructive depth resolved stress and texture analysis [182,209,344], can also be extended to depth profiling of corrosion products.

While Method II is recommended for comprehensive characterization of corrosion products from laboratory scale exposures, it is important to note that it is a time consuming procedure. Hence, Method I including ED XRD will be suitable for characterization of corrosion products from plant exposed samples due to the relatively higher thickness of such corrosion products. However, this use of this method will be limited to availability of synchrotron beamtime.

7.2 Effect of gas chemistry on corrosion

In accordance with the literature [38,79,80] (chapter 2.1.3), the results presented in chapters 5.1–5.3 show that corrosion attack is generally accelerated in the presence of a deposit. The gas chemistry did not influence this general trend because the corrosion attack on deposit coated samples was always greater than that on deposit-free samples exposed to similar atmospheres. Hence, it can be concluded that more corrosion attack will occur once KCl deposits on the superheater surface.

Specifically, for the deposit-free samples, it is observed that corrosion under oxidizing conditions results in a discontinuous double layered oxide (Figure 7.1a) which changed to a uniform double oxide layer with grain boundary attack when HCl is added to such gas mixture (Figure 7.1b). Interestingly, for the exposures involving SO$_2$ in the gas mixture, the formation of double layered oxide was significantly reduced (Figure 7.1c, d). This positive effect of SO$_2$ is in agreement with data in literature which attributes this to strong adsorption of sulphates [241], or the ability of S to promote formation of Cr$_2$O$_3$ due to its strong affinity for Cr [255].

![Figure 7.1](image_url)

**Figure 7.1.** Schematic illustration of the corrosion products observed after exposure of deposit-free TP 347H FG samples at 560 °C for 72 h under different gas atmospheres: (a) oxidizing (b) oxidizing-
chlorinating (c) oxidizing-sulphidizing and (d) oxidizing-chlorinating-sulphidizing (i.e. straw-firing) gas mixtures. The volume of H₂O in all gas mixtures was 13.4 vol%.

The corrosion products on deposit-coated samples after corrosion exposure under different gas atmospheres are schematically summarized in Figure 7.2. It is observed that the gas chemistry during corrosion exposure influenced the interaction of deposits with gas species, as well as the nature of corrosion attack on the investigated material (austenitic stainless steel, TP 347H FG).

Based on the microstructure and elemental composition of corrosion products (chapters 5.1–5.3), it is obvious that chlorine always influenced the corrosion attack. The particular influence of the gas chemistry was based on its ability to modify the microclimate at the deposit/sample interface and the chlorine partial pressure during corrosion.

The corrosion attack on deposit coated samples exposed under oxidizing (Figure 7.2a) and oxidizing-chlorinating (Figure 7.2b) atmospheres clearly reveals the influence of chlorine partial pressure during corrosion. Although the presence of KCl, in agreement with data in the literature [115,116,149,164], show that corrosion attack is increased under oxidizing atmospheres relative to its absence, the additional presence of HCl in the gas results in higher volatilization of metal chlorides of the alloying elements. Consequently, melting of the deposits was pronounced after exposure conducted under oxidizing-chlorinating atmospheres. Nonetheless, the results in chapter 5.1 show that the average internal attack on deposit-coated samples exposed under oxidizing and oxidizing-chlorinating atmospheres are similar (about 8 μm). These observations suggest that while HCl may not significantly influence the extent of corrosion attack, its ability to enhance melting of deposits can enhance the possibility for subsequent deposition of species on superheater surfaces. As also shown in chapter 5.1, the average internal attack on deposit-coated samples (about 8 μm) surpassed that on deposit-free samples (< 4.2 μm) after exposures under oxidizing and oxidizing-chlorinating atmospheres. Therefore it can be concluded that under these conditions, the effect of KCl on corrosion attack outweighs the effect of gas chemistry.
Figure 7.2. Schematic illustration of the typical microstructure of corrosion products on deposit-coated TP 347H FG samples following exposure at 560 °C for 72 h to (a) oxidizing (b) oxidizing-chlorinating (c) oxidizing-sulphidizing and (d, e) oxidizing-chlorinating-sulphidizing gas mixtures. Gas mixtures (a-d) contained 13.4 vol% H$_2$O, while (e) contained 3 vol% H$_2$O.

With respect to the effect of H$_2$O, the results obtained in this work demonstrates that the influence of this specie on corrosion extends beyond the current understanding in literature, which is based on evaporation of Cr from oxides [52,53]. By consideration of the Deacon process (reaction 7.1) [132,156] as well as the competition for adsorption sites during sulphation of KCl (reaction 7.2) [196,271,272], it is realized that H$_2$O also possesses the ability of influencing the chlorine partial pressure during corrosion. As schematically illustrated in Figures 7.2d and e, a decrease in thicknesses of the sulphate and oxide layer occurs with high water vapour in the gas mixture. This suggests that water vapour in the gas mixture (within the range investigated in this work), will exert a positive effect on corrosion, as addressed in chapter 5.3.

$$2\text{HCl}(g) + \frac{1}{2}\text{O}_2(g) \rightleftharpoons \text{Cl}_2(g) + \text{H}_2\text{O}(g)$$  \hspace{1cm} (7.1)
$$2\text{KCl}(s) + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{K}_2\text{SO}_4(s) + 2\text{HCl}(g) \quad (7.2)$$

In agreement with data in literature [111,112,127,246], gas mixtures containing \(\text{SO}_2\) always resulted in formation of \(\text{K}_2\text{SO}_4\) due to sulphation of \(\text{KCl}\) (Figures 7.2c, d, e). Under an oxidizing-sulphidizing atmosphere, this sulphate layer is observed to minimize corrosion attack as evidenced by reduction in oxide thickness. This is also in agreement with previous investigations [119,127,131,230] in which \(\text{K}_2\text{SO}_4\) is reported to cause lesser corrosion attack compared to \(\text{KCl}\). However, results from this work also show that the microclimate created by the sulphate layer under this atmosphere can also induce severe pitting attack (Figure 7.2c). Such serious attack may be encountered when thick sulphate layers form due to sulphation of adherent \(\text{KCl}\) on the superheater tube.

### 7.3 Sulphation of KCl and its influence on corrosion

Except for the exposures in which the gas mixture did not contain \(\text{SO}_2\) (chapter 5.1), all samples in this work showed the presence of \(\text{K}_2\text{SO}_4\) resulting from sulphation of \(\text{KCl}\) during the corrosion exposures. As discussed in the previous chapters, HCl is released during sulphation of \(\text{KCl}\) and part of this can dissociate into \(\text{Cl}_2\) according to reaction 7.1, to induce chlorination of alloying elements.

It has been argued in literature that sulphation is necessary to reduce corrosion by \(\text{KCl}\) because \(\text{K}_2\text{SO}_4\) is not able to react with \(\text{Cr}_2\text{O}_3\) layers as does \(\text{KCl}\) [119,127]. However, based on this work, it is evident that HCl released from the sulphation of \(\text{KCl}\) also plays a role in the corrosion process. In this regard, sample surfaces that can promote sulphation of \(\text{KCl}\) are likely to suffer more corrosion attack. According to literature, \(\text{Fe}_2\text{O}_3\) and \(\text{CaO}\) can catalyze the oxidation of \(\text{SO}_2\) to \(\text{SO}_3\) (reaction 7.3) [330–332]. Consequently, the sulphation of \(\text{KCl}\) and the release of HCl will be enhanced on samples with the tendency to form such surface oxides. On the contrary, literature suggests that samples that can form \(\text{SiO}_2\) and \(\text{TiO}_2\) will suppress the sulphation of \(\text{KCl}\) [330,331], hence they will sustain less corrosion attack.

$$2\text{SO}_2(g) + \text{O}_2(g) \rightleftharpoons 2\text{SO}_3(g) \quad (7.3)$$

This is clearly revealed by the results presented in chapters 6.1 and 6.3, from which it is observed that the composition of the preoxidation layer influenced the degree of sulphation. For the Nimonic 80A samples (chapter 6.3), it was observed that in addition to the low driving force for the reaction between \(\text{KCl}\) and \(\text{TiO}_2\) in the preoxidation layer (see discussion in chapter 7.6.1 below), the sulphation of \(\text{KCl}\) was relatively reduced on such samples relative to the non-preoxidized samples. Accordingly, a lesser amount of HCl was released on the preoxidized samples and possibly responsible for the insignificant corrosion attack observed. In contrast, severe corrosion attack was observed on the non-preoxidized sample possibly due to enhanced sulphation of \(\text{KCl}\) on the sample.
It may be argued that the sulphate layer resulting from sulphation of KCl may impede the transportation of corrosive species to the corrosion front, and consequently serve as a barrier layer to curtail progression of corrosion attack. As illustrated in the left edge of Figure 7.2c, this can locally happen under oxidizing-sulphidizing atmospheres due to faster sulphation of KCl. However, under oxidizing-chlorinating-sulphidizing atmospheres, results presented in chapter 5.4 suggest that the sulphate layer does not inhibit corrosion because the thicknesses of the corrosion product layers after exposures up until 672 h, all increased with time. In addition, the results in chapter 5.4 reveal that the previous suggestion of fast sulphation of KCl [127] depends either on the thickness of the deposit layer, or on the amount of applied deposit. For the approximately 1mm thick deposit employed in the present work, the steady increase of the K₂SO₄ containing layer suggests that complete sulphation may take longer than 672 h.

As shown in chapter 5.2 (Figure 7.2c), the sulphate layer may provide a suitable microclimate (reducing conditions) which provokes severe pitting attack. Although the exact mechanism for such attack still needs to be clarified, it is probable that Cl-facilitated hot corrosion is favoured under the reducing atmospheres provided by thick sulphate layers. Based on the results obtained in this work, it is clear that corrosion problems will arise once sulphation of KCl occurs close to the superheater surface. This will of course be influenced by the contact between deposits and the superheater surfaces, which in real plants, may be different from the conditions applied during laboratory exposures in this work.

7.4 The effect of temperature

Ideally, temperature increase promotes diffusivity in the alloy [281], so the formation of oxide layers should be favoured with increase in temperature due to a faster supply of oxide forming elements to the alloy/oxide interface. However, as observed from the results in chapter 5.4, the conditions during biomass firing prevents formation of protective oxides even when the metal temperature is increased from 560 °C to 600 °C. Consequently, an increase in thickness of the corrosion product layers occurred.

As highlighted in chapter 5.4, this may be due to the temperature dependence of the following processes/parameters:

a. the driving force for the reaction of deposits with the oxide layer
b. the reaction of chlorine with alloying elements
c. the partial pressure of the KCl, thus its evaporation
d. the sulphation of KCl to K₂SO₄
e. the vapour pressure of metal chlorides resulting from ‘b’

In chapter 5.4, it was suggested that the increase in corrosion attack with temperature observed may result from a combined effect of temperature on the above listed processes. While temperature increase will lead to more HCl generation form processes ‘a’, ‘b’ and ‘d’, temperature effect process ‘e’ will result in more metal wastage due to their removal in the form of volatile metal chlorides. Furthermore, the temperature promoted diffusivity of alloying elements through grain boundaries implies that the
probability of grain boundary attack will increase with temperature. Compared to isothermal exposure at 560 °C for 168 h in this work, a fivefold increase in the average depth of internal attack results when a similar exposure is conducted at 600 °C (see chapter 5.4).

Based on the considerations in the preceding paragraph, the chlorine generated during corrosion at high temperatures should continue to propagate corrosion attack upon subsequent exposure at lower temperatures. This memory effect has been observed from laboratory corrosion tests with HCl under oxidizing conditions [128]. Thus, it is expected that in real power plants where steam temperatures fluctuate either due to changes in load conditions, or fuel choice, initial operation at high steam temperatures should result in high corrosion attack even if the plant later operates at lower steam temperatures. This was indicated by results presented in chapter 5.4, from corrosion exposures involving thermal cycling between 560 °C and 600 °C. On the basis of average thickness values, it was observed that an appreciable increase in thickness of corrosion product layers results when exposures involved thermal cycling from 600 °C to 560 °C, compared to exposures that involved thermal cycling in the reverse direction (from 560 °C to 600 °C). Further, by comparison of results from these thermal cycling exposures, with results from isothermal exposure at 560 °C, it is reasonable to conclude that a material will corrode more once it has experienced a higher temperature.

7.5 Selectivity of corrosion attack towards alloying elements in commercial alloys

According to literature [76,134,156,157] (chapter 2.2.2.4), the relative stabilities of alloying elements to chlorination attack influences the corrosion performance of a given alloy. Alloying elements such as Ni and Mo are known to exhibit relatively low driving force for chlorination compared to Fe and Cr [56,76,156]. This effect was observed for the commercial steels investigated in this work. From the results in chapters 4, 5 and 6.5, it is observed that for the investigated austenitic stainless steels (TP 347H FG/CG and Esshete 1250), Ni which has the lowest driving force for chlorination was always enriched at the corrosion front because of the selective attack of Fe, Cr and Mn (Figure 7.3a, b). By a similar consideration of the commercial FeCrAl alloys (chapters 6.1 and 6.4), the high driving force for chlorination of Fe, Cr and Al resulted in attack of these elements as shown in Figure 7.3c.
Figure 7.3. Selective attack of alloying elements in commercial alloys investigated in this work. (a and b) Attack of Fe, Cr and Mn and enrichment of Ni at the corrosion front, in austenitic stainless steels. (c) Attack of Fe, Cr and Al in FeCrAl alloys.

However, the dependence of corrosion attack on the driving force for chlorination, observed for commercial steels does not appear to hold for the Nimonic 80A, a Ni-based superalloy. It is expected that for this alloy, only Cr, Al and Ti should be attacked leaving behind a Ni rich layer. On the contrary, but in agreement with an observation in literature [122], Ni was attacked together with Cr, Al and Ti. Nonetheless, a Ni rich layer was established at the corrosion front thereby suggesting a faster attack of other alloying elements. On the basis of this observation, it is possible that kinetics also plays a role regarding the resistance of alloying elements to corrosion attack under biomass firing conditions.

The vapour pressure of metal chlorides, and the oxygen partial pressure required for their conversion to oxides, are factor that can potentially influence selective attack in commercial alloys [345]. This effect is manifested in the corrosion of Esshete 1250 (chapter 6.5) which contains 6.3 wt% Mn. Following favourable chlorination of Mn, the high vapour pressure of the metal chloride results in the presence of Mn in the outermost part of the corrosion product (Figure 7.3b) where the oxygen partial pressure was appropriate for its conversion to the oxide. Considering associated release of chlorine from such process, alloying elements forming metal chlorides with low volatility and low oxygen partial pressures for conversion to their oxides, may not be desirable because they result in release of chlorine close to the corrosion front.

The vapour pressure of metal chlorides is of importance once an element can be chlorinated as it also influences the rate at which the metal chloride is removed from the corrosion front. In this regard, the lower vapour pressure of Ni-chloride as well as its requirement of high oxygen partial pressures for
conversion to oxides, relative to that of Fe [76,134,345], implies that Ni-based alloys will exhibit more stability to chlorination attack under biomass firing conditions, compared to Fe-based alloys.

It is important to note that in real power plants, the thermal gradients from the flue gas to the superheater surface, as well as contact between the deposit and superheater surface, may influence the rate at which metal chlorides of alloying elements are removed from the corrosion front. However, based on the experimental conditions applied in this work, it can be concluded that in the as-received condition of the investigated alloys, alloying elements such as Al, Ti, Cr and Fe will not be able to form protective oxides during operation in biomass fired power plants.

7.6 Surface modification approaches and factors which may affect their use to prevent corrosion

7.6.1 Preoxidation

As commercial alloys are unable to form protective oxides under corrosive conditions, another approach would be to form such oxides before exposure to the corrosive environment, i.e. by preoxidation. Based on the commercial FeCrAl alloy (Kanthal APM) and the Ni-based superalloy (Nimonic 80A) studied in this work (chapters 6.1–6.3), oxides produced by preoxidation are observed to be dependent on the alloy composition and preoxidation conditions. Al-rich oxides are produced from preoxidation of Kanthal APM while for Nimonic 80A, a Cr-Ti-rich oxide results. In Nimonic 80A, the concentration of Al (about 1.3 wt%) is below the reported limit for external formation of an Al-rich oxide (3.2 wt%) [300]. Moreover, according to Figure 2.2, Al$_2$O$_3$ formation at 900 °C requires lower oxygen partial pressure compared to Cr$_2$O$_3$. Consequently, Al was only identified in the internal oxidation zone of Nimonic 80A and hence confirms the fact that the concentration (and diffusivity) of an alloying element as well as the partial pressure of oxygen required to stabilize its oxide, influence external/internal oxidation [34].

Based on the results obtained in this work, it is also observed that the stable polymorph of Al$_2$O$_3$ obtained after 168 h of preoxidation of Kanthal APM, depends on the preoxidation conditions, particularly, the preoxidation temperature. In contrast to data in the literature (see for example [51]), the oxide formed at 900 °C in both O$_2$ and O$_2$ + 10 vol% H$_2$O did not consist solely of α-Al$_2$O$_3$. However, only after preoxidation at 1100 °C in O$_2$, was the formation of α-Al$_2$O$_3$ evident.

In accordance with thermodynamic calculations, the results in chapters 6.1 and 6.2 show that the corrosion performance of an alloy is influenced by the composition of the oxide layer above it. As only the reaction between gaseous KCl and α-Al$_2$O$_3$ exhibits a low driving force (a positive Gibbs energy) at 560 °C, only the oxide layer on Kanthal APM preoxidized at 1100 °C was chemically stable after exposure to biomass firing conditions\textsuperscript{xiii}. On this basis, it is suggested that if preoxidation of Al$_2$O$_3$

\textsuperscript{xiii} This generalized consideration excludes corrosion attack induced by mechanical failures in the oxide layer.
forming alloys is to be utilized as an approach to prevent corrosion of superheater tubes, the preoxidation temperature is a vital parameter to be considered.

The observed stability of the Cr-Ti-containing oxide formed on Nimonic 80A after corrosion exposures to biomass firing conditions (chapter 6.3), is in line with data in literature reporting that TiAlN coatings do not suffer corrosion attack under NaCl deposits at 450 °C [161]. Literature suggests that Cr-rich oxides should be unstable in KCl containing environments (see for example [164]).

\[
(Cr_xFe_{1-x})_2O_3(s) + 4xKCl(s) + 1.5xO_2(g) + 2xH_2O(g)
\]
\[
\rightleftharpoons (1 - x)Fe_2O_3(s) + 2xK_2CrO_4(s) + 4xHCl(g)
\] (7.4)

In contrast to the reaction between KCl and Cr₂O₃, TiO₂ exhibits a low driving force for reaction with KCl. Thus, the intriguing corrosion resistance exhibited by the Cr-Ti-rich oxide layer on Nimonic 80A is suggested to be associated with the presence of Ti in its outer part. Based on the corrosion performance of preoxidized Nimonic 80A samples in this work, it can be concluded that superheater preoxidation leading to formation of unreactive oxide layers, offers an approach to prevent the corrosion of superheaters during biomass firing. However, as a drawback from practical applications, it does imply the need of an additional treatment to form the protective oxides, which cannot form on operation temperature of the superheaters in the plant.

It is also pertinent to note that mechanical stability is a vital challenge that needs to be addressed for preoxidation to be considered as an approach for protecting superheaters against corrosion attack. This is because the corrosion attack suffered by Kanthal APM samples preoxidized at 1100 °C in O₂ was mainly initiated on places were the oxide layer failed mechanically before the corrosion exposure. Although the Cr-Ti-rich oxide formed on Nimonic 80A showed no evidence of mechanical failure, its mechanical integrity needs to be tested under thermal cycling conditions. This is in view of the fact that in real power plants, the oxide is likely to experience thermal variations during service as well as during plant start-up and shutdowns.

7.6.2 Si and Ni-Al based coatings

To explore the positive effect of Si reported in the literature for the corrosion of model Fe-Cr alloys in the presence of alkali chloride deposits [152,170], a SiOₓ coating was investigated in this work. As shown in chapter 6.4, the coating was able to locally withstand corrosion attack. This positive effect of Si-based coatings towards corrosion attack may be due to their ability to act as a diffusion barrier or possibly due to the low driving force for its reaction with KCl. Moreover, literature shows that even in the case of molten chlorides, SiO₂ exhibits low solubility and thus, will not dissolve in such corrosive melts [346].

The localized positive effect of SiOₓ towards corrosion attack may be attributed to the inhomogeneous coating of the sample before corrosion exposure. The results in chapter 6.4 show that rough surfaces may not be optimal for application of these coatings. Moreover, as with the preoxidation approach, a major
factor to be considered for these coatings is mechanical stability because, even for the non-attacked regions of the SiO$_x$ coated samples, delamination and cracking of the coating was observed after the corrosion exposure.

For the NiAl coating (chapter 6.4), the relative stabilities of the different elements towards chlorination as discussed above (chapter 7.5), also influenced the observed local corrosion attack. This is because similar to the selective attack observed on the investigated austenitic stainless steels (TP 347H and Esshete 1250), local selective attack of Al was occurred on the NiAl coating leading to Ni enrichment in the near surface region. In literature [153], this selective attack caused the formation of a protective alumina layer on the NiAl alloy. However, the voluminous nature of such oxides as observed in the present work (Figure 12 in chapter 6.4) suggests that it lacks the capability of offering protection against further corrosion attack where Al$_2$O$_3$ was probably, not initially formed. This disparity is likely due to the difference in exposure conditions: the positive effect reported for NiAl in literature was realized after corrosion exposure of NaCl-KCl coated samples under an inert atmosphere [153]. Under oxidizing-chlorinating-sulphidizing gas atmospheres similar to the conditions applied in the present work, literature reports that voluminous Al$_2$O$_3$ also results from the corrosion of FeAl coating (Figure 7.4) [162]. From comparison of Figure 7.4 and Figure 10 in chapter 6.4, it is evident that the NiAl coating investigated in the present study exhibits a higher resistance to corrosion attack under biomass firing conditions and thus presents a potential surface modification approach to reduce the corrosion of superheaters in biomass fired power plants.

Following the previous considerations in chapter 7.5, Ni coatings are expected to exhibit stability towards corrosion attack propagated by chlorine. However, according to the results in chapter 6.4, resistance to sulphidation may be more important for Ni coatings. It has been suggested in literature that NiSO$_4$ in the outer parts of a preoxidized NiO layer may react with HCl to propagate corrosion attack [130]. Considering the low driving force for chlorination of Ni, it is probable that its severe corrosion as reported in chapter 6.4, may have been facilitated by sulphidation and subsequent reaction with chlorine to form Ni chlorides. As suggested in chapter 6.4, it is suspected that sulphidation attack was propagated through cracks in the Ni coating. It is therefore evident that resistance to both chlorination and sulphidation attacks have to be considered during design of surface modification approaches for superheaters in biomass fired power plants.
It is essential to clarify that while the Cr-Ti-rich oxide on Nimonic 80A did not show any sign of corrosion, the attack on both the SiO$_x$ and NiAl coatings investigated in this project were all locally observed. Besides, comparisons of the magnitude of the corrosion attack on these coatings (chapter 6.4) to that on the corresponding uncoated substrates (chapters 4 and 6.5) reveal that these coatings remarkably resisted corrosion attack. With further optimization, in particular with respect to mechanical integrity, these coatings present opportunities to prevent corrosion of superheaters in biomass fired power plants.
Chapter 8 – Summary

The main objectives of this work were to a) develop methodologies that can enable comprehensive characterization of complex corrosion products formed under biomass firing conditions, b) understand the influence of process parameters on the corrosion process and c) evaluate candidate materials for the use in superheaters in biomass fired power plants.

The obtained results demonstrated the ability of combining the complementary information from LOM, SEM, EDS and XRD via two characterization methods, for the comprehensive characterization of corrosion products from both full and laboratory scale exposures. Specifically, the plan view top down methodology (Method II) is effective in revealing local details relevant for understanding the corrosion mechanisms. Results in this work also show that improved analysis of cross sections of corrosion products is affordable with depth resolved energy-dispersive synchrotron diffraction facilitated by small gauge volumes (Method I). A complementary application of Methods I and II enables comprehensive characterization of complex corrosion products in which information on microstructure, elemental composition in addition to phase analysis can be obtained.

The mechanism of corrosion attack under biomass firing conditions is mainly controlled by a chlorine-catalyzed process involving chlorination, evaporation of metal chlorides, their oxidation and possible re-chlorination at the corrosion front (the so-called chlorine cycle). Results from this work show that the gas phase chemistry has an effect on the corrosion process. Under oxidizing-chlorinating atmospheres, severe evaporation of corrosion products as well as melting of deposits results. Such melts have effects on both corrosion and adhesion of deposits on the superheater. In all SO₂ containing gas mixtures, sulphation of deposits occurs and the microclimate provided by the sulphate layer can provoke localized pitting attack. There are indications from results in this work that both HCl and H₂O in the gas mixture influence the sulphation of deposits and by extension, the degree of corrosion attack. Based on the limited comparison made in this work, it appears that high water vapour content in the flue gas will not make corrosion worse.

Although sulphidation is a possible mechanism for corrosion under biomass firing conditions, the severity of chlorination facilitated attack is higher due to the vapour phase transport of intermediate species (metal chlorides) involved in the corrosion process. As a result, the resulting oxides are porous and do not provide protection against corrosion even after exposures lasting for 672 h. An increase in temperature (from 560 °C to 600 °C) was observed in this work to cause an about fivefold increase of the depth of internal attack of TP 347H due to the influence of temperature on diffusivity, generation of corrosive species during corrosion as well as the vapour pressure of metal chlorides. Both under isothermal and thermal cycling conditions, Fe, Cr and Mn were selectively attacked in the investigated austenitic stainless steel (TP 347H FG) resulting in the presence of a Ni-rich layer at the corrosion front. This was also observed for the identical alloy exposed to a biomass fired power plant, thereby suggesting that the laboratory conditions applied in this work moderately mimicked the conditions in power plants.
For the exposure conditions investigated in this work, alloying elements in the commercial alloys (Kanthal APM, Nimonic 80A, TP 347H and Esshete 1250) were unable to form an oxide that prevented further corrosion attack. However, results in this work also show that there are potentials for surface modification of these alloys, using corrosion resistant oxides (α-Al₂O₃, TiO₂) or coatings (SiO₂, NiAl), to facilitate protection against corrosion during biomass firing. This needs to take into account the mechanical integrity of the surface layers and in-situ healing of damaged layers.
Chapter 9 – Outlook

Although the results and observations of the present work revealed important new insights into high temperature corrosion, they also indicate the need for additional research in order to fully understand high temperature corrosion of superheaters under biomass firing conditions. Some of these imperative studies are outlined as follows:

- The assumption that the innermost layer of deposits on superheaters consists mainly of KCl may not hold for all boiler configurations. Deposition investigations have shown that the deposits in suspension fired boilers are rich in Si, Ca and Al. The oxides of these elements may influence the interaction of gas species with the deposit, and in the event of melt formation, they can also influence the corrosiveness of such melts. Accordingly, dedicated research on the additional influence of these species on the corrosion mechanism is vital.

- The isothermal conditions between the gas, deposit and metal surface employed in the present work may not correlate exactly with the situation in real power plants. Thermal gradients exist between the flue gas and metal temperature and its influence on corrosion under biomass firing conditions needs to be properly understood. Dedicated experiments, however, are difficult due to the often unknown temperature variations.

- The porosity of the deposit layer as well as the contact between the deposit layer and sample surface will influence the transport of gas species to and from the corrosion front. Consequently, systematic studies focusing on these parameters are necessary for improved understanding of corrosion under biomass firing conditions.

- An important observation from this study is the molten morphology exhibited by KCl and K$_2$SO$_4$ rich features after exposures at temperatures below the melting point of these compounds. Metal chlorides (M$_x$Cl$_y$) were suggested to assist in melt formation due to the low solidus temperature of its eutectic with KCl. To obtain detailed information on the possibility of accelerated corrosion due to such melt formation on superheater surfaces, the melting properties of the KCl-K$_2$SO$_4$-M$_x$Cl$_y$ system needs to be properly studied. The implications of such studies should also extend to shedding of deposits since melt formation may increase the adhesion of deposits to superheater surfaces.

- The investigation of corrosion performance of other Al, Si and Ti based coatings are important. Furthermore, such studies should incorporate thermal cycling to evaluate both the chemical and mechanical integrity of the coatings.

- The transport pathway of chlorine during both the initiation and propagation stages of corrosion still needs to be understood. Isotopic labelling exposures will probably be valuable to obtain insights on this.
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