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Nucleation and Growth of Internal Diesel Injector Deposits: The Study of a Reactive Interface

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I declare that this thesis, and the work reported herein, was composed by and originated from me. Information derived from the published and unpublished work of others has been acknowledged in the text and references are given.

Emma Naomi Antonio (2019)

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Abstract

The formation of deposits within diesel injectors leads to reduced engine performance, lower fuel economy and increased emissions. Internal diesel injector deposits, first identified in 2009, differ from other engine deposits as they form from hot fuel on hot engine surfaces. Despite the prevalence of these deposits, a mechanistic understanding of how they form, and specifically the role of iron in deposition, is poorly defined. This work aims to develop a mechanistic understanding of these systems to facilitate the development of fuel formulations which prevent deposition and therefore maintain optimal engine performance for the duration of the lifetime of a vehicle.

A model system was formulated in collaboration with an industrial partner BP, to elucidate key parameters in deposition; hexadecane was used as a model diesel compound due to its chemical and physical properties. Using secondary ion mass spectrometry, the injector steel Fe-13Cr was characterised, over engine relevant temperatures (RT–400°C), to be predominantly iron-based. As the chemical state of the iron within the injector is undefined, three model iron surfaces, with differing chemistries, were used to reveal key factors in the deposition mechanism.

Deposits were simulated by refluxing hexadecane with the model surfaces at 200°C and subsequently characterised using X-ray photoelectron spectroscopy, scanning electron microscopy and secondary ion mass spectrometry. The level of hexadecane oxidation in solution was analysed by electrospray ionisation mass spectrometry. Compared to silicon surfaces, iron surfaces were found to promote oxidation and deposition of hexadecane. The iron surface chemistry was found to affect the amount and morphology of deposition, with the interplay between oxidation and solubility determining deposition levels.

Comparisons between the various surface chemistries of iron demonstrate that i) iron surfaces promote the degradation of hexadecane, ii) regardless of the original surface chemistry, an iron (III) oxide (and/or hydroxide) surface is formed and iii) further fuel degradation can occur with this surface when the system is cooled to room temperature.

A rig and cell were developed to facilitate *in situ* measurements of the transitions occurring at the iron surface. Grazing incidence wide angle X-ray scattering and X-ray absorption fine structure were used to investigate the structural and chemical transitions of iron; these findings further support the formation of an iron oxide hydroxide.

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We shall not cease from exploration, and the end of all our exploring will be to arrive where we started and know the place for the first time.

T.S. Elliot

Publications

- (1) Antonio, E. N.; Wicking, C.; Filip, S; Ryan, M. P.; Heutz, S. The Role of Iron Speciation in the Oxidation and Deposition at the Hexadecane-Iron Interface. **2019**, *Submitted to ACS Applied Materials and Interfaces*.

Impact

The work presented in this thesis contributed to the development of BP Ultimate Diesel with ACTIVE technology. This fuel is marketed as BP's 'best ever anti-dirt fuel' and is reported to reduce CO₂ emissions by up to 4% per journey.

<https://www.bp.com/en/global/corporate/news-and-insights/press-releases/bp-rolls-out-its-best-ever-anti-dirt-ultimate-fuels.html> Accessed on 2019-08-28

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Nomenclature

List of Abbreviations

AES	Auger electron spectroscopy
APS	Advanced Photon Source
BAS	Basic autoxidation scheme
bcc	body centred cubic
CEC	Coordinating European Council
CIF	Crystallographic information file
COD	Crystallography open database
CRC	Coordinating Research Council (USA)
DDSA	Dodecenyl succinic acid
EBSD	Electron backscatter diffraction
EDX	Energy dispersive X-ray spectroscopy
EELS	Electron energy loss spectroscopy
EXAFS	Extended X-ray absorption fine structure
FAME	Fatty acid methyl ester
fcc	face centred cubic
FTIR	Fourier transform infrared
FTS	Fischer Tropsch Synthesis
FWHM	Full width half maximum
GI-WAXS	Grazing incidence wide angle X-ray scattering
hcp	hexagonal close packed

HDSA Hexadecenyl succinic acid
HPCR High pressure common rail
HR-MS High resolution mass spectrometry
ICDD International Centre for Diffraction Data
ICP Inductively coupled plasma
IDID Internal diesel injector deposits
ISCD Inorganic crystal structure database
LCF Linear combination fitting
LEL Lower explosion limit
NMR Nuclear magnetic resonance
PC Principal component
PCA Principal component analysis
PEEK Polyether ether ketone
PIBSI Polyisobutylene succinimides
PTFE Polytetrafluoroethylene
RTFO Renewable Transport Fuel Obligation
SAXS Small angle X-ray scattering
SEM Scanning electron microscopy
SIMS Secondary ion mass spectrometry
SMMT Society of Motor Manufacturers and Traders
SMSS Shape memory stainless steel
TED Transmission electron diffraction
TEM Transmission electron microscopy
ToF Time of flight
ULSD Ultra low sulfur diesel
WAXS Wide angle X-ray scattering
XAFS X-ray absorption fine structure
XANES X-ray absorption near edge spectroscopy
XAS X-ray absorption spectroscopy
XPS X-ray photoelectron spectroscopy

Chapter 1

Introduction

1.1 Overview

Over the duration of this PhD, attitudes towards and policies on diesel fuel have seen a significant acceleration; the sale of diesel cars is set to end in the UK by 2040, whilst in the short term, increased taxes and surcharges have been announced for diesel vehicles.¹ The ‘Volkswagen emissions scandal’, whereby from 2009 – 2015 Volkswagen fitted their cars with devices to reduce emission levels during emissions tests, brought to the public’s attention the car industries’ failure to meet emissions targets under real-world conditions. Alongside these legislative changes and an increased awareness of pollution from diesel vehicles, frequent media coverage of studies on the health and environmental impact of pollution has seen a shift in public attitude,² with the Society of Motor Manufacturers and Traders (SMMT) reporting a decline in the sale of diesel vehicles over recent years.³

Diesel fuel was previously promoted in the UK due to its decreased production of the greenhouse gas carbon dioxide per unit energy compared to petrol fuel, however the generation of nitrogen oxides and particulates are an undesirable feature of diesel engines. Nitrogen oxides include nitrogen dioxide (NO_2) which is a toxic gas, nitrous oxide (N_2O) which is a greenhouse gas and nitric oxide which will react to form nitrogen dioxide. Particulates are known to cause air pollution, leading to respiratory problems.

Over the last decade, efforts to reduce the environmental impact of diesel use and to meet

increasingly stringent emissions targets have led to numerous changes in fuel formulations and engine design. The introduction of ultra-low sulfur diesel (ULSD) aimed to mitigate the environmental and health side effects caused by the production of sulfurous oxides from sulfur-containing fuel. Legislation on the sulfur content of fuel reduced the concentration of sulfur in the fuel from 500 ppm to 50 ppm (since 2005 in the UK) and subsequently 10 ppm (widely available by 2008). In 2007, the Renewable Transport Fuel Obligation (RTFO) was introduced, a measure aimed at improving the sustainability of fuel which required all fuel sold in the UK to contain 5 % renewable fuel, meaning all diesel fuel sold in the UK contained 5 % biodiesel.⁴

The diesel common rail, which is a direct injector system, was first commercialised by the injector manufacturer DENSO in 1995 and aims to improve the performance of engines. The high pressure common rail (HPCR) typically consists of four injectors that inject precise quantities of diesel into the combustion chamber as a fine mist, as part of a sophisticated injection strategy involving several discrete injections per single combustion cycle.^{5,6} A simplified schematic of a common rail system is shown in Figure 1.1. These systems currently operate at high pressures, up to 1800 bar, with pressures anticipated to reach 3000 bar in future. High pressures require small clearances and result in high operating temperatures; channels within the injector are reported to be less than 10 μm while the engine temperature is reported to exceed 150°C. Changes in engine design have potential to significantly improve efficiency and reduce emissions, for example in 2013 DENSO reported a 3 % increase in fuel efficiency, a 50 % reduction in the formation of particulate matter and an 8 % decrease in the formation of nitrogen oxides for their new diesel common rail system.⁷

However at the ‘International Colloquium Fuels’ conference in 2009, a key finding within the research community was the formation of deposits within diesel injectors. These deposits can result in adverse effects for engine performance, fuel economy and emissions.⁸ The direct cause of deposition was unknown, however, recent changes in engine design and fuel formulation were postulated as possible causes for the onset of these deposits. The reduction of sulfur content in the fuel reduces the stability of the fuel to oxidative stress, due to the anti-oxidant properties of sulfur-containing species. The introduction of biodiesel into the fuel also introduces the associated contaminants from fatty acid methyl ester (FAME) production into the engine, whilst

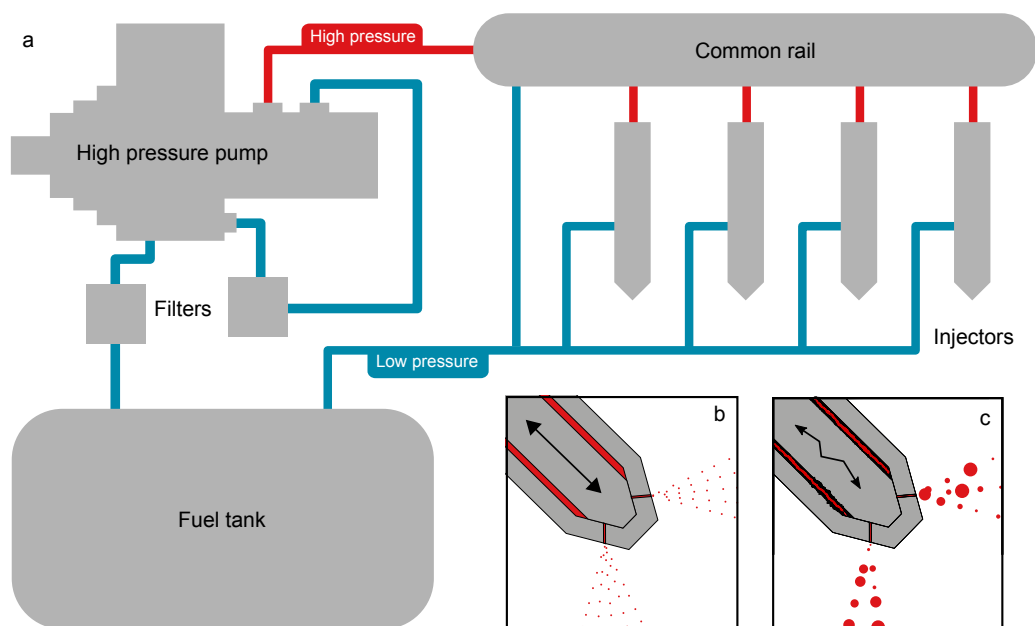


Figure 1.1: a) Simplified schematic of a diesel common rail system showing the pathways of fuel including high and low pressure regions in the engine and the re-circulation of fuel. Electrical connections and sensors are not shown. Enlarged schematic of the injector b) before and c) after deposition, leading to reduced engine performance. Internal diesel injector deposits (IDID) studied in this work are illustrated in c).

changes in injector design have resulted in higher temperatures and pressures creating a more reactive environment as well as smaller tolerances within the injector. The moving parts in injectors are up to an order of magnitude smaller and lighter than earlier models, meaning these new parts do not have the inertia to overcome the effects of deposition, therefore reducing the overall tolerance of the engine to deposits. In addition, the recycling of pressurised fuel back to the fuel tank is also believed to allow further fuel degradation. Deposits forming within the injector have been reported to cause sticking and even blockages within the injectors, disrupt the injector timing patterns, vary the injection volume, slow the injector response and result in irregular and uneven spray into the combustion chamber.⁶

Internal diesel injector deposits (IDID), illustrated in Figure 1.1, differ from nozzle or coking deposits as they form from the fuel onto hot metal surfaces in the absence of combustion gases or evaporation processes. The pressures and temperatures at which these deposits form are undefined. Significant work has been invested into understanding the causes and nature of these deposits. In 2013 the US Coordinating Research Council differentiated IDID into four categories: amide lacquers; inorganic salts; carbonaceous deposits and carboxylate soaps.^{6,9}

Deposits found in fouled European injectors included all these types of deposition, however deposits found in North America were primarily soap-based. Studies in France and Spain found sodium-containing deposits to correlate with the introduction of biodiesel, despite regulations on biodiesel limiting the sodium concentration in the fuel to below 5 mg/kg (EN 14214 standard).¹⁰ Other studies on fouled injectors across Europe and North America did not find any conclusive correlations between their observations and the proposed causes of IDID.¹⁰ Nonetheless, the advent of these deposits is widespread in light and heavy duty vehicles, on and off road vehicles and in marine applications.

Due to widespread use of diesel vehicles, modifying the fuel formulation provides a practical, simple and relatively immediate way to address some of the environmental and health concerns associated with diesel fuel. The fuel formulation also provides a means of maintaining engine performance and emissions standards throughout a vehicle's lifetime, which can be up to 1.6 million kilometres for heavy duty vehicles.¹⁰

1.2 Amide Lacquers and Inorganic Salts

Despite the use of the polymer polyisobutylene succinimides (PIBSI) for several decades as a deposit control additive, the formulation of 'amide lacquer' deposits has been attributed to PIBSI.¹¹ PIBSI is a generic term used to describe any species formed from the reaction of polyisobutylene (PIB) with maleic anhydride and an undefined amine.¹¹ PIBSI therefore covers a wide mixture of species with varying chemical structures and mass distributions. In recent studies low molecular mass PIBSI was found to be responsible for deposition,¹¹ whilst earlier studies showed the reaction between PIBSI and acid to be responsible for deposition.⁸ Inorganic salts including calcium and sodium oxides and sulfides have been observed on injector surfaces.⁶ Amide lacquers and inorganic salts are outside the scope of this work and therefore will not be discussed further.

1.3 Carboxylate Salt Deposits

Carboxylate salts, often referred to as soap or waxy deposits, are believed to be the most prevalent type of IDID in Europe and North America.^{6,10} These deposits form from acidic compounds and trace metal contaminants producing deposits that are white in colour.¹² The onset of carboxylate salts may be a consequence of the reduced solubility of metal ions in ULSD leading to metal precipitation at high temperatures and/or the increase in the sodium concentration as a result of the introduction of biodiesel.⁶ Predominantly sodium metal is found, however potassium, calcium and zinc are also observed. As well as the introduction of sodium from biodiesel production, where sodium hydroxide is used as a catalyst, fuel extraction and refining processes may provide further sources of sodium contamination.⁵ Sodium nitrate is used as a corrosion inhibitor; sodium hydroxide and sodium sulfate are used in the refining process and sodium chloride is used as drying agent in conventional diesel production.⁵ The concentration of metal is believed to be the rate limiting parameter in carboxylic salt formation, due to the prevalence of acidic species in diesel systems.

Potential sources of carboxylic functionality include: carboxylic acids formed as a result of thermal degradation of diesel, lubricity additives with carboxylic functionality and corrosion inhibitors.¹⁰ Two types of alkenyl succinic acid corrosion inhibitors - dodecenyl succinic acid (DDSA) and hexadecenyl succinic acid (HDSA) - were identified in European injector deposits by Fourier transform infrared (FTIR).⁶ Engine tests using sodium and calcium with DDSA or HDSA were found to effectively reproduce carboxylate salt deposits observed in the field, as discussed further in Section 1.6.⁶

1.4 Carbonaceous Deposits

Carbonaceous deposits - widely accepted to form from the thermal degradation of the fuel - are a long standing problem in a range of hydrocarbon stream systems, however a mechanistic understanding of deposition is still incomplete. The formation of carbonaceous deposits is the primary focus of this work and will be discussed in detail in Chapter 4.

Insights gained from the characterisation of deposits in fouled injectors are presented below

alongside protocols and studies which aimed to replication deposit formation.

1.5 Investigations into Fouled Injectors

Fouled injectors have been studied with a range of analysis techniques including microscopy - scanning electron microscopy (SEM) and transmission electron microscopy (TEM) - spectroscopy - energy dispersive X-ray spectroscopy (EDX), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR) - and spectrometry - time of flight secondary ion mass spectrometry (ToF-SIMS).^{12–14} These studies have provided a variety of valuable insights into the properties of carbonaceous deposits. The elemental composition of these deposits was found using EDX to be predominantly carbon and oxygen, although the ratio of these elements was not determined.¹⁰ Using Raman spectroscopy, ordered and disordered regions of carbonaceous material were found.¹³ The chemistry of deposits within a fouled diesel injector was found using ToF-SIMS to vary as a function of depth,¹⁵ with a higher concentration of polycyclic aromatic hydrocarbons (PAHs) at the injector surface.¹² Peaks associated with carboxylic acid salts were identified using FTIR for carboxylate deposits.

These studies focus on characterising the chemistry and morphology of injector deposits and therefore do not provide any insights into the mechanisms of deposition. Several studies made comments on the role of iron based on their observations of deposits. Lacey *et al.* suggested that iron is ‘unlikely’ to play a role in deposit formation due to its burial under micrometer-thick deposits,¹⁰ whilst Dallanerga *et al.* reported that the sharp change in chemical composition at the metal-fuel interface, observed by a ToF-SIMS depth profile, suggested that the surface did not play a role.¹⁴

Studies, both applied and fundamental, relating to the role of iron in oxidation and deposition in other hydrocarbon stream systems are presented in detail in Sections 4.3.6–4.3.8.

1.6 Simulating Deposition

Standards for industrial engine tests have been produced to enable the evaluation of methods for mitigating deposition, such as new fuel formulations or additive packs. A method for assessing

the potential of fuels to form internal injector deposits, the ‘Internal Diesel Injector Deposit Test’ (CEC F-110-16 (S)), was released by the ‘Coordinating European Council (CEC) for the Development of Performance Tests for Fuels, Lubricants and Other Fluids’ in 2017.¹⁶ However there have been reports of limited success in reproducing deposition with this method.¹⁷ In 2010 Schwab *et al.* developed an engine test in which sodium salts and alkenyl succinic acids were added to the fuel; this test is found to successfully reproduce the behaviour and chemical composition of soap deposits.⁵ This test was partially approved by the CEC and is widely used in engine testing.¹⁸ Sodium naphthanate is commonly used as the sodium salt and dodecenyl succinic acid (DDSA) is commonly used as the alkenyl succinic in these tests. Whilst these tests are fundamental to the development of fuel formulations to mitigate deposition, they do not further a mechanistic understanding of deposition.

There are limited studies which aim to reproduce carbonaceous deposits under laboratory conditions. One such study was conducted by Venkatarman and Eser who formed deposits in a flow reactor at 160°C and 31 bar from hexadecane.¹⁹ They found a good correlation between the fouled injectors which they analysed and the deposition they simulated in their complex laboratory set up. Deposits in both systems were found to contain poly-aromatic hydrocarbons with oxygen moieties, demonstrating that their set-up provided a valuable model system for simulating injector deposition.¹⁹

1.7 The Aims of This Work

Understanding the deposition mechanism and subsequently preventing deposition is key in rectifying the adverse effects on engine performance, fuel economy and emissions caused by deposits. This work aims to gain a mechanistic understanding of the deposition of carbonaceous material formed from hot fuel on engine surfaces.

Chapter 2 details the experimental methods used to simulate deposition, including the experimental set-up used for performing *in situ* experiments at synchrotron facilities. The underlying theory behind the characterisation techniques used in this work is discussed in this Chapter, along with the experimental parameters used for these analyses.

In Chapter 3, the surface composition of the engine steel 13 chrome (Fe-13Cr) was characterised by ToF-SIMS and TEM. These analyses identified the surface to be predominantly iron-based at engine relevant temperatures. Three model iron surfaces with varying surface chemistry were developed and characterised to enable subsequent studies into the effect of the surface chemistry on deposition.

The effect of surface chemistry on the formation of carbonaceous deposits is investigated in Chapter 4. Here the relationship between fuel oxidation, deposition and the surface chemistry was studied to determine key parameters in deposition. The effect of solubility on deposition is also investigated here.

Chapter 5 studies the transitions occurring at the iron surface during the formation of carbonaceous deposits. Iron thin films were used here as the substrate due to practical considerations. Grazing incidence wide angle X-ray scattering (GI-WAXS) and X-ray absorption fine structure (XAFS) spectroscopy were used to characterise the structural and chemical changes occurring on iron surfaces *in situ*.

In Chapter 6, a summary of the work is presented. The implications of this work for industry are outlined. Suggestions for future work include advanced analysis of the data presented in this thesis and possible routes forward to further understand and explore this complex system.

References

- (1) Office for Low Emission Vehicles Reducing Emissions From Road Transport: Road to Zero Strategy - GOV.UK., 2018.
- (2) Mudway, I. S. et al. Impact of London’s low emission zone on air quality and children’s respiratory health: a sequential annual cross-sectional study. *The Lancet. Public health* **2019**, *4*, e28–e40.
- (3) Fall in New Car Market Wake Up Call to Policy Makers as Environmental Goals at Risk - SMMT., <https://www.smmt.co.uk/2019/01/fall-in-new-car-market-wake-up-call-to-policy-makers-as-environmental-goals-at-risk/> (accessed 05/26/2019).
- (4) The Department for Transport The Renewable Transport Fuel Obligations Order 2007., <http://www.legislation.gov.uk/uksi/2007/3072/made> (accessed 08/29/2019).
- (5) Schwab, S. D.; Bennett, J. J.; Dell, S. J.; Galante-Fox, J. M.; Kulinowski, A. M.; Miller, K. T. Internal Injector Deposits in High-Pressure Common Rail Diesel Engines. *SAE International Journal of Fuels and Lubricants* **2010**, *3*, 2010–01–2242.
- (6) Deposit Analysis Panel, CRC Diesel Performance Group *Internal Diesel Injector Deposits CRC Project No. DP-04-13a Report No. 665*; tech. rep.; Alphaseta: Coordinating Research Council Inc., 2013, pp 3 –15.
- (7) DENSO Develops a New Diesel Common Rail System With the World’s Highest Injection Pressure — News — DENSO Global Website., <http://www.globaldenso.com/en/newsreleases/130626-01.html> (accessed 02/11/2019).
- (8) Ullmann, J.; Geduldig, M.; Stutzenberger, H.; Caprotti, R.; Balfour, G. Investigation into the Formation and Prevention of Internal Diesel Injector Deposits. *SAE Technical Paper 2008-01-0926* **2008**.
- (9) Arters, D.; Goodrich, B.; Millard, A.; Hess, D.; Gunter, G. *Internal Diesel Injector Deposits (CRC Project No DP-04-13a)*; tech. rep.; Coordinating Research Council, 2013, p 15.

- (10) Lacey, P.; Gail, S.; Kientz, J. M.; Milovanovic, N.; Gris, C. Internal Fuel Injector Deposits. *SAE International Journal of Fuels and Lubricants* **2011**, *5*, 2011–01–1925.
- (11) Reid, J.; Barker, J. Understanding Polyisobutylene Succinimides (PIBSI) and Internal Diesel Injector Deposits. *SAE Technical Paper 2013-01-2682* **2013**.
- (12) Barker, J.; Snape, C.; Scurr, D. Information on the Aromatic Structure of Internal Diesel Injector Deposits From Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). *SAE Technical Paper 2014-01-1387* **2014**.
- (13) Barker, J.; Reid, J.; Piggott, M.; Fay, M. W.; Davies, A.; Parmenter, C.; Weston, N.; Snape, C.; Scurr, D.; Angel-Smith, S. In *JSAE/SAE 2015 International Powertrains, Fuels and Lubricants Meeting*, SAE International: 2015.
- (14) Dallanegra, R.; Caprotti, R. Chemical Composition of Ashless Polymeric Internal Diesel Injector Deposits. *SAE Technical Paper 2014-01-2728* **2014**, DOI: <https://doi.org/10.4271/2014-01-2728>.
- (15) Barker, J.; Snape, C.; Scurr, D. A Novel Technique for Investigating the Characteristics and History of Deposits Formed Within High Pressure Fuel Injection Equipment. *SAE International Journal of Fuels and Lubricants* **2012**, *5*, 1155–1164.
- (16) CEC - The Co-ordinating European Council — Test Methods and Publications., https://www.cectests.org/listdoctypeforsale1.asp?subdoc_type=Fuels (accessed 05/26/2019).
- (17) Lubrizol Internal Diesel Injector Deposits - Lubrizol., <https://www.lubrizol.com/Lubricant-and-Fuel-Additives/Fuel-Additives/Products/Lubrizol-9040-Zer0-Series/Performance/Diesel-Injector-Deposits> (accessed 04/16/2019).
- (18) De Goede, S.; Barbour, R.; Velaers, A.; Sword, B.; Burton, D.; Mokheseng, K. The Effect of Near-Zero Aromatic Fuels on Internal Diesel Injector Deposit Test Methods. *SAE International Journal of Fuels and Lubricants* **2017**, *10*, 2017–01–0807.

- (19) Venkataraman, R.; Eser, S. Characterization of deposits formed on diesel injectors in field test and from thermal oxidative degradation of n-hexadecane in a laboratory reactor. *Chemistry Central Journal* **2008**, *2*, 25.

Chapter 2

Materials and Methods

2.1 Materials

2.1.1 Reagents

The hexadecane used in this work has been sourced from Sigma Aldrich ('Reagent Plus(R), 99 % H6701') and Acros Organics ('n-hexadecane 99% pure 120465000').

2.1.2 Substrates

The 13 chrome substrates (Fe-13Cr) used in Chapter 3 were sourced as $73 \times 22.3 \times 3.2$ mm Coupon, GRD Material S42000 101 from European Corrosion Supplies Limited, Kidderminster, UK. The composition, as specified by the supplier, is presented in Table 2.1. The iron substrates used in Chapter 4 were 99.98 % iron substrates (thickness: 1 mm, temper: as rolled, condition:ARMCO(R) soft ingot Iron) (FE000413) from Goodfellow, UK. The iron target used to make iron films for synchrotron experiments was a 75 mm diameter, 2 mm thickness, 99.95 % purity iron target (FE009200) from Goodfellow, UK. The silicon substrates used in Chapter 4 were <100> silicon substrates from Virginia semiconductor, cut into $1 \text{ cm} \times 1 \text{ cm}$ squares.

Table 2.1: Atomic percentage chemical composition of Fe-13Cr coupons given by European Corrosion Suppliers limited. The remaining composition is iron.

Cr	Mn	Si	C	Ni	Cu	N	Nb	Mo	Al	V	Co	P	S
13.0	0.5	0.3	0.2	0.2	0.09	0.03	0.03	0.03	0.02	0.02	0.02	0.02	0.003

2.2 Experimental Techniques

2.2.1 Cleaning of silicon substrates

1 cm $\times$ 1 cm $\langle 100 \rangle$ silicon substrates (Virgina semiconductor) were cleaned by sonicating in acetone and then propan-2-ol for 10 minutes each and dried with nitrogen.

2.2.2 Metal Substrate Preparation - Mounting and Polishing

The iron or Fe-13Cr substrates were manually cut to 1 cm $\times$ 1 cm and mounted in Bakelite. The samples were ground with silicon carbide paper (Kemet, UK) with grit sizes of 800, 1200, 2500, 4000 under a force of 15 N and a speed of 300 rpm. The samples were subsequently polished using 3 μm diamond polish on a Struers MD-Dac cloth (5 mins) followed by 1 μm (5 mins) and then 0.25 μm (10 mins) diamond polish on a Struers MD-Nap cloth to achieve a mirror finish. The polished iron substrates were cut out of the Bakelite and washed with ethanol, methanol then cleaned for 10 minutes with UV-ozone in a UVOCS T0SOS Ultraviolet Ozone Cleaning System.

2.2.3 Heat Treatment of Fe-13Cr Steel

Fe-13Cr substrates, polished according to Section 2.2.2, were subsequently heated to temperatures of 100, 200, 300 and 400°C for 2 hours in a vacuum tube furnace, pumped down to 0.3 mbar with a rotary pump.

2.2.4 Controlling the Surface Chemistry of Iron Substrates

To achieve the annealed surface finish, the iron substrate (polished according to Section 2.2.2), was heated at 300°C for 2 hours in a partial vacuum (0.3 mbar) whilst the oxidised surface finish was achieved by heating the polished iron substrate at 300°C for 2 hours in air.

2.2.5 Magnetron Sputtering

Magnetron sputtering is a physical vapour deposition technique, used here to produce iron thin films. Magnetron sputtering has several advantages for thin film preparation including: high deposition rates; high purity films; high adhesion; excellent coverage and the ability to sputter a wide range of materials. In magnetron sputtering, the target material is bombarded with high energy ions, ejecting atoms from the targets surface that then deposit on surfaces in the chamber including the substrates.

2.2.5.1 The argon plasma

Magnetron sputtering requires a high vacuum, typically $10^{-6} - 10^{-8}$ mbar. Argon gas is added into the vacuum chamber increasing the pressure, in this case to 10^{-2} mbar. An argon plasma is generated through the ionisation of argon atoms with accelerated electrons. Argon ions are then accelerated by an electric field to bombard the negatively charged metal target or cathode, ejecting some metal atoms.

The pressure of argon is selected to maximise the number of argon ions for sputtering, whilst limiting the scattering of argon ions by argon atoms, which reduces the number of argon ions impacting the target surface. Increasing the ratio of argon ions to atoms is desirable as it would decrease the pressures required whilst maintaining sputtering rates.

2.2.5.2 Sputtering of the Target

Upon impact of the argon ions onto the target, a collision cascade occurs, ultimately ejecting some atoms which are close to the surface and whose energy overcomes the surface binding energy. These collisions can also ionise atoms in the target releasing secondary electrons. These

electrons are contained by a magnetic field over the target generated between a ring magnet and a central magnet under the target. These electron move in helical path around the magnetic field lines and are used to further ionise argon atoms, enhancing the sputter rate. The sputtering yield is the number of ejected atoms per incident ion and depends on a variety of properties including the relative mass and binding energy of the target atoms and the mass, energy and angle of incidence of the incident ions.

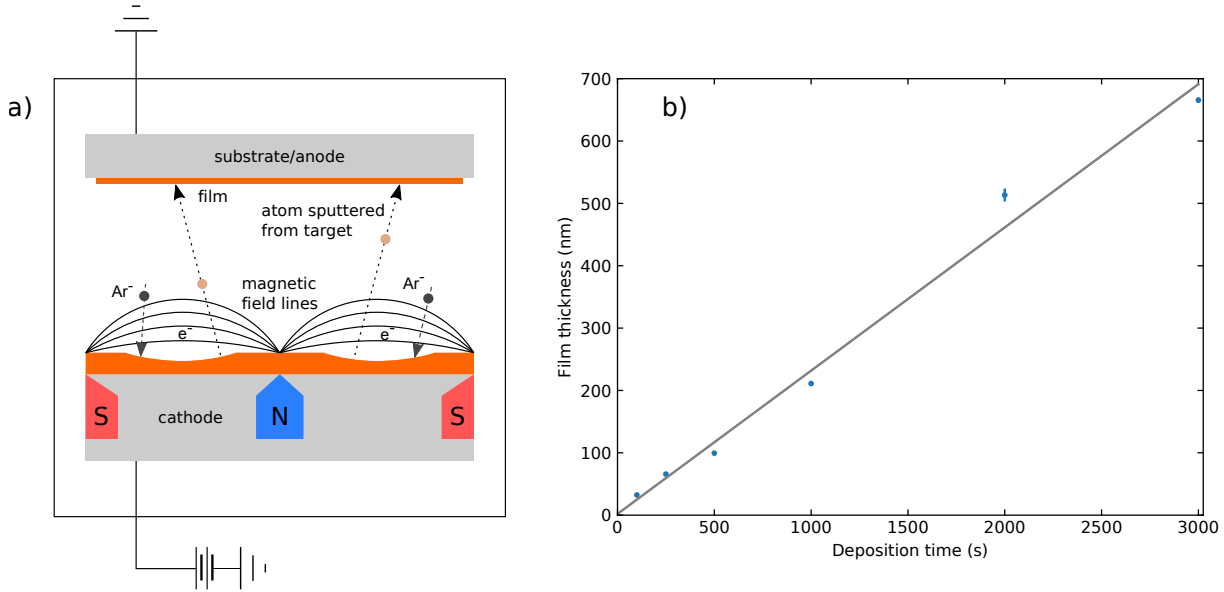


Figure 2.1: a) Schematic of a magnetron sputtering chamber. Argon ions are accelerated by an electric field towards the iron target. Iron atoms are sputtered from the target and deposit on the substrate. A magnetic field is used to trap secondary electrons which also served the increase the ionisation rate of argon. b) Calibration of the film thickness against the sputter time for iron films produced by magnetron sputtering. Where error bars are not visible, they are smaller than the point.

2.2.5.3 Film Growth

A Kurt Lesker LAB 18 Thin Film Deposition System was used to prepare iron thin films. Iron films were grown at an argon pressure of 6.7 mbar and a power of 300 W. The deposition rate for iron thin film growth was determined by measuring the film thickness at several sputtering times. Titanium dioxide, dissolved in propa-2-nol, was used as a mask on the sample's surface during film growth and subsequently removed by sonicating the films in propan-2-ol following film growth. A Dektak profilometer was used to determine the film thickness over this region; the calibration curve is presented in Figure 2.1b.

For X-ray absorption spectroscopy studies, iron thin films with thicknesses of 10 nm (35 s), 50 nm (209 s) and 100 nm (427 s) were grown on kapton substrates. For transmission electron microscopy analyses, a 10 nm (35 s) film was grown on silicon nitride grids. For grazing incidence wide angle scattering measurements, 150 nm (642 s) were grown on silicon substrates.

2.2.6 Heat Treatment of the Iron Thin Film

The oxidised film was produced by heating the iron film at 300°C for 2 hours in air.

2.2.7 Treatment with Hexadecane

The substrate (an iron substrate or an iron thin film) and 12 ml of hexadecane (Figure 2.2b) were refluxed for 1 hour at 200°C as shown in Figure 2.2a. The sample was removed from the solution following a soaking time of 0.5, 24 or 72 hours and dried with nitrogen. The substrates were then characterised with secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS) and scanning electron microscopy (SEM). *Ex situ* wide angle X-ray scattering and X-ray absorption spectroscopy were also used to characterised these substrates. The resulting solutions were analysed by mass spectrometry.

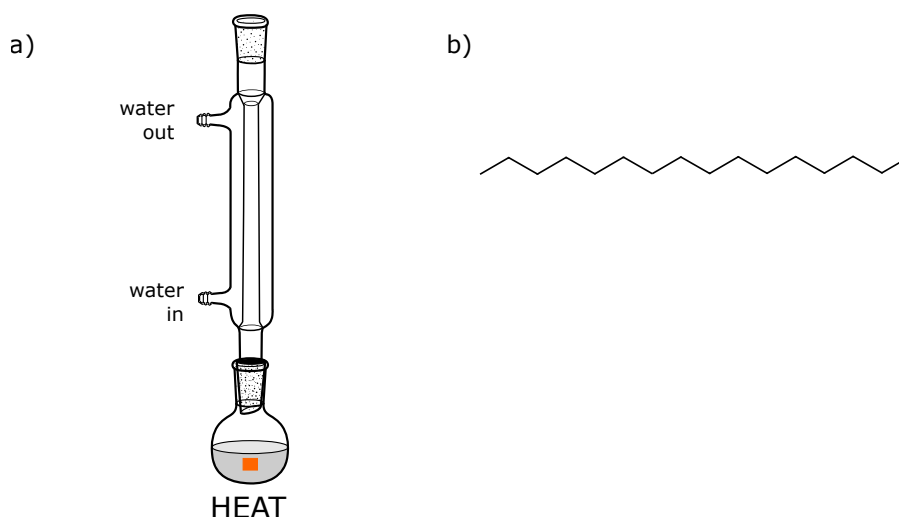


Figure 2.2: a) Schematic of the experimental set-up for the treatment of substrates (orange) with hexadecane. b) Hexadecane - The model diesel component used in this work.

2.3 Preparation For *In Situ* High Temperature Flow Studies

2.3.1 Practical considerations

A custom-made experimental set-up was required to facilitate *in situ* investigation into the chemical and structural changes occurring at the surface. The requirement for high temperatures was the primary safety and practical consideration in this work. Experiments into the interaction between hexadecane and iron surfaces were conducted at 200°C, which is above the flash point for hexadecane (135°C) and close to its auto-ignition temperature (215°C). The flash point and auto-ignition temperatures refer to the temperature at which vapours will ignite with and without an ignition source respectively.

Two main approaches were taken to ensure that these experiments could be completed safely; the volume of hexadecane used was minimised and equipment rated for use in hazardous areas was used. The lower explosion limit (LEL) refers to the concentration in air at which the fuel is ‘too lean’ to burn; for hexadecane the LEL is quoted as 40 g m⁻³. Assuming that the experiment is conducted in a very confined space of 2 m³, 80 g of hexadecane can be used, corresponding to ~ 103 cm³.

Using this overly cautious volume of hexadecane for experiments significantly reduces the risks associated with these high temperatures. The reaction cavity volume inside the cell must be minimised to enable flow experiments with this limited total volume. In addition, ATEX-rated components were used where possible; the use of components designed for potentially explosive environments further reduces the risk of explosion by ensuring that if electrical components do spark, that these sparks are fully contained.

The aim of these experiments was to investigate the interaction of iron surfaces with hexadecane at elevated temperatures, therefore, contact between hexadecane and other metal surfaces was avoided. The cell was made from polyether ether ketone (PEEK) as it has a good chemical-resistance to diesel and has a melting point well above the target temperature for the experiment (343°C).

For spectroscopic measurements, as the iron K edge is at 7.112 keV, it is essential to minimise the X-ray path length through the cell and therefore X-ray attenuation. The attenuation of the X-ray intensity, I , as it passes through a material is given by:

$$I = I_0 e^{-Ax} \quad (2.1)$$

where I_0 is the incident X-ray intensity, A is the linear attenuation coefficient and x is the path length through the material. As $A = \mu \times \rho$, where μ is the mass attenuation coefficient (or absorption coefficient) and ρ is the density, and the attenuation length is defined as the distance when the X-ray intensity drops to $\frac{1}{e}$ its original value, the attenuation length, x_A , for a given material is defined by:

$$x_A = \frac{1}{A} = \frac{1}{\mu\rho} \quad (2.2)$$

The X-ray attenuation can subsequently be determined using:

$$\frac{I}{I_0} = e^{-\frac{x_{Fe}}{x_A Fe}} e^{-\frac{x_{kapton}}{x_A kapton}} \quad (2.3)$$

as an example for X-ray attenuation through two materials, where x_{Fe} and x_{kapton} are the path lengths through iron and kapton respectively and $x_A Fe$ and $x_A kapton$ are the attenuation lengths for these materials.

Two experimental set-ups were tested for *in situ* spectroscopic studies. Multiple layers of iron films were measured in solution in transmission mode. Alternatively, experiments were performed in a fluorescence geometry with an incident angle of 45°. To minimise X-ray attenuation, the ‘iron substrate’ was sputtered onto the kapton window. These cell designs are discussed in Section 2.3.2.

For structural characterisation of the iron surface, a grazing incident cell geometry is required, therefore, significant X-ray attenuation through the cell cannot be avoided. As there is no requirement on the X-ray energy used for these measurements, a balance must be achieved between adequate sampling of the sample surface and the attenuation of the X-rays through the

cell. This cell is discussed in Section 2.3.2.

2.3.2 Cell Design

Despite the varying geometrical and practical requirements for these cells, they share many design features. The cells were made from PEEK with kapton window with the volume contained in each cell kept to a minimum, as discussed in Section 2.3.1. To avoid exposure of the fuel to the seal, it was placed on the outside of kapton. A compressible material, which would deform over the course of the experiment, was successfully used to achieve a seal.

A schematic of the cell used for spectroscopic measurements in transmission mode is given in Figure 2.3a. This cell was tested at the Advanced Photon Source on the MR-CAT beam line. To achieve sufficient signal from the iron thin films, layers of 10, 20 and 40 films were used for film thicknesses of 100 nm, 50 nm and 10 nm respectively. Unlike all the other cells, Torlon (polyamide-imide) was used to make this test cell which, whilst having excellent physical properties at high temperatures, is a very effective insulator resulting in poor heat distribution across the cell. This system does not facilitate flow. Due to the practical difficulties associated with this cell design as well as problems with heat distribution over Torlon, this cell design and material were not used in further work.

Figure 2.3b demonstrates the cell design that was used for all subsequent *in situ* spectroscopic measurements presented in this work. This cell was used on the I20 beam line at the Diamond Light Source, as shown in action in Figure 2.5b. In this cell, iron thin films are sputtered onto the kapton window. The iron film is sampled through the kapton in the fluorescence mode, with an X-ray incident angle of 45° . A fluorocarbon O-ring was used to form a seal between the PEEK cell and the kapton window; it was compressed as the cell parts and heating block were clamped together. The heating block is made from two pieces of metal that are clamped together around two cartridge heaters, ensuring good thermal contact. A thermocouple was used to measure the temperature of the heating block and the measured temperature is used in a feedback loop to control the temperature. Details of the temperature controller are given in Section 2.3.3.

Figure 2.3c illustrates a front and side view of the cell used for performing structural

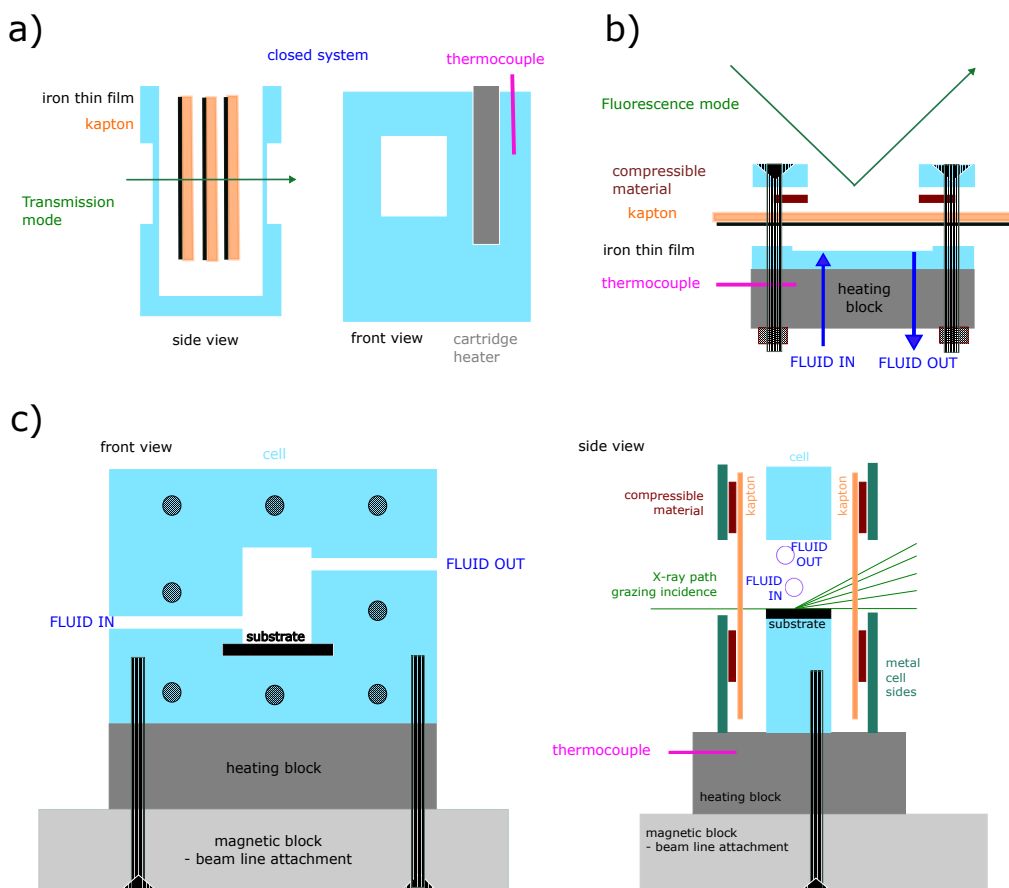


Figure 2.3: Schematic of the cell designs use in this work for a) spectroscopic measurements in a transmission geometry; b) spectroscopic measurements in a fluorescence geometry and c) structural measurements with a grazing incidence geometry.

measurements at the Australian Synchrotron. Similarly to above, the hexadecane will only come into contact with PEEK and kapton surfaces. Rubber was used as the compressible material in this cell, unlike above where two seals are required. Metal plates were used to sandwich the PEEK cell partly due to their structure and strength but also to improve the heat distribution across the cell. A photograph of this cell is shown in Figure 2.5c and with the cell on the beam line in Figure 2.5d.

2.3.3 Rig Development

To facilitate investigation into the interaction of iron substrates with flowing hexadecane at 200°C, a rig was developed. This system was designed not only to meet the practical and safety requirements of these experiments, but to enable higher pressures and faster flow rates for future work. A schematic of the rig developed is shown in Figure 2.4a. The parts are as follows:

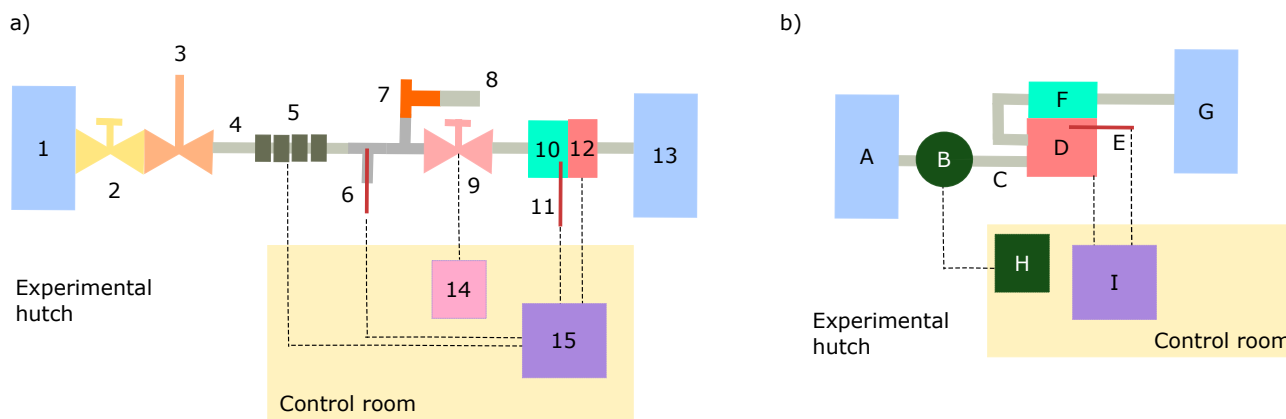


Figure 2.4: Rigs developed for *in situ* a) spectroscopic and b) structural measurements performed on the I20 beam line at the Diamond Light Source and SAXS/WAXS beam line at the Australian Synchrotron respectively.

1. **Syringe Pump** - A Harvard Apparatus syringe pump was used to control the flow rate of hexadecane.
2. **Metering Valve** - A Swagelok[®] meter valve was used to isolate the pump from the system.
3. **3-way Valve** - A Swagelok[®] 3-way valve was used to drain the system by flushing it with nitrogen when the experiment was complete.
4. **Tubing** - Swagelok[®] polytetrafluoroethylene (PTFE) tubing was used in this system, as it is non metallic with excellent chemical (resistance to hexadecane) and physical (its melting point (326°C) is significantly higher than 200°C) properties.
5. **Heating Tape** - Omega Engineering heating tape was used to heat the hexadecane before it entered into the cell.
6. **Thermocouple** - A TC ATEX-rated in-line K-type thermocouple was used to measure the temperature of hexadecane during heating with the heating tape and feed back to the temperature controller.
7. **Pressure Release Valve** - A Swagelok[®] pressure relief valve, set to 2 bar, was incorporated into the set up. It serves to release any over pressure building up in the system, and also provides an alternative pathway for flowing hexadecane if the actuator valve was

closed to isolate the cell.

8. **Waste** - A large waste container was connected to the pressure release valve, to collect hexadecane, should this valve open.
9. **Actuated Valve** - A Valpes electric actuator was used so the cell could be isolated.
10. **Cell** - A schematic for the custom-made PEEK cell used in this work is shown in Figure 2.3b.
11. **Thermocouple** - An RS K-type thermocouple was used to measure the temperature of the heating block and feed back to the temperature controller.
12. **Heat Block** - A custom-made heating block was heated with two RS cartridge heaters.
13. **Waste** - The hexadecane that passed through the cell entered the waste and was not re-circulated.
14. **Actuator Controller** - In the case of a leak, the cell could be isolated remotely from the flow. In this case, the pressure release valve would open and the fuel would enter a separate waste container.
15. **Temperature Controller** - A Eurotherm Nanodac Temperature controller/monitor with two separate feedback loops was used between: 1) the in-line thermocouple and the heating tape and 2) the cartridge heaters and the thermocouple in the heating block. This controller was located in the control hutch and could be used to remotely change the temperature and turn off the heating.

Despite the potential for flow experiments, the *in situ* measurements performed in this work were conducted in closed (no flow) systems. The rig in action is shown in Figure 2.5.

The system designed for experiments at the Australian Synchrotron was stream-lined compared to that used at the Diamond Light Source. As spectroscopic measurements were performed in a closed system, flow experiments were not conducted, nevertheless, the potential use of a peristaltic pump is shown in Figure 2.4b. Therefore, the total volume of fuel used in these



Figure 2.5: Photographs of the a) rig and b) cell on the I20 beam line at the Diamond Light Source. Images of the c) cell and d) beam line set up for measurements completed on the SAXS/WAXS beam line at the Australian Synchrotron.

static experiments was significantly reduced and precautions included previously (the actuated valve and the pressure release valve) were no longer required. The set-up was further simplified by plugging the pump in inside the control room. The size of the tubing was also reduced. The use of Newport kinematic bases to attach the cell to the beam line whilst maintaining its alignment enabled the whole flow system to be dismantled in the fume hood, removing the requirement to flush the cell with nitrogen inside the experimental hutch.

A schematic for this system is shown in Figure 2.3.3b; the parts are as follows:

A **Tank** - The hexadecane reservoir for flow experiments

B **Peristaltic Pump** - A peristaltic pump could be incorporated here, but was not used for this work.

C **Tubing** - PTFE tubing with a 1 mm inner diameter was used.

D **Heat Block** - The heating block was heated with two cartridge heaters. Both the cell and the hexadecane in the tubing were heated here (the PTFE tubing was passed through the heating block).

E **Thermocouple** - An RS K-type thermocouple was used to measure the temperature of the heating block and feedback to the temperature controller.

F **Cell** - A schematic for the custom-made PEEK cell used in this work is shown in Figure 2.3c.

G **Waste** - As above.

H **Pump Plug** - In contrast to the complex system used previously for isolating the cell, in this case, the pump was plugged in inside the control hutch so it could be turned off remotely.

I **Temperature Controller** - As above.

2.4 Characterisation Techniques

2.4.1 Mass Spectrometry

Through measuring the mass of ionised species, mass spectrometry provides information on the chemical composition of a sample. Two types of mass spectrometry were used in this work; secondary ion mass spectrometry (SIMS) and high resolution positive/negative ion electrospray ionisation mass spectrometry (ESI-MS). Dynamic SIMS was used in Chapter 3 to characterise the oxide forming on Fe-13Cr, an engine steel containing 13 % chromium, under varying heat

treatments. In Chapter 4, static SIMS was used to characterise changes in the deposit and surface composition as a function of experimental parameters.

High resolution mass spectrometry (ESI-MS) was conducted at BP Technology Centre Pangbourne by Dr. Chrissie Wicking. ESI-MS was used in Chapter 4 to investigate the solution from which the deposits formed, providing insights into the extent of free radical oxidation in solution.

2.4.2 High Resolution Electrospray Ionisation Mass Spectrometry (ESI-MS)

Mass spectrometry was conducted by Dr Chrissie Wicking at BP Technology Centre in Pangbourne using a QExactive Plus Orbitrap with enhanced resolution equipped with a HESI source. The mass range measured was $133.4 - 2000\ m/z$ at a resolution of 280, 000 FWHM. Capillary temperatures of 350°C or 300°C and a spray voltage of 3 kV or 4 kV was used for the analysis of negatively-ionising and positively-ionising species respectively.

For positive analysis, 1 μl of sample was mixed with 900 μl of toluene/methanol (6:4) and 100 μl of 100 mM sodium nitrate in methanol. For negative analysis, 1 μl of sample was mixed with 1000 μl of toluene/methanol (6:4) and 1 μl of 35 % ammonium hydroxide solution in water. The background subtraction was completed using Excalibur software. The scans were normalised to the most intense peak between compared scans based on the assumption that these solutions ionise consistently, regardless of their components. The relative abundance was filtered for the positively-ionising and negatively-ionising species at 0.3 and 0.7 respectively to remove noise.

2.4.2.1 The Kendrick Mass Defect

The Kendrick mass defect (KMD) was proposed by Edward Kendrick in 1963 with the aim of reducing the complexity of the mass spectra of organic mixtures upon the introduction of mass spectrometry techniques with ultrahigh resolution and limited fragmentation.¹ The Kendrick mass scale takes the mass of CH_2 to be 14.0000 mass units, with the Kendrick mass defined as:

$$Kendrick\ mass = IUPAC\ mass \times \frac{14}{14.01565} \quad (2.4)$$

Therefore, homologous series (with species differing by CH₂ groups) will have the same Kendrick mass defect. The Kendrick mass defect is determined by:

$$Kendrick\ mass\ defect = (nominal\ Kendrick\ mass - exact\ Kendrick\ mass) \quad (2.5)$$

Historically, Kendrick mass defects were used to identify homologous series with reference tables and determine their identity without reference tables over a large range of masses. In 2001, Hughey *et al.* demonstrated that a 2D plot of the nominal mass against the Kendrick mass defect was an effective way to visualise and assign elemental composition patterns in high resolution mass spectra of complex organic mixtures.² KMD plots allow several thousand elemental compositions to be resolved into a two dimensional display, with their empirical formula (class), carbon to hydrogen ratio (type) – and hence cyclisation/unsaturation – and alkylation easily visualised. 3-dimensional KMD plots, which include the mass spectral signal magnitude/relative abundance, are also commonly used.

KMD plots are frequently used by the oil and gas industry to find correlations between chemical structures in highly complex mixtures analysed using high resolution mass spectrometry. All mass spectra presented in this work are presented as KMD plots. An example of an annotated KMD plot is shown in Figure 2.6. Homologous series varying by CH₂ appear as horizontal lines, while species increasing in oxygen content as displayed as diagonal lines.

2.4.3 Secondary Ion Mass Spectrometry (SIMS)

In SIMS, a beam of primary ions bombard a sample surface producing an array of sputtered material including some ionised atoms and molecules. These ionised species, referred to as secondary ions, are extracted and their mass to charge ratio is measured against their intensity, producing a mass spectrum.

The characteristic surface sensitivity of SIMS is a result of secondary ions originating from

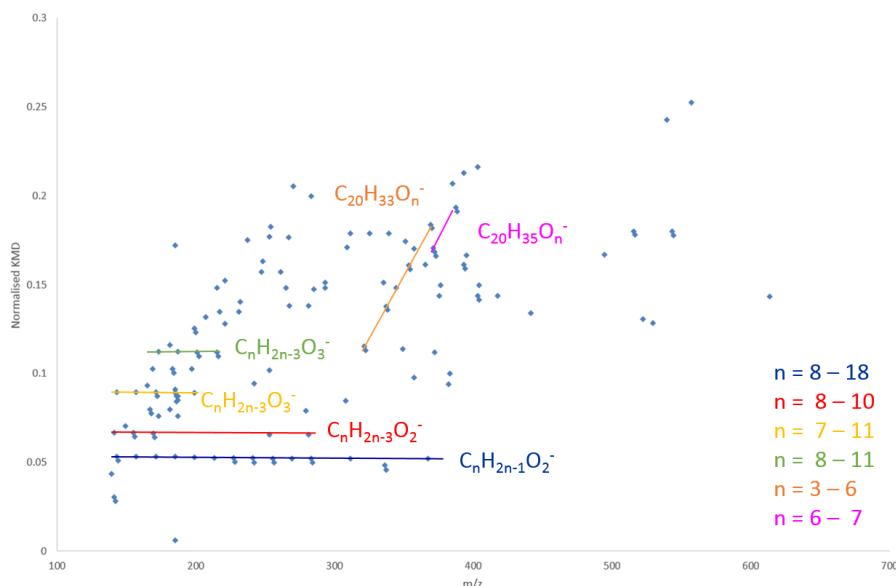


Figure 2.6: An example of a Kendrick mass defect (KMD) plot of electrospray ionisation mass spectrometry data showing homologous series changing by CH_2 along horizontal lines and oxygen content along vertical lines.

the first few mono-layers, although this is material-dependent.³

2.4.3.1 Static and Dynamic SIMS

Static and dynamic SIMS refer to two types of SIMS whereby the measurement is surface sensitive, or mass spectra of the sample are measured as a function of depth. Static SIMS uses very low beam currents and limits the ion dose to ensure surface sensitivity, with secondary ions originating from the first few monolayers. The ion dose limit or static limit is materials dependent, reported to be 10^{15} ions cm^{-3} in inorganic materials and $10^{10} - 10^{13}$ ions cm^{-3} in organic systems. The ion dose limit corresponds to 10 % of the analysis area experiencing primary ion beam impact and the removal of less than 1 % of material from the analysis area.^{4,5} At these low beam doses and reduced ion beam interactions with the surface, SIMS is reported to be essentially a ‘non-destructive technique’.⁶

Dynamic SIMS refers to the use of high ion beam currents to remove material facilitating measurements as a function of depth and enabling chemical compositions analyses of the near surface and bulk. The development of dual-beam instruments facilitates the attainment of complex mass spectra as a function of depth, with different parameters for each beam. A sputter beam is used in conjunction with the primary analysis beam, alternating to remove damaged

layers and analyse the sample. Depth profiles of molecular and elemental species are produced.

2.4.3.2 Primary Analysis Beam

A bismuth primary ion beam was used in this work. The bismuth beam is produced by a liquid metal ion gun/source (LMIG/S) by field emission, collimated and accelerated in short pulses towards the sample. The resulting beam is very focused, with a reported diameter of 10 nm.⁴ The primary ion beam is then rastered across the analysis area, generating ions through desorption ionisation.

The use of clusters, as opposed to monoatomic primary ions, significantly reduces the damage to the surface and subsequent layers. Although the clusters and monoatomic ions typically have the same energy, the energy of individual atoms within the cluster is lower compared to monoatomic ions. Therefore, the depth of damage is significantly reduced. Simulations of Ar_n^+ ion beams also showed an increase in the lateral area sputtered compared to monoatomic ion beams,⁷ resulting in less fragmentation producing to intact parent molecules and a cleaner mass spectrum.⁶ These characteristics make clusters particularly useful for studying variations in molecular structures, as opposed to elemental compositions.

The pulse lengths of the ion beam can be adjusted depending on whether high mass resolution or high lateral resolution information is desired. High mass resolution is facilitated by very short pulse duration's (~ 0.6 ns) enabling greater separation of the secondary ions. Mass resolution is defined as the ability to separate two adjacent peaks by their full width half maximum and equal to $m/\delta m$. This mode is referred to as the bunched mode, or 'high current bunched mode' (HCBM) on the ION-ToF instrument used for this work. The lateral resolution in HCBM mode is significantly reduced to a few microns. The burst or 'pulsing-enabled burst alignment mode' (BAM), achieving high lateral resolution, was not used in this work and hence will not be discussed here.

2.4.3.3 Secondary Ion Generation

Upon impact, energy from the primary ion beam is transferred to the surface species in billiard-ball type collision, generating a collision cascade which can cause beam-induced mixing of

surface species.⁸ The depth of this interaction is referred to as the penetration depth. If atomic or molecular species have sufficient energy to overcome the surface binding forces, then they will be released. The depth of origin of these ejected species (information depth) is quoted to be from the first 2 – 3 atom layers, however due to multiple collision processes, this is not always the case.⁹ Of the ejected species, including neutral molecules, atoms, radicals, electrons and ions, it is only the ions that are analysed by SIMS. Ionisation occurs at or near the surface in subsequent processes meaning that ionisation is strongly influenced by the chemical state at the surface. This effect is called the matrix effect and acknowledges that the surrounding chemistry can suppress or enhance the ionisation of surface species and alter their deflection. The matrix effect is described by:

$$I_n = I_p Y \alpha_n T C_n \quad (2.6)$$

where I_n is the intensity of secondary ion species n , I_p is the primary ion beam current, Y is the sputter yield, α_n is the ionisation probability and C_n is the concentration of species n . T is the instrumental transmission factor. The ionisation probability depends on the identity of n , the local chemistry, the primary ion beam energy and the angle of incidence. Variations in the ionisation probability due to the local chemical environment convolutes the dependency of intensity on concentration. In some scenarios, for example isotopic measurements in well-defined systems, it is possible to quantify the mass spectra. Due to the variable and poorly defined chemical environment in this work, the absolute secondary ion intensities do not provide any valuable quantitative insights and therefore ratios are considered.⁸

2.4.3.4 Species Detected

Secondary ions can form through a range of processes. The addition or loss of an electron or a proton can generate molecular ions (M^+ or M^-) or protonated/deprotonated species ($[M+H]^+$ or $[M-H]^-$) respectively. Cationisation refers to the the formation of metal adducts ($[M+Na]^+$); sodium is a common source of surface contamination. Fragmentation of molecular species will also produce ions.

2.4.3.5 Mass Analysis and Ion Detection

Once secondary ions are generated, they are accelerated through an extraction plate into the time of flight (ToF) analyser so they have the same kinetic energy. To account for the variations in kinetic energy of secondary ions of the same mass/charge ratio, a reflectron - a series of high voltage ring electrodes at the end of the analyser - is used to ensure all species reach the detector at the same time, narrowing the bandwidth of the output signals and improving the mass resolution.^{4,6}

A ToF analyser is used to measure the m/z ratio of the secondary ions to generate a mass spectrum. Ions are separated by the flight time in a flight tube in the absence of any electric or magnetic fields according to:

$$E_k = \frac{1}{2}mv^2 \quad (2.7)$$

where E_k is the kinetic energy of the ions, m is their mass and v is their velocity. The mass separation is given according to:

$$m/z = \frac{2Vt^2}{L^2} \quad (2.8)$$

where m/z is the mass separation, V is the accelerating potential, L is the length of the flight tube and t is the time taken for ions to drift down the flight tube and hit the detector.⁶ A microchannel plate (MCP) is used to detect and amplify the secondary ions exiting the analyser. The use of solely atomic or molecular peaks is recommended for subsequent mass calibration.⁴

2.4.3.6 Sputter Beam

For dynamic SIMS studies, a sputter beam is used in conjunction with the primary analysis beam. A wide range of ions can be used for the sputter beam depending upon the materials studied and the information required. The dual source column on the ION-TOF instrument enables the use of oxygen or caesium as a sputter beam. The advantage of a dual beam system is that the parameters for the primary and sputter beams can be independently optimised. Oxygen ions are produced via electron impact, however caesium ions are produced by the thermal ionisation of atoms. Oxygen is used to enhance the yields of electropositive elements,

whilst caesium is used for electronegative elements as it can readily lose 6 electrons to these species. Argon clusters are alternative sputter ions. A high current, low energy caesium sputter beam was used in this work to study the surface metal oxides.

2.4.3.7 Chemometric Analysis

Multivariate analysis refers to a series of statistical analysis techniques used to interpret spectral data. Principal component analysis (PCA) can be used to identify the largest mass co-variance between large and complex data sets, such as those obtained using SIMS.^{10,11} Spectral peaks which have a dependence, linearly or inversely, can provide insights into the effect of different conditions and surface compositions on deposition.

Prior to PCA, several pre-processing steps are used: Poisson scaling, sum normalisation and mean centring. Poisson scaling is applied to correct for the loss in counts, and hence secondary ion yield, due to detector dead time at high masses.^{12,13} The total ion intensity is normalised to 1 to account for variations in data acquisition, for example changes in the primary ion current, that may not relate to chemical differences between samples.¹¹ The data are subsequently mean-centred; the mean intensity from each data set is subtracted from each intensity within the data set. Centring the intensity of the spectra around zero ensures that the differences found between samples are due to chemical variances within the samples.^{11,14}

A matrix of the processed data is generated, with rows as the spectra and columns as the peak area for every m/z values. Characteristic vectors (eigenvectors) and characteristic roots (eigenvalues) are determined for the variance-co-variance matrix, which together are a linear combination of the original variables.¹¹ PCA determines the directions of greatest variation within the data; successive principal components are aligned along the direction of the next greatest variance in the data. In practice, only a few PCs are necessary to describe the variance in the data set as each PC is orthogonal to and therefore independent of the previous PC.¹¹

The number of PCs necessary to describe the variance is commonly determined using a scree plot; the number of PCs which describe the greatest variance in the data is determined by the ‘elbow’, as shown in Figure 2.7a. Scores (Figure 2.7b) relate the identified PCs to the sample/analysis area they refer to, whilst loadings plots (Figure 2.7c) are used to identify the

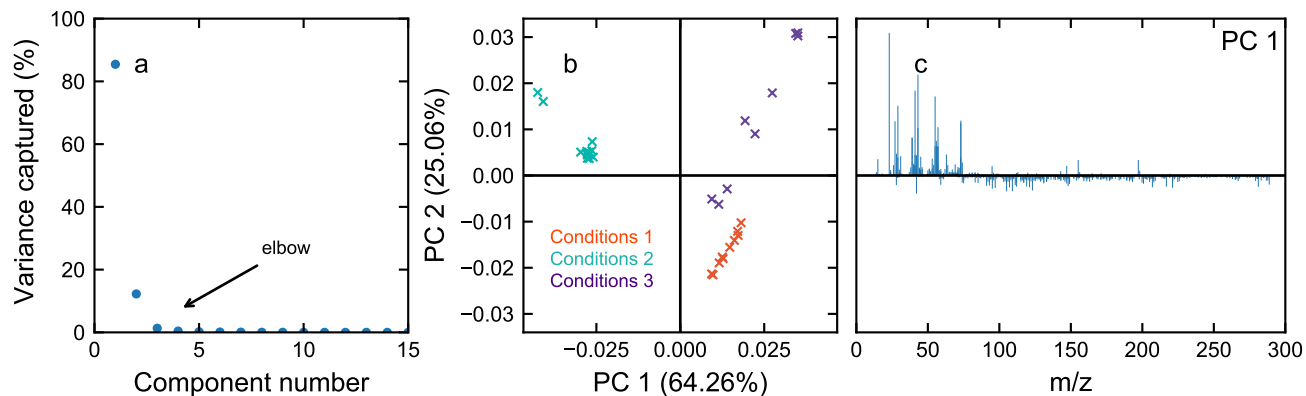


Figure 2.7: a) Scree plot for determining the number of principal components. b) Scores plots demonstrating the distribution of scans between two principal components. Each data point here corresponds to one measurement of the surface. c) Loadings plots relate the principal components to the masses they correspond to within the sample.

masses corresponding to each principal component. Within each principal component, the masses shown in the positive side of the loadings plots correspond to species found in the samples shown on the positive side of the scores plot.

2.4.3.8 Experimental Settings

A dual-beam TOF-SIMS V instrument (ION-TOF GmbH, Münster, Germany) was used for this work. A Bi_3^+ ion cluster was used as the primary analysis beam (25 keV, ~ 3 pA). All presented measurements were obtained in the high current bunch mode, providing high mass resolution, but poor lateral resolution. For the depth profiles or dynamic SIMS experiments presented in Chapter 3, a Cs^+ was used as the sputter beam (1 kV). A crater size of $250 \mu\text{m} \times 250 \mu\text{m}$ was used to avoid crater edge effects. In the static measurements in Chapter 4, 30 scans were taken of 10 different analysis areas ($100 \mu\text{m} \times 100 \mu\text{m}$, 128×128 pixels) in both the positive and negative modes, ensuring the ion dose remained well within the static limit. The positive spectra are calibrated with: C^+ , CH^+ , CH_2^+ , CH_3^+ , C_2H_3^+ , C_2H_4^+ , C_2H_5^+ , C_3H_3^+ , C_3H_5^+ , C_3H_7^+ , C_4H_3^+ , C_4H_4^+ , C_4H_5^+ , C_4H_6^+ , C_4H_9^+ , C_5H_2^+ , C_5H_3^+ , C_5H_5^+ , C_5H_9^+ , $\text{C}_5\text{H}_{11}^+$, C_6H_5^+ , C_7H_7^+ .

The Matlab package PLS-Toolbox, version 6.2.1 (Eigenvector Research, Inc, Manson, WA, USA) was used for principal component analysis. These data were Poisson-scaled, sum normalised and mean-centred prior to analysis.

2.4.4 Interactions of X-rays With Matter

The interaction of X-rays with matter can provide a vast array of insights into the materials properties including structure, morphology and chemical speciation. Several X-ray characterisation techniques, including X-ray photoelectron spectroscopy - XPS - (Section 2.4.5), X-ray Absorption spectroscopy - XAS) - (Section 2.4.6) and wide angle X-ray scattering - WAXS - (Section 2.4.7) are used in this work to acquire information on the chemical states, chemical speciation, local geometry and structure.

When X-rays pass through a material they could be transmitted, absorbed or scattered. When an X-ray photon is absorbed, a core electron can be emitted leaving behind a core hole; this phenomenon is referred to as the photoelectric effect. A higher energy electron then decays into the core hole, emitting either a secondary photon or an Auger electron, with an energy characteristic of that energy transition. XAS, used in this work, is the measurement of absorption as a function of incident photon energy, whilst XPS measures the photoelectrons' kinetic energy over a range of incident photon energies. X-ray fluorescence spectroscopy (XFS) is the measurement of the emitted photon energy and will not be discussed here.

The scattering of incident photons by electrons within the sample can be coherent or incoherent. Coherent or Rayleigh scattering arises from elastic collisions where the incident electron energy remains unchanged and retains some relationship to the phase of the incident photon. In incoherent scattering, there is an energy transfer between the incident X-ray photon and an electron within the material, resulting in a decrease in the photon energy or increase wavelength. Constructive interference between the incident and scattered photons is not possible here due to the discrepancy between the wavelengths and the phase of the photons. A summary of these processes are given in Figure 2.8.

2.4.5 X-ray Photoelectron Spectroscopy (XPS)

As mentioned above, XPS measures the kinetic energy of photoelectrons as a function of incident photon energy. The kinetic energy is characteristic of the elemental and chemical environment from which the electron originates and given by:

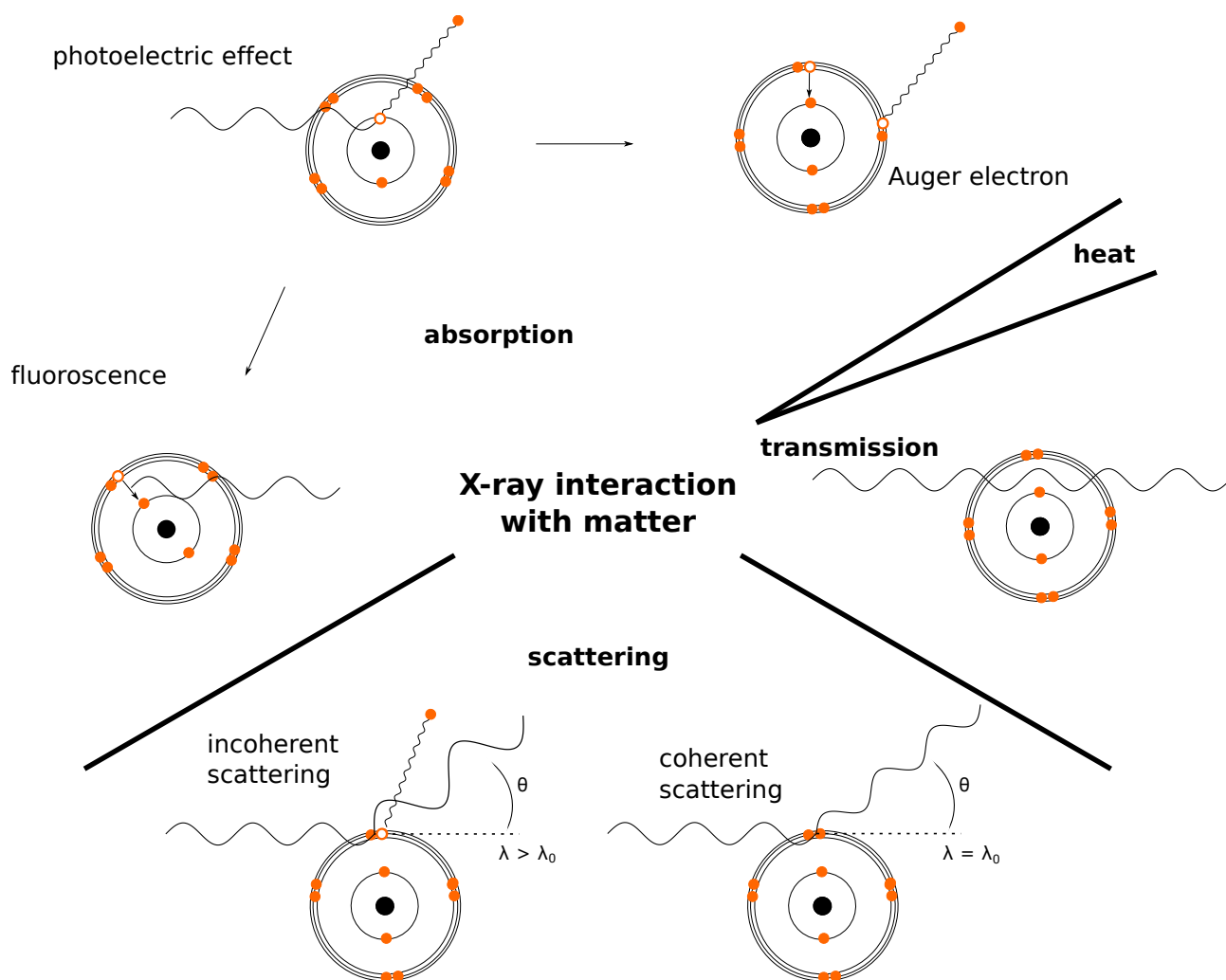


Figure 2.8: Schematic of the interaction of X-rays with matter

Schematic of the interaction of X-rays with matter, including the generation of heat, transmission, scattering (incoherent or coherent) and absorption (photoelectric effect followed by fluorescence or the emission of a Auger electron).

$$E_K = h\nu - E_{binding} - \phi \quad (2.9)$$

where E_K is the kinetic energy, $h\nu$ is the incident photon energy, $E_{binding}$ is the binding energy of an atomic or molecular orbital and ϕ is the work function of the detector. The unique electronic configurations of different elements lead to characteristic and independent core lines at different binding energies. The oxidation state and local chemical environments of different elements can cause a shift in binding energies of electrons and hence is observed as a shift in the XPS spectra.

The surface sensitivity of XPS is attributed to inelastic scattering of photoelectrons within

the sample, with the electron intensity attenuating according to the Beer-Lambert law, given by:

$$I = I_0 e^{-\mu t} \quad (2.10)$$

where I is the intensity transmitted through the sample, t is the sample thickness, I_0 is the incident X-ray intensity on the sample and μ is the absorption coefficient. Therefore only photoelectrons from the first few monolayers of the sample will be detected, providing information on the chemical and electronic states of the sample surface. The inelastic mean free path was given by Seah and Dench as:¹⁵

$$\lambda_m(E) = \frac{A_m}{E^2} + B_m E^{\frac{1}{2}} \quad (2.11)$$

where $\lambda_m(E)$ is the path length in monolayers, A_m and B_m are empirical parameters and E is the energy. The probing depth is defined as the depth from which 90 % of all electrons are scattered by the time they reach the surface; the probing depth is commonly reported to be approximately 10 nm, however this is material-dependent with lighter materials having a larger probing depth.

2.4.5.1 Spectral Features

In this work the core lines of carbon 1s (C1s), oxygen 1s (O1s) and iron 2p (Fe2p) were studied. Variations in chemical states are detected by shifts in binding energy, typically up to 5 eV. The iron core line appears as a doublet; this is a result of spin-orbit coupling between the electron spin and the angular momentum vector of the orbital. The peak ratios of 2:1 is attributed to the orbital degeneracy of the $2p_{\frac{3}{2}}$ and $2p_{\frac{1}{2}}$ respectively. The physical processes responsible for spectral features will be outlined here.

Satellites are generated when the photoelectron interacts with a valence electron; satellites can provide information on oxidation states, electronic coupling, final state effects and valence bonds. There are two types of satellites; shake up satellites, caused by the transition of an electron to an excited state, and shake off satellites, where the electron is excited into the continuum.

Shake up satellites are observed in conjugated organic systems, for example for 1-methyl naphthalene, the C1s satellite is a broad peak at 291 eV, at a binding energy 6 eV higher than that for adventitious carbon. This satellite is a result of $\pi - \pi^*$ transitions involving the two highest filled orbitals and the lowest unfilled valence orbitals. Satellites have intensities 5 – 10 % of the main peak and can have separations of up to 15 eV.

Very strong satellites are observed in inorganic systems for transition and rare earth metals. The strong configuration interactions taking place in the final state leads to complex spectra. The position of the satellites observed for the Fe2p core line are used as a fingerprint region for distinguishing between iron chemical environments.

There are several other spectral features that are either not observed for the core lines studied or measured in this work. Auger lines appear at high binding energies and are a result of emission of Auger photoelectrons. The electron relaxing into the core hole, which has a lifetime of 10^{-15} s, will emit a photon (fluorescence). This photon can then excite a third electron called the Auger electron. Auger lines can be used as fingerprints to aid identification of oxidation states and local chemical environment. Measuring the valence band, which is related to emission of electrons from the highest occupied orbital, provides an insight into the electronic properties of a material. Plasmons are typically observed on metal samples and are produced when the exiting photoelectron loses energy to oscillating conduction electrons resulting in an energy loss at characteristic frequencies.

2.4.5.2 Quantification

It is possible to quantify not only elemental compositions, but also the chemical states of the element with XPS. According to:

$$N_i = \frac{I_i}{K\lambda_i\sigma_i} \quad (2.12)$$

where N_i is the average atomic concentration, I_i is the intensity of photoelectrons, λ_i is the inelastic mean free path of a photoelectron, K is related to detection which should be consistent for a given measurement and σ_i is the photoionisation cross section. The photoionisation cross section is a measure of the photoelectrons generated for a specific orbital at a given photon energy.

2.4.5.3 Instrumentation

X-rays are generated by a metallic anode upon bombardment with high energy electrons. Electrostatic hemispherical analysers consist of two concentric hemispheres with radii R_1 and R_2 . Potentials applied to the hemisphere give an electrostatic field between them that disperses photoelectrons depending on their kinetic energy. Electrons entering the analyser with an energy E_0 at radius R_0 follow a circular path where E_0 is the pass energy, before entering the detector. A schematic of an XPS spectrometer is shown in Figure 2.9.

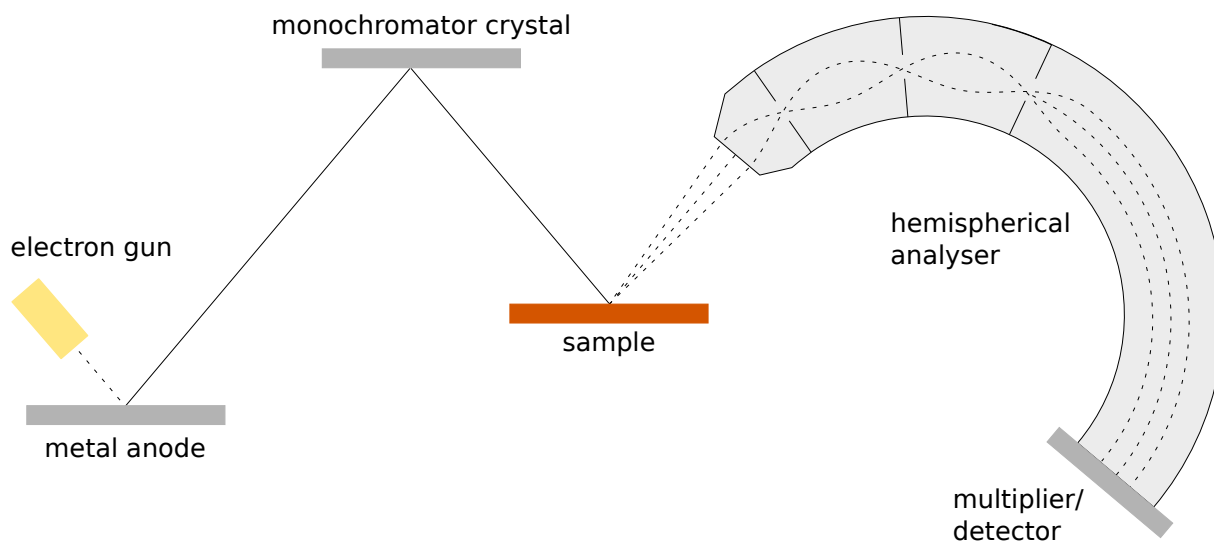


Figure 2.9: Schematic of an XPS spectrometer; monochromatic X-rays (generated through bombarding a metal target with high energy electrons) interact with the sample generating photoelectrons whose kinetic energies are measured.

2.4.5.4 Experimental settings

The surfaces of the deposits were characterised using a Thermo Scientific K-Alpha+ X-ray Photoelectron Spectrometer (base pressure 2×10^{-9} mbar) with a monochromated, microfocused Al $K\alpha$ source ($h\nu = 1486.6$ eV) and a 180° double focusing hemispherical analyser with a 2D detector. The X-ray source was operated with a 6 mA emission current and 12 kV anode bias. The samples were mounted with conductive carbon tape and a flood gun was used to minimise charging. Data collected at pass energy of 200 eV for survey and 20 eV for core level spectra (O1s, C1s and Fe2p) using an X-ray spot size of 400 m^2 .

2.4.5.5 Analysis

The background in XPS spectra originates from inelastic collisions of photoelectrons, lowering their kinetic energy. To account for this phenomenon several types of background are commonly used in XPS, each with their own limitations. A linear background is effective when there is a small difference in background height (small differences between E_{min} and E_{max}), but it is also poorly defined, the least accurate and does not mathematically relate to the process of inelastic scattering. On the other hand, the Tougaard background is based on the energy loss cross section; the probability that an electron undergoes a loss event and becomes part of the background. The Tougaard background works very well for some systems, for example semiconductors, but is however difficult to apply. The Shirley background is a non-linear background that increases with decreasing kinetic energy and is dependent on the signal. The origin of this is that the higher the signal intensity, the more electrons are decelerated by inelastic events at the same time; the Shirley background is commonly used for metals.

The C1s peak was fitted with a convolution of Lorentzian and Gaussian line shapes, a fitting parameter that is referred to as the L/G ratio. The Lorentzian line shape corresponds to the intrinsic line width caused by lifetime broadening, whilst the Gaussian line shape corresponds to the X-ray spread and spectrometer broadening.

These data were analysed with the Advantage software package; in the carbon peak fit, L/G ratios and FWHM were constrained to $\pm 2\%$ and ± 0.2 eV respectively for each substrate termination. The carboxylic peak at 288.5 eV was also constrained ± 0.2 eV. The spectra were aligned to the C1s core line binding energy assigned at 285.0 eV. Spectra were either normalised to the total area of the carbon, iron and oxygen signal or the peak fitted to the C-C oxidation state as stated in the text.

2.4.6 X-ray Absorption Spectroscopy (XAS)

In XAS, the absorption of the sample is measured as a function of incident photon energy. If the incident photon has an energy that is larger than the binding energy of the electron, the photon may be absorbed and a bound core electron will be lost. The attenuation of incident X-ray

photons within the material is given by Beer-Lambert's law in Equation 2.10. The absorption coefficient μ is a smooth function of energy with a value that depends on the sample density ρ , the atomic number Z , atomic mass A and the X-ray energy E , roughly as:

$$\mu \approx \frac{\rho Z^4}{AE^3} \quad (2.13)$$

The absorption coefficient has a strong dependence on both E and Z , with the Z^4 dependence resulting in absorption coefficients span several orders of magnitude. XAS can be used to selectively probe the electronic structure of any given element. Absorption energies are well known ($\pm 10\%$) and tabulated for different elements. The absorption edge refers to the sharp rise in absorption when the photon energy equals the binding energy of a core electron. In an isolated atom this would appear as a sharp step as electrons are promoted to the continuum. However, in reality, the exiting photoelectron will interact with other electrons in the material; there is a phase shift associated with scattering and thus the outgoing and scattered waves interfere producing complex spectra. Following absorption, the atom remains in the excited state for a few femtoseconds. The atom returns to the ground state through the emission of a photon (fluorescence) or an Auger electron.

As a result of the photoelectron scattering off neighbouring atoms and the subsequent interference of the outgoing and incoming wave, XAS spectra are sensitive to the formal oxidation state, nearest neighbour chemistry (amplitude), coordination chemistry (amplitude), nearest neighbour distances (frequency) of the probed atom. Therefore, from XAS insights into the chemical state and local atomic structure of the probed element can be attained.

2.4.6.1 Spectral Features

The spectral features discussed here are annotated on Figure 2.10. The absorption edge accounts for the step function in the X-ray absorption spectra, whereby core shell electrons are promoted to the continuum. The pre-edge is a small feature with slightly lower energy than the absorption edge which is caused by transitions between the threshold and the Fermi energy. The white line is the prominent peak above the edge, which are particularly commonly found for L or M

core electrons. The ‘near edge’ corresponds to characteristic features above the absorption edge. Interpretation of these spectra are split into two parts. X-ray absorption near edge spectroscopy (XANES) refers to the edge and the region near the edge, whereas extended X-ray absorption fine structures (EXAFS) refers to the oscillatory region further from the edge.

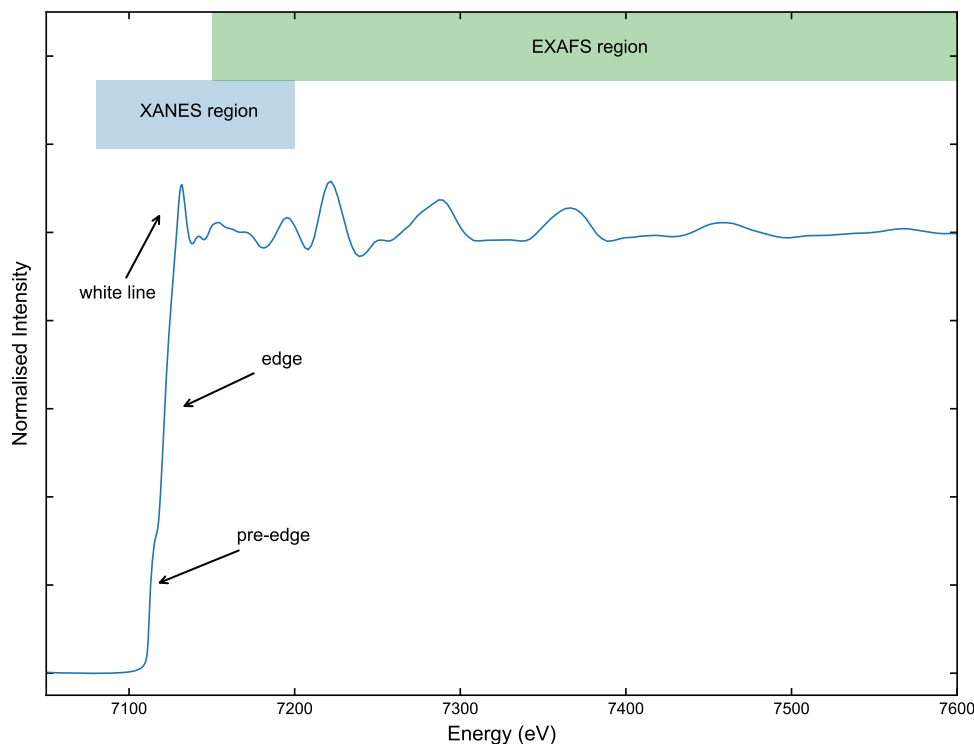


Figure 2.10: Annotated X-ray absorption fine structure spectra for an iron thin film highlighting key spectral features including the pre-edge, absorption edge, white line, and the XANES and EXAFS regions.

2.4.6.2 Analysis of XANES Data

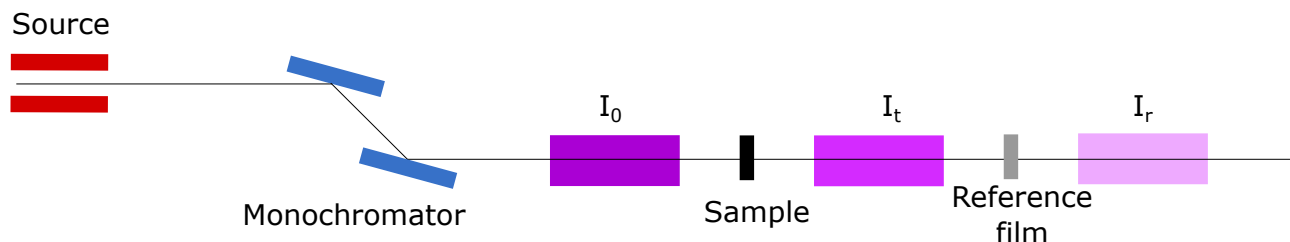
X-ray absorption near edge spectroscopy (XANES) was previously referred to as ‘near-edge X-ray absorption fine structure’ (NEXAFS). Following normalisation, where the edge-step is set to 1, there are several methods of data interpretation for XANES data, including fingerprinting, linear combination fitting, principal component analysis and peak fitting methods. Fingerprinting involves qualitatively comparing the measured spectra to reference standards, whilst linear combination fitting fits combinations of measured standards to the measured data. Principal component analysis can be used to determine the number of chemical environments within

the sample using an orthogonal mathematical basis to reconstruct the data. Peak fitting is often used to compare changes between characteristic peaks in spectra, whilst the modelling of XANES spectra is complex and not widely implemented.

2.4.6.3 Synchrotron Facilities

XAS is typically conducted at synchrotron facilities due to the requirement for an intense and energy-tunable X-ray source. The XAS experiments included in this work were performed on the MR-CAT beam line at the Advanced Photon Source (APS), Illinois, US and on the I20-scanning beam line at the Diamond Light Source, UK. A simplified schematic of the beam line configuration for XAS measurements in transmission mode is given in Figure 2.11a and fluorescence mode is given in Figure 2.11b. Measurements were taken at the iron edge (7.112 keV).

a)



b)

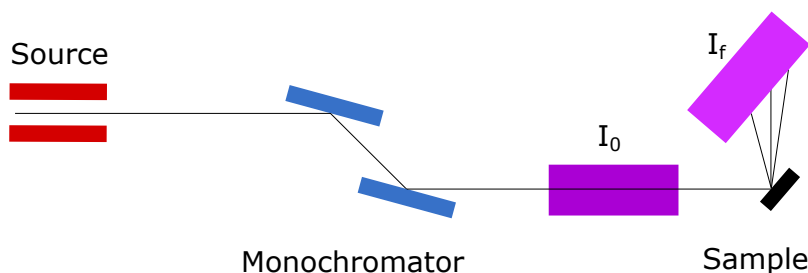


Figure 2.11: Simplified schematic of X-ray absorption spectroscopy beam lines for measurements in the a) transmission and b) fluorescence geometry. I_0 , I_t , I_r and I_f refer to ionisation chambers used for determining the intensity of the beam at its incident energy, following transmission through the sample, following transmission through a reference film and in the fluorescence geometry respectively.

Table 2.2: Scan parameters for EXAFS measurements at Diamond Light Source.

Start energy eV	End energy eV	Step size eV
6912	7072	5
7072	7098	5 – 0.4
7098	7126	0.4
7127	7129	0.5
7129	8000	0.5 – 4

2.4.6.4 Experimental Settings

On the MR-CAT beam line at the APS, measurements were taken in the transmission geometry (Figure 2.11a). Extended X-ray absorption fine structure measurements were taken from 6.9 keV to 7.7 keV with a step size of 0.25 eV. Each scan lasted 1 second; 10 scans were averaged for each sample to improve the signal to noise ratio. Measurements were aligned to the iron edge on the reference iron film.

On I20 at the Diamond Light Source, *ex situ* measurements were taken in both the transmission (Figure 2.11a) and fluorescence (Figure 2.11b) geometry whilst *in situ* measurements were performed in fluorescence mode. Extended X-ray absorption fine structure (EXAFS) measurements were taken for *ex situ* samples and before and after *in situ* experiments using the parameters shown in Table 2.2. As I20 is not a quick-EXAFS beam line, the scan parameters were varied, as shown in Table 2.3, to achieve a faster scan speed for *in situ* measurements.

2.4.7 Grazing Incidence Wide Angle X-ray Scattering (GI-WAXS)

WAXS is commonly used to qualitatively compare the degree of crystallinity between different samples, to determine the lattice spacing of observable peaks and to determine the grain size or coherence length. The coherent scattering of X-rays, illustrated in Figure 2.8, can be used to obtain information on both crystalline and amorphous samples. As X-rays propagate through crystalline materials, some X-rays are diffracted by periodic planes of atomic or molecular

Table 2.3: Scan parameters for XANES measurements at Diamond Light Source.

Start energy eV	End energy eV	Step size eV
7000	7100	5
7100	7150	0.5
7150	7200	1.5
7200	7248	3
7248	7250	2
7250	7345	2

species.¹⁶ A spot of high intensity X-rays is produced by the constructive interference of scattered X-rays from adjacent planes, according to Bragg's law:

$$n\lambda = 2d\sin\theta \quad (2.14)$$

where n is the order of diffraction, λ is the X-ray wavelength, d is the inter-planar spacing and θ is the X-ray incident angle. The diffraction angle is related to the inter-planar spacing while the direction of the diffracted beam is related to the the orientation of the planes.¹⁶ The magnitude of the scattering vector is:

$$q = \left(\frac{4\pi}{\lambda}\right)\sin\theta \quad (2.15)$$

for a given scattering angle 2θ and an X-ray wavelength λ .¹⁶ The Bragg condition is:

$$q = q_B = \frac{2\pi}{d_{hkl}} \quad (2.16)$$

where h, k, l are the Miller indices for particular planes whilst q_B is orthogonal to the lattice planes, which are spaced by d_{hkl} .¹⁶ In WAXS, scattered X-rays are typically measured at angles larger than 5° by an area detector at a camera length of 0.3 – 1 m as shown in Figure 2.12. The scattering resolution of the recorded profile depends on the detector, source intensity, diffracting volume and crystalline quality,¹⁶ In contrast, in small angle X-ray scattering (SAXS),

the scattering intensity is typically measured at angles close to 0° with the detector at a camera length of 1 – 4 m.

2.4.7.1 Synchrotron Facilities

The GI-WAXS measurements presented in this work were performed on the SAXS/WAXS beam line at the Australian Synchrotron. A simple schematic of the set up is given in Figure 2.12. Using an area detector, enables data to be rapidly collected over a large range of scattering angles, however these measurements have lower accuracy and resolution than point detectors.¹⁶

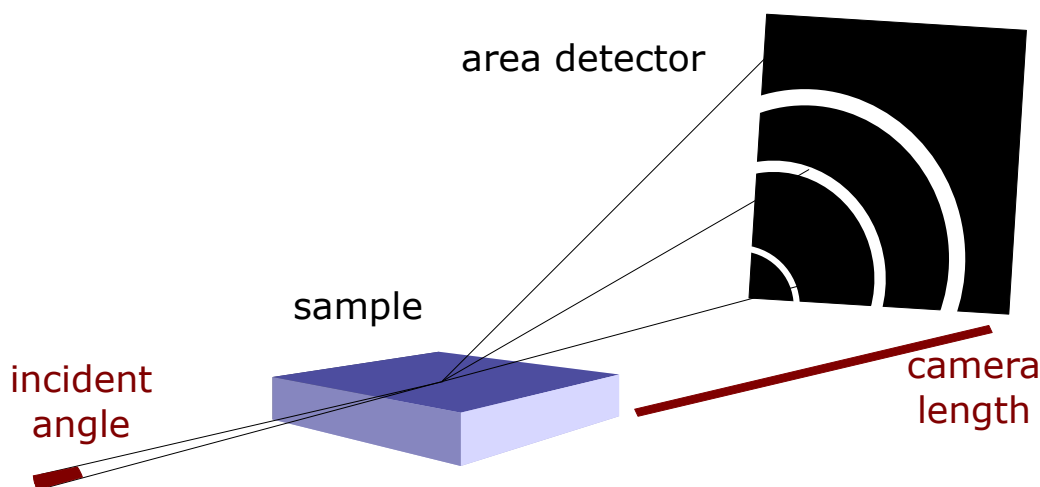


Figure 2.12: Simplified schematic of a grazing incidence wide angle scattering set up with a 2D area detector. The incident angle α is typically below 3° , the camera length is typically 0.3–1 m

2.4.7.2 Experimental Settings

Measurements were taken at the a beam energy of 20 keV. Incident angles of 0.1, 0.11, 0.12, 0.13, 0.14, 0.15, 0.16, 0.17, 0.18, 0.19, 0.2, 0.25, 0.3, 0.5, 1.0° were measured for *ex situ* samples, before and after *in situ* experiments as well as following a realignment of the beam onto the sample surface during *in situ* experiments. *In situ* measurements were taken at an incident angle of 0.15° . All scan lasted for 1 second.

2.4.8 Scanning Electron Microscopy (SEM)

Scanning electron microscopy is an imaging technique that uses a focused electron beam, as opposed to photons, as an illumination source to acquire surface-sensitive information on the

morphology and composition of a sample.

A beam of high energy electrons is produced by a field emission gun and accelerated by an electric field (1 – 30 kV) towards the sample through the electron column. Field emission guns have the advantage over other electron sources of increased spatial resolution and improved signal-to-noise ratio. The beam is focused and directed by a series of electromagnetic lenses. The interaction of the electron beam with the sample surface can produce secondary electrons, backscattered electrons and characteristic X-rays, each providing different and independent insights into the sample. Wave-particle duality enables electrons to image features on the nanometer-scale due to the wavelength of electrons being orders of magnitude smaller (approximately 0.012 nm) than visible light photons. The sample is measured under high vacuum to ensure a sufficiently long mean free path. An image is measured by rastering the electron beam across the sample surface and measuring the signal received. Two detectors are used in this work, the in-lens detector that detects high angle electrons and a detector to the side of the chamber detecting electrons emitted at lower angles. The interaction volume is dependent on the sample density, the Z-number of the material and is proportional to the acceleration voltage of the electrons.

The characteristic X-rays mentioned above, which are used to acquire elemental maps and quantification, will not be discussed here.

2.4.8.1 Secondary Electrons

Secondary electrons are emitted as a result of inelastic scattering interactions between the incident electron beam and valence electrons on the sample. Secondary electrons have a kinetic energy of <50 eV by definition and typically originate from the outermost surface due to the energy required to escape the surface.¹⁷ Escape depths of between 5 – 50 nm are reported depending on the material.¹⁷ The generation of secondary electrons is highly dependent on the incident angle of the electron beam, with electrons that travel a greater distance close to the surface generating more secondary electrons. More secondary electrons will originate from edges, ridges and corners leading to brighter areas on the images and hence providing topographical contrast but no chemical information.

2.4.8.2 Backscattered Electrons

Backscattered electrons (BSE) are incident electrons that have been reflected or deflected as a result of elastic scattering by the electron clouds within the sample. Backscattered electrons are significantly higher in energy than secondary electrons, they tend to scatter at high angles and are produced over a much larger depth range.¹⁷ Sample atoms with a higher number of electrons will have a larger scattering cross section and therefore a greater probability of elastic collision.¹⁷ The contrast for backscattered electrons is related to the atom size and therefore provides a very crude indication of varying chemical composition.

2.4.8.3 Experimental Parameters

A LEO Gemini 1525 FEG-SEM system (Carl Zeiss AG, Germany) was used in this work to image deposits formed on iron substrates. Samples were measured at 10^{-6} mbar with a 5 keV electron beam at working distances between 5 – 7 mm. Images for secondary electrons and backscattered electrons were measured for all samples. Samples were mounted using conductive carbon tape and coated with 10 nm of chromium using a Quorum Technologies Q150T S turbomolecular-pumped coating system.

References

- (1) Kendrick, E. A Mass Scale Based on $\text{CH}_2 = 14.0000$ for High Resolution Mass Spectrometry of Organic Compounds. *Analytical Chemistry* **1963**, *35*, 2146–2154.
- (2) Hughey, C. A.; Hendrickson, C. L.; Rodgers, R. P.; Marshall, A. G.; Qian, K. Kendrick Mass Defect Spectrum: A Compact Visual Analysis for Ultrahigh-Resolution Broadband Mass Spectra. *Analytical Chemistry* **2001**, *73*, 4676–4681.
- (3) Briggs, D, *Surface Analysis of Polymers by XPS and Static SIMS*, eng; Cambridge solid state science series; Cambridge University Press: Cambridge, 1998.
- (4) Vickerman, J. C.; Briggs, D., *ToF-SIMS : Materials Analysis by Mass Spectrometry*, eng, 2nd edition., 2013.
- (5) Briggs, D; Hearn, M. Interaction of ion beams with polymers, with particular reference to SIMS. *Vacuum* **1986**, *36*, 1005–1010.
- (6) Fearn, S., *An Introduction to Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and its Application to Materials Science*; 2053-2571; Morgan & Claypool Publishers: 2015.
- (7) Kayser, S.; Rading, D.; Moellers, R.; Kollmer, F.; Niehuis, E. Surface spectrometry using large argon clusters. *Surface and Interface Analysis* **2013**, *45*, 131–133.
- (8) McPhail, D. S. Applications of Secondary Ion Mass Spectrometry (SIMS) in Materials Science. *Journal of Materials Science* **2006**, *41*, 873–903.
- (9) Winters, H. F.; Coburn, J. W. Influence of the altered layer on depth profiling measurements. *Applied Physics Letters* **1976**, *28*, 176–179.
- (10) Wagner, M. S.; Graham, D. J.; Ratner, B. D.; Castner, D. G. Maximizing information obtained from secondary ion mass spectra of organic thin films using multivariate analysis. *Surface Science* **2004**, *570*, 78–97.
- (11) Graham, D. J.; Wagner, M. S.; Castner, D. G. Information from complexity: Challenges of TOF-SIMS data interpretation. *Applied Surface Science* **2006**, *252*, 6860–6868.

- (12) Stephan, T.; Zehnpfenning, J.; Benninghoven, A. Correction of dead time effects in time-of-flight mass spectrometry. *Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films* **1994**, *12*, 405–410.
- (13) Langer-Hansel, K.; Schintlmeister, A.; Fleig, J.; Hutter, H. Oxygen transport in electroceramics investigated by electrochemical $^{18}\text{O}/^{16}\text{O}$ isotope exchange and ToF-SIMS. *Surface and Interface Analysis* **2013**, *45*, 486–489.
- (14) Bro, R.; Smilde, A. K. Centering and scaling in component analysis. *Journal of Chemometrics* **2003**, *17*, 16–33.
- (15) Seah, M. P.; Dench, W. A. Quantitative electron spectroscopy of surfaces: A standard data base for electron inelastic mean free paths in solids. *Surface and Interface Analysis* **1979**, *1*, 2–11.
- (16) Rivnay, J.; Mannsfeld, S. C. B.; Miller, C. E.; Salleo, A.; Toney, M. F. Quantitative determination of organic semiconductor microstructure from the molecular to device scale. *Chemical Reviews* **2012**, *112*, 5488–5519.
- (17) Goldstein, J.; Newbury, D. E.; Joy, D.; Lyman, C. E.; Echlin, P.; Lifshin, E.; Sawyer, L.; Michael, J. R., *Scanning Electron Microscopy and X-ray Microanalysis*, eng, 3rd ed.; Plenum Press: New York ; London, 2003.

Chapter 3

Identifying A Model Engine Surface

3.1 Overview

The use of a model system to understand the depositions mechanism reveals key parameters by reducing the intrinsic complexity of hydrocarbon stream systems. Hexadecane was identified by BP as a diesel-range molecule, representing the chemical and physical properties of diesel. Injectors are made of a steel containing 13 % chromium referred to as Fe-13Cr. This chapter focuses on characterising the Fe-13Cr steel under engine-relevant conditions to identify a model surface for subsequent studies with hexadecane.

3.2 Aims and Experimental Details

1. Determine the elemental composition of the surface of a Fe-13Cr substrate (Section 3.4)
 - *Substrate:* Fe-13Cr.
 - *Sample preparation:* Polished (Section 2.2.2) and heat treated under vacuum (Section 2.2.3).
 - *Characterisation:* SIMS (Section 2.4.3.8); TEM.
2. Characterise three model iron surfaces for subsequent studies (Section 3.5)

- *Substrate:* 99.9 % iron substrate.
- *Sample preparation:* i) Polished substrate (Section 2.2.2); ii) Annealed substrate — heat treated under vacuum — (Section 2.2.2 and Section 2.2.4) and iii) Oxidised substrate — heat treated in air — (Section 2.2.2 and Section 2.2.4).
- *Characterisation:* SEM (Section 2.4.8.3); SIMS (Section 2.4.3.8); XPS (Section 2.4.5.4 and Section 2.4.5.5).

3.3 Literature Review

Steels are ferrous alloys in which the composition of alloying elements is determined by the desired mechanical and chemical properties of the steel. Some alloying elements include chromium, nickel, molybdenum, aluminium, manganese, carbon and sulfur. Chromium-rich steels are used for their corrosion-resistant properties, afforded by a passive oxide layer which forms on these steels. Often referred to as a passive film or oxide, and sometimes scale, the passive oxide acts as a kinetic barrier to dissolution as a result of the very low rate of metal dissolution through the layer.¹ Under atmospheric conditions, films forming on iron do not have passive characteristics and are commonly known to enable elements, such as carbon and sulphur, to penetrate into the bulk through pores and channels.² It is however possible to form passive films on iron substrates under specific conditions through electrochemical processes or the use of highly oxidising agents.¹

The term stainless steel refers to iron-chromium alloys that have the necessary atomic percentage of chromium for a passive chromium oxide film to form spontaneously.¹ The minimum atomic percentage of chromium required for a passive film to spontaneously form in a ferritic iron alloy was reported as 11 at.% by Ostwald *et al.*,² however there is some disagreement over the atomic percentage of chromium required. The passive properties of this surface scale are of paramount importance to a number of industries, however the mechanism that enables this behaviour is poorly understood, partly due to difficulties with studying an oxide layer that is typically 1 – 4 nm thick.¹ An understanding of the oxides formed on chromium-containing steels is required for developing a model system for subsequent studies of deposition.

3.3.1 The Formation of a Surface Oxide

The formation of oxide layers on metals has been determined to consist of four main stages on metals with moderate reactivity such as nickel; these are:^{3,4}

1. Primary dissociative chemisorption of environmental oxygen occurs relatively quickly on the metal surface as shown in Figure 3.1a.⁴
2. Adsorption will continue until a 2-D layer of oxygen covers the surface;⁵ this process is accompanied by a reduction in oxygen reactivity as the surface becomes saturated and oxide islands begin to form (Figure 3.1b).⁴
3. A thin oxide forms due to lateral growth of oxide islands (Figure 3.1c) and hence the oxygen uptake increases to a constant level.^{4,6}
4. Following the formation of a film that covers the surface, an inhomogeneity, such as a surface defect, grain boundary or dislocation, will nucleate three-dimensional oxide growth as shown in Figure 3.1d.^{6,7}

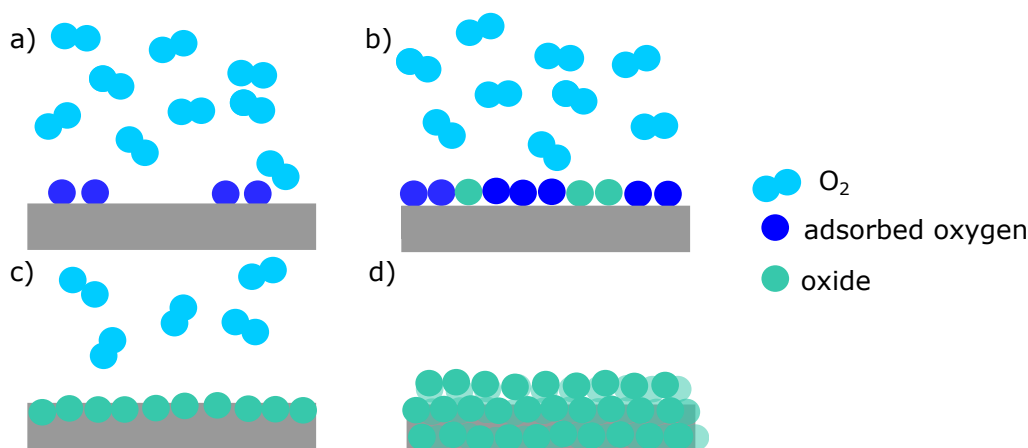


Figure 3.1: Schematic showing the four main stages in the formation of oxide layers on metal surfaces. These illustrations represent the a) Dissociative chemisorption of oxygen on the metal surface, b) Adsorption of oxygen until a 2D layer covers the surface and oxide islands begin to form, c) Formation of a thin oxide by lateral growth of islands and d) A three dimensional oxide whose growth was nucleated by a surface defect

On more reactive surfaces, such as chromium and iron, it is difficult to resolve the first three steps.⁴ In an alloy, the composition of the thin oxide formed in stage three is related to the bulk

Table 3.1: The free energies for oxide formation, ΔG_f , for various different oxides.⁹

	Cr ₂ O ₃	Fe ₂ O ₃	Fe ₃ O ₄
ΔG_f (kcal mol ⁻¹)	253	177	243

composition. A transient oxide is formed on alloys, which may be less stable than protective oxides formed on single-component metals.⁶ Further growth of the surface oxide requires the combination of oxide and metal ions from opposing sides of the oxide scale (it becomes diffusion controlled); with the rate diffusion limited, oxide growth is relatively slow at low to intermediate temperatures.⁷ As metal and oxide ions are believed to react very quickly, the rate determining step for oxide growth is the lattice diffusion of these reacting ions/atoms, as outlined by Wagners theory.⁷ The diffusion rates of different ions and their oxygen affinities govern the composition of the oxide film formed.

3.3.2 Solid State Diffusion

Three-dimensional growth of the film is driven by the free energy change associated with the formation of a metal oxide; the values for the free energies of chromia (Cr₂O₃), hematite (Fe₂O₃) and magnetite (Fe₃O₄) are given in Table 3.1.⁷ The transport of metal ions, from the bulk, and oxygen ions, from the surface, across the oxide, which is required for the further growth of the oxide layer, facilitates the formation of the protective oxide from the initial transient oxide.^{6,7} As well as lattice diffusion, other pathways such as oxide grain boundaries may facilitate transport.^{7,8} The overall result is a concentration gradient of oxygen and metal through the oxide layer, with the higher concentrations of oxygen at the atmosphere-oxide interface decreasing towards the metal-oxide interface.⁷

Defects within the lattice facilitate diffusion;⁷ ions and atoms will diffuse along dislocations and grain boundaries as these areas have lower densities than the grains themselves. Surface treatments such as polishing, electropolishing and machining can introduce dislocations at the surface which then provide fast diffusion pathways for scale-forming elements such as chromium, manganese, silicon and aluminium.^{2,6}

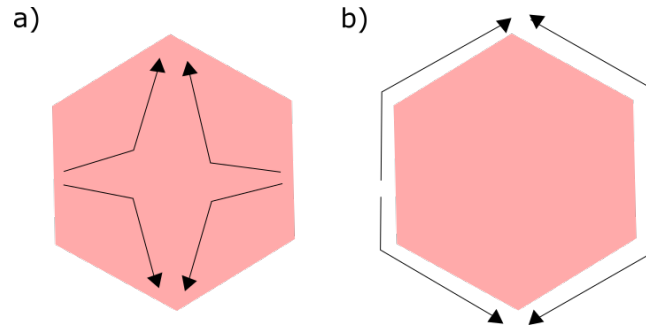


Figure 3.2: Schematic of diffusion mechanisms through the steel a) volume or lattice diffusion through the bulk b) solid state diffusion along grain boundaries.

The microstructure of the steel influences diffusion as a finer microstructure will result in multiple grain boundaries and sub-grain boundaries, providing fast diffusion paths for scale-forming elements.^{6,10} The oxidation temperature determines the microstructure; a finer microstructure will form when the oxidation temperature is higher than the re-crystallisation temperature.⁶ An extreme case of this was demonstrated by Xia *et al.* who used a mechanical treatment of the steel (surface mechanical attrition treatment SMAT) to produce a nanocrystalline structure on martensitic steel.¹¹ The rate of diffusion was greatly increased, with fast oxidation occurring both in the early stages of oxidation and in the growth of the film.^{11–13} The diffusivity of chromium increases by 4-5 orders of magnitude compared to conventional treatments, while iron and oxygen experience significant enhancements.^{11,14}

The solid-state diffusion mechanisms outlined above are also known as short circuit diffusion; diffusion occurs along grain boundaries, surfaces or dislocations as shown in Figure 3.2b. Volume or lattice diffusion is another mechanism whereby diffusion occurs through the bulk of the lattice, as shown in Figure 3.2a.¹⁵ Lattice diffusion occurs through the movement of point defects; the mechanism depends on the type of defect, such as vacancy or interstitial mechanisms.⁷

3.3.3 Factors Influencing Oxygen Diffusion

Elements are selectively oxidised depending upon the enthalpy of metal-oxide bond formation, as shown in Table 3.2. Manganese and chromium are preferentially oxidised over iron which is the bulk material in steels.^{4,16} Nickel has the lowest bond energy and hence is often observed as a metallic nickel enriched layer beneath the oxide.⁴ In addition, chromium is often depleted

Table 3.2: Enthalpy of formation of metal oxide bonds according to the NBS Tables of Chemical Thermodynamic Properties.¹⁷

	Cr	Mn	Fe	Ni
ΔH_f (M-O) (kJ mol ⁻¹)	-383	-385	-272	-240

beneath the oxide layer due to oxide-induced chromium segregation, meaning the chromium near the surface has diffused towards the oxide layer and oxidised, leaving a chromium deficient area beneath the oxide.⁴ Transport of metal ions towards the oxide and oxygen ions towards the bulk is required for further film growth; the transport of metals prevents the depletion of elements below the film.

3.3.4 Factors Influencing Metal Diffusion

Iron ions are known to be mobile in steel at relatively low temperatures, with iron mobility observed between 50°C and 150°C.¹⁸ Chromium however requires significantly higher temperatures for significant ion mobility; typically temperatures higher than 700°C are required to avoid chromium depletion beneath the oxide.^{2,18} However from observations relating to film thickness, chromium ion mobility has been suggested to occur at temperatures as low as 350°C.¹⁹ At temperatures where chromium has limited mobility, some chromium oxide will form at the metal/oxide interface, but iron oxides will dominate.^{19,20} Therefore, at low temperatures iron oxides are formed, whereas at high temperatures the formation of chromium oxide (Cr₂O₃-based) is more favourable than the formation of iron oxide.^{19,21,22}

Whilst iron and chromium ions are transported through the steel along fast diffusion pathways such as grain boundaries, manganese is predominantly transported by lattice/volume diffusion, as reported by Doyle *et al.* following a study using radiotracers.¹² The rate of manganese transport to the surface is higher than that of iron and chromium, resulting in the formation of surface manganese oxides.^{6,12}

In general metal ions can continue to pass through the passive layer, albeit at reduced rate. Chromia acts as a passive film with an extremely low rate of metal dissolution through the layer.¹ It provides a barrier to ion diffusion, even for elements as small as hydrogen.²³ An

approximately stoichiometric film will ensure the lattice transport of metal and oxide ions is low (minimisation of lattice defects).²⁴

Kurokawa *et al.* determined the relative speeds of metal ion diffusion through the chromia layer to be: $D_{Mn} > D_{Fe} > D_{Ni} > D_{Cr}$.^{6,25} Manganese can rapidly diffuse through the chromia layer using vacant cation lattice sites which, combined with manganese's low solubility in chromia, results in an outer manganese oxide.⁶ At long timescales, the concentration of manganese at the surface will be enhanced by the continued diffusion of manganese, leading to depletion in the bulk.² A thick inner chromia layer will reduce the amount of manganese formed, by limiting the flux of manganese ions towards the surface.⁶

3.3.5 A Limiting Oxide Thickness

The native oxide has a limited thickness (typically reported as ~ 4 nm) due to the diffusion limit of oxygen across the layer.²⁶ As mentioned above, the diffusion of ions is widely accepted to be the rate determining step in oxidation and thus, the rate of oxidation is proportional to the ion flux across the oxide scale.^{6,7} As the limiting oxide thickness is reached, the kinetics depart from dependence on the diffusion rate of ions.²⁷ Through observing a change in kinetics upon reaching the limiting oxide thickness, Tedmon found that the limiting oxide thickness increases as a function of temperature, with the limiting oxide thickness reached more rapidly at higher temperatures.²⁷

3.3.6 Structure of Surface Oxides

The structures of oxides commonly found on steel will be discussed; these structures include spinel-type structure, chromia and other iron oxides including hematite, magnetite, maghemite and wüstite.

3.3.6.1 Spinel Structures

Spinel structures commonly have the formula $(A^{2+})(B^{3+})_2O_4$, where the O^{2-} anions are packed into a face-centred cubic lattice, with the cations partially occupying both tetrahedral ($\frac{1}{8}$ of the available sites) and octahedral ($\frac{1}{2}$ of the available sites) holes in this lattice, for example

$(\text{Fe}^{2+})_{tet}(\text{Fe}^{3+})_{oct}(\text{Fe}^{3+})_{oct}\text{O}_4$ for normal spinels. In a normal spinel structure, divalent cations occupy the tetrahedral sites whilst trivalent cations occupy the octahedral sites. However, in an inverse spinel, $\text{B}(\text{AB})\text{O}_4$, the divalent cations occupy the octahedral sites along with half of the trivalent: $(\text{Fe}^{2+})_{oct}(\text{Fe}^{3+})_{oct}(\text{Fe}^{3+})_{tet}\text{O}_4$. The remaining trivalent cations occupy the tetrahedral sites. Most iron-containing spinels have an inverse spinel structure; for example in magnetite (Fe_3O_4). More complex spinel-type structures have been observed as the outer oxide on the surface of steels as discussed above, for example $(\text{Mn,Fe})\text{Cr}_2\text{O}_4$, whereby Mn^{2+} and/or Fe^{2+} and Cr^{3+} occupy the octahedral sites whilst Cr^{3+} occupies the tetrahedral sites.²

3.3.6.2 Chromia

Chromia (Cr_2O_3) is believed to act as a passive layer reducing ion transport between the surface and the bulk metal. Above 700°C , chromia will form at the surface, whilst at lower temperatures, chromia is observed beneath a surface iron oxide. The oxygen anions form a hexagonal close-packed lattice and Cr^{3+} ions fill two thirds of the octahedral sites.

3.3.6.3 Wüstite

In a stoichiometric FeO , Fe^{2+} cations fill all the octahedral holes in a cubic close packed oxygen lattice.²⁸ Wüstite (Fe_{1-x}O) however is not stoichiometric with x varying between 0.05 and 0.15 leaving some octahedral sites empty.²⁸ The discrepancy in charge is compensated for by the oxidation of Fe^{2+} to Fe^{3+} . A schematic of the structure of wüstite is shown in Figure 3.3a.

3.3.6.4 Magnetite

As mentioned above, magnetite (Fe_3O_4) has an inverse spinel structure; the oxygen anions form a close-packed face-centred cubic lattice with divalent iron ions in octahedral sites and trivalent iron ions divided between the octahedral and tetrahedral sites: $(\text{Fe}^{3+})_{tet}(\text{Fe}^{3+}\text{Fe}^{2+})_{oct}\text{O}_4$.²⁸ In between the oxide layers, iron ions form two types of layers as shown in Figure 3.3b: Kagom layers and mixed trigonal layers.²⁸ Kagom layers are dense, containing multivalent iron ions in octahedral sites; one third are divalent, whilst the remaining two thirds are in a $3+$ oxidation state.²⁸ Between the Kagom layers there are three trigonal layers forming a sandwich of tetrahedrally

coordinated Fe^{3+} ions on the outside, with a middle layer of octahedrally coordinated Fe^{3+} .²⁸

3.3.6.5 Hematite

Haematite ($\alpha\text{-Fe}_2\text{O}_3$) has a rhombohedral corundum structure; oxygen anions are arranged in a hexagonal close packed (hcp) lattice with Fe^{3+} ions in two thirds of the octahedral sites as shown in Figure 3.3c.²⁸

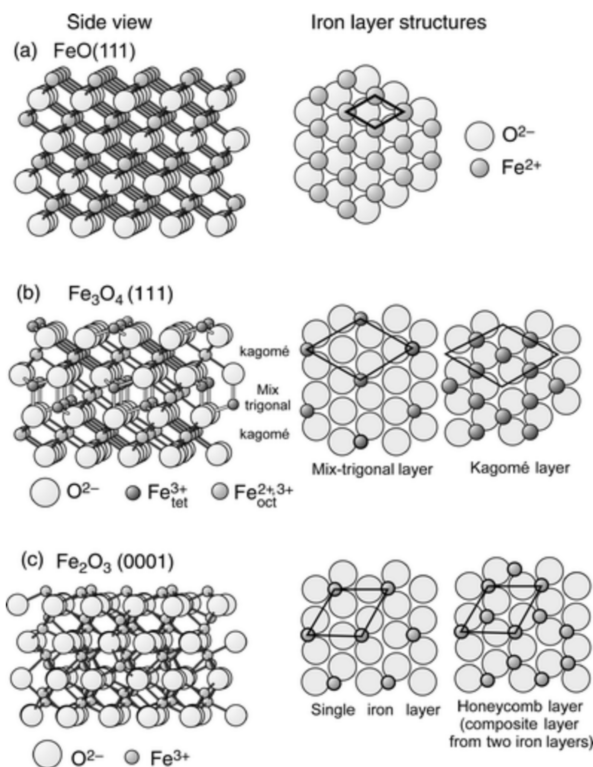


Figure 3.3: Schematics of side views and top views of a) $\text{FeO}(111)$; b) $\text{Fe}_3\text{O}_4(111)$ and c) $\alpha\text{-Fe}_3\text{O}_4(0001)$. Reprinted with permission from [28].

3.3.6.6 Maghemite

Maghemite ($\gamma\text{-Fe}_2\text{O}_3$) has the same formula as hematite (Fe_2O_3), however adopts an inverse spinel structure similar to magnetite. It can be considered an iron(II)-deficient magnetite, with trivalent cations (and vacancies) occupying both tetrahedral and octahedral sites.²⁹

3.3.7 Case Studies

The chemistry and structure of the oxide layer forming on steels has been found to be highly dependent on the steel composition, its thermal history, the type of oxidising gases used, the concentration of oxidising gases and any surface pre-treatments. Whilst the composition of the engine steel Fe-13Cr is known, there is no further information on the thermal or processing history of this steel before it is used in engines. Here we review studies on a variety of steels to evaluate how these different factors govern the surface and near-surface composition and structure in these highly complex systems.

3.3.7.1 Temperature

Table 3.3 provides a summary of the work discussed in detail here. As mentioned above, there are a plethora of factors that can influence the nature and composition of the oxide forming on the surface of steels. However, regardless of the oxidising conditions and the composition of the steel, some general trends relating to temperature are observed. For example, at low temperatures, due to iron's high mobility the steel surface tends to form iron oxides regardless of its composition. Similarly, above 700°C, where chromium's ion mobility is high, chromia tends to form on the surface.

Greeff *et al.* studied the oxidation of sputter-cleaned Fe-9Cr-1Mo steel at temperatures from 157°C to 758°C following exposure to 1000 L of oxygen at a pressure of 1.1×10^{-5} Pa *in situ* using XPS and Auger Electron Spectroscopy (AES).²⁰ A summary of their work is given in Figure 3.4. At 157°C and low oxygen exposures (2 L), the concentration of oxygen at the surface linearly increases as oxygen covers the surface, nucleating the lateral growth of oxide islands as shown in Figure 3.1.²⁰ The surface concentration of oxygen then continues to increase as determined by the diffusion of ions through the film, reaching a steady state following 200 L of oxygen.³⁰ The ratio of iron to oxygen then remains constant after exposure to 200 L of oxygen.²⁰ No chromium can be detected after 1000 L of oxygen exposure at 157°C.³⁰

At 481°C, a different trend is observed; Greeff *et al.* attributed this to their earlier work, which found the increased mobility of sulfur at this temperature resulted in site competition between sulfur and chemisorbing oxygen, which was accompanied by a decrease in diffusion as

Table 3.3: Summary of findings on the effect of temperature on surface oxide.

Temp. (°C)	Steel	Oxide	Reference
50	Fe-20Cr-18Ni	magnetite surface oxide	[19]
	Fe-40Cr	mostly hematite with some chromia	[9]
157	Fe-9Cr-1Mo	surface iron oxide, no Cr detected	[20, 30]
164	Fe-9Cr-1Mo	spinel surface and chromia sub-surface, total oxide thickness - 9.5 nm	[19, 30]
275	Fe-40Cr	iron oxide surface, chromium oxide sub-surface	[9]
300	Fe-20Cr-18Ni	oxide thickness 29 Å, chromia rich layer on surface	[19]
350	Fe-(18-20)Cr-(8-10)Ni	Mn and Cr rich surface	[9]
445	Fe-40Cr	chromia surface, iron barely detectable at surface	[9]
450	Fe-(18-20)Cr-(8-10)Ni	Cr concentration increases	[9]
481	Fe-9Cr-1Mo	iron oxide surface layer, sub-surface chromium containing layer	[20, 30]
484	Fe-9Cr-1Mo	5 at. % chromium at the surface, diffuse interface between oxide and alloy, total oxide thickness - 60 nm	[20, 30]
726	Fe-9Cr-1Mo	chromia surface, no iron oxide	[20, 30]
758	Fe-9Cr-1Mo	increase in chromium oxide observed at surface	[20, 30]
800	Fe-(16-18)Cr/ Fe-19Cr/Fe-22Cr	outer Mn-rich spinel (Cr,Mn) ₃ O ₄ , inner Cr-rich chromia Cr ₂ O ₃	[6]

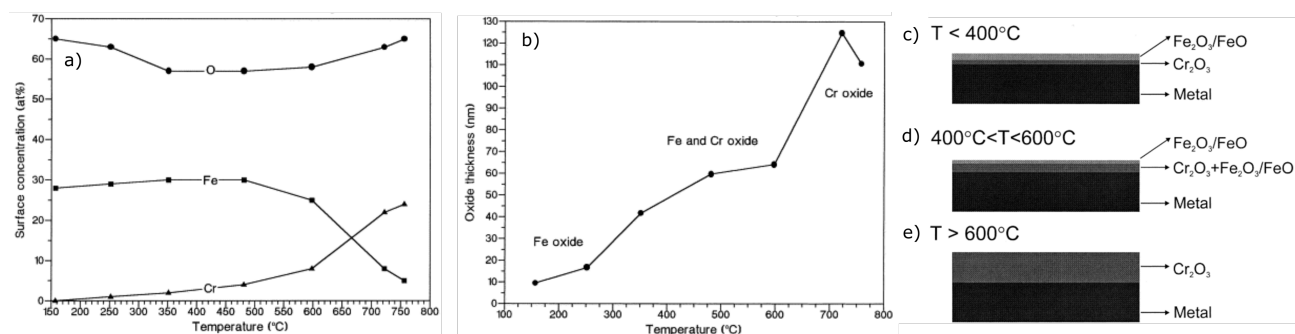


Figure 3.4: a) Plot of surface concentration of oxygen, chromium and iron in Fe-9Cr-1Mo as determined by AES at increasing temperatures. b) Plot of the oxide thickness at increasing temperatures. Schematic of the surface oxide at temperatures: c) below 400°C ; d) between 400°C and 600°C and e) above 600°C . Reprinted with permission from [20].

sulfur provides a diffusion barrier.^{20,30} At 481°C , chromium is initially observed in the oxide layer, but as the oxide layer increases in thickness the concentration of chromium decreases.²⁰ This is consistent with other findings of a surface iron oxide and a sub-surface chromium-containing oxide.⁹

At 758°C , chromium is preferentially oxidised and its mobility increases significantly with temperature resulting in a significant increase in chromium oxide.²⁰ At room temperature, 0 at.% chromium was observed, which gradually increases up to 600°C , when there is a significant increase in chromium at the surface, which is accompanied by a drop in the surface concentration of iron.²⁰ These findings are supported by other studies.²¹

As well as studying the surface chemistry, Greeff *et al.* investigated the composition of the oxide as a function of depth. Following exposure to 1000 L of oxygen, XPS and AES depth profiles through the oxide scale, at approximately 164°C , 484°C and 726°C , found the composition and relative ordering of the film to changes with temperature. At temperatures below 200°C the surface is iron oxide with a sub-surface mixed chromium and iron oxide approximately 9.5 nm in thickness, assigned to have a spinel and chromia structure respectively.^{19,30} At 484°C the concentration of chromium at the surface increases to 5 at.% due to chromium's enhanced mobility, with the concentration of chromium increasing towards the bulk. At this temperature, the oxide layer has grown in thickness to 60 nm, the surface is predominantly iron oxide and the distinction between the oxide and the metal interface becomes more diffuse. Above 720°C chromia is observed at the surface, with no iron oxides present, due to the thermodynamic

stability of chromium oxide and chromium's fast diffusion to the surface at these temperatures.

Cooper *et al.* studied the oxide layer forming on three stainless steels (Fe-(16-18)Cr, Fe-19Cr and Fe-22Cr) at 800°C.⁶ Using X-ray diffraction they observed an outer and inner oxide with a spinel structure (Cr,Mn)₃O₄ and chromia structure (Cr₂O₃) respectively. At 800°C a chromium-rich iron-depleted oxide layer is expected due to chromium's high bond formation energy and high mobility at these temperatures. Cross-sectional SEM-EDX maps showed chromium to be primarily localised in the inner oxide with manganese localised in the outer oxide. The concentration of manganese decreased from the surface towards the bulk, due to the fast diffusion of manganese to the surface and the thermodynamic stability of manganese oxides. SEM-EDX also showed the inner chromium layer to be a continuous structure whilst Cr-Mn spinel particles were observed on the outer layer. Upon exposure of a sputter-cleaned surface to oxygen at 800°C, islands of spinel structure formed immediately on the surface.

Van Staden *et al.* used AES to follow the formation of an oxide on sputter cleaned chromium-rich steel (Fe-40Cr) exposed to low partial pressures of oxygen (1.33×10^{-6} Pa) from room temperature to 657°C.⁹ Below 50°C at oxygen exposures above 30 L, the surface is mostly haematite (Fe₂O₃) with some chromia. At both 270°C and 445°C, chromium oxidation occurs with 0.6 L of oxygen, with no further changes after 2.5 L of oxygen. Iron oxide formation begins upon 10 L of oxygen exposure at 270°C. Despite chromium oxide forming first on the surface at 275°C due to its high free energy of formation (Table 3.1), following long oxygen exposures iron oxide will cover the chromium oxide layer forming a film at the surface. At 445°C, the iron is barely detectable at the surface; with surface ratios of Cr/Fe = 5.1, the iron does not undergo oxidation. At 450°C, the surface remains as Cr₂O₃ due to the enhanced mobility of chromium ions. Under all the conditions discussed, iron oxidation occurs following the complete oxidation of surface chromium.

Through heating the 304-steel (Fe-(18-20)Cr-(8-10)Ni) under vacuum (partial pressure 1×10^{-4} Pa) Doyle *et al.* observed similar trends using XPS.¹² Above 350°C the concentration of iron at the surface decreased with a corresponding increase in the manganese and chromium concentrations at the surface. Upon heating, the Fe(0) peak on the XPS corresponding to metallic iron increases due to the diffusion of metallic iron to the surface, however it is not

oxidised due to the limited supply of oxygen. Above 450°C the Cr(0) peak becomes more dominant; the increase in metallic chromium is attributed to the enhanced mobility of chromium at these temperatures. When the 304-steel was heated in air, the signal associated with iron oxide increases with increasing temperature while the metallic iron signal decreases as the iron is oxidised.¹² Throughout the heating profile in air, the chromium peaks remained mostly unchanged.¹²

The surface of 316-steel was mostly unaffected by the change in temperature, however above 450°C a slight increase in iron and oxygen concentrations and a slight decrease in chromium and manganese concentrations was observed.¹² Using XPS, the concentration of nickel was observed to decrease as the steel was heated; this decrease can be attributed to the increased thickness of the oxide film and the surface sensitivity of XPS.¹⁹ The chromium peak was consistent with a chromia oxide layer which was mostly unchanged by the increasing temperature.¹²

Lampimäki *et al.* used XPS to look at the effect of temperature on the formation and thickness of films forming on austenite Fe-20Cr-18Ni at constant volumes of oxygen (1000 L) at a pressure of 2.7×10^{-4} Pa.¹⁹ A summary of their results is presented in Figure 3.5. The increased thickness of oxides at higher temperatures is attributed to the increased mobility of ions at higher temperatures.^{20,21} The authors observed an approximately linear increase in thickness up to temperatures of 300°C where the film reached a maximum thickness of 29 Å.¹⁹ At 50°C the surface oxide was identified as magnetite, with an iron-chromium mixed oxide observed at depths of 7 Å to 11 Å. The iron oxide surface layer is due to the mobility of iron ions through the oxide film at relatively low temperatures.¹⁹ However at 300°C, a Cr₂O₃-rich layer forms on the surface of the oxide as the formation of a chromium oxide is more thermodynamically favourable and chromium has an increased diffusion mobility at this temperature.¹⁹ The oxide increases in thickness at 300°C, with the iron oxide stretching from a depth of 6 Å to 28 Å into the steel.¹⁹ At the higher temperatures of 350°C, the oxide becomes significantly thinner,¹⁹ perhaps due to the oxidation of Cr₂O₃ to gaseous CrO₃. Exposure to larger volumes of oxygen (10 000 L as opposed to 1 000 L) results in a mixed amorphous Fe(Cr,Fe)₂O₄ instead of a layered oxide structure.¹⁹

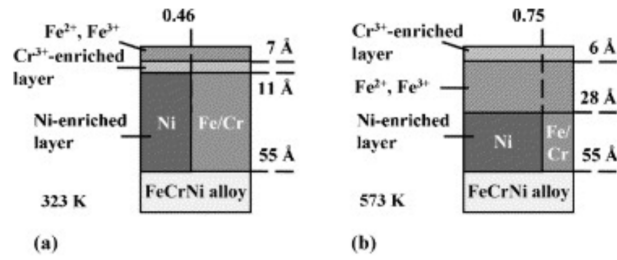


Figure 3.5: Schematic of oxide layer segregation determined by XPS following exposure to 1000 L O₂ at a) 50°C and b) 300°C. Reprinted with permission from Lampimäki et al. [19].

3.3.7.2 Other Alloying Elements

The bulk composition of the stainless steel is found to determine the characteristics of the oxide. Cooper *et al.* found an outer spinel and an inner chromia oxide on several stainless steels (Fe16-18Cr, Fe-19Cr and Fe-22Cr) oxidised at 800°C.⁶ The spinel is believed to form through the interaction of its constituent parts (Cr^{3+} , Mn^{2+} and O^{2-}) as opposed to the combination of manganese and chromia. A higher concentration of manganese will result in more spinel at the surface. The bulk composition will determine the ratio of Cr:Mn in the surface spinel with reported values varying between a 2:1 and 1:1 ratio. At higher bulk compositions of chromium and manganese, the oxide layer will be thicker and richer in spinel respectively.

Due to nickel's relative nobility compared to other alloying elements and its slow diffusion rate through the bulk steel, it is commonly observed in a metallic state segregated at the bulk/oxide interface.^{4,12,19,31} At oxidation temperatures of 50°C, nickel is determined to be between 15 Å and 55 Å from the surface, suggesting that grain boundaries do not have a significant effect on nickel segregation.¹⁹ As the oxide thickness increases at elevated temperatures, the depth of nickel from the surface increases, maintaining metallic nickel's position below the growing surface oxide; at 300°C nickel is found between 28 Å and 55 Å into the sample.¹⁹ At higher temperatures, the concentration of nickel at this interface will also increase.

3.3.7.3 Pre-Treatments

The potential of surface pre-treatments to influence oxide formation on a ferrite, martensite and austenite steel was investigated by Ostwald *et al.*² The degree of oxide formation was shown to depend upon the extent to which the surface was deformed; the five surface treatments

studied, with increasing levels of surface deformation, were electropolishing, polishing, grinding and sandblasting (fine and then coarse). For electropolishing and polishing, deformation only extends $1 - 2 \mu\text{m}$ towards the bulk and hence these surface modifications are not drastic enough to form fast diffusion pathways and hence prevent the depletion of oxides beneath the scale. However, grinding and sandblasting cause significant surface deformation, forming fast diffusion paths through the steel, enabling the formation of a Cr-oxide scale on ferritic Fe-16Cr which prior to surface treatment was predominantly iron oxide.

3.3.7.4 Oxidising Conditions - Temperature and Oxidising Gases

Ostwald *et al.* also investigated the effect of varying the oxidising gas on the surface composition and structure of several steels at 700°C .² A reducing mixture of $\text{H}_2-2.5\%\text{H}_2\text{O}$ produced a spinel $((\text{Mn,Fe})\text{Cr}_2\text{O}_4)$ and chromia (Cr_2O_3) surface. In $\text{N}_2-20\%\text{H}_2-0.5\%\text{H}_2\text{O}$ a fine-grained even chromia scale is rapidly produced due to the Cr-N intermediate that favours chromia nucleation. In synthetic air $\text{N}_2-20.5\%\text{O}_2$, there is a greater partial pressure of oxygen and hence many oxides, and spinels of these oxides, can be formed, especially iron oxides Fe_2O_3 and Fe_3O_4 . Oxidation in synthetic air leads primarily to iron oxide due its stability in synthetic air and the rapid growth rate of iron oxide compared to chromia and manganese/chromium containing spinels. Manganese ions diffuse quickly through the steel and chromia layer towards the surface forming an outer layer of spinel. Over time manganese continues to diffuse outwards through the chromia scale, hence after long time periods manganese was always observed at the surface in this study.

3.3.8 Summary

In the literature presented in the previous pages, the composition and structure of the oxide on the steel is found to depend on the composition of the steel, the oxidising conditions and the thermal history of the sample. The surface and near-surface composition and structure is controlled by the microstructure of the steel, the bulk composition and the temperature. Above 700°C , where chromium ions are mobile, a protective chromium film will form on the surface. Depending on the bulk composition of the steel, a manganese outer spinel may form on the

surface. At low temperatures the surface will be predominantly iron oxide due to the mobility of iron to diffuse to the surface at these temperatures and the stability of iron oxide in air, with evidence of iron oxide growing on top of chromium oxides formed when surface chromium was first exposed to oxygen. Nickel is widely observed in its metallic state at the oxide/alloy interface due to a combination of its low reactivity and its slow diffusion rate.

3.4 Characterisation of The Oxide Layer on Engine Steel Fe-13Cr

The engine injectors of interest to BP were identified to be made from the steel Fe-13Cr, however the pre-treatments used in the processing of this steel and the steel's thermal history are both unknown. As the composition and structure of the surface oxide is shown to be determined by the treatment of the steel, the identity of the surface is therefore unknown. In order to gain a fundamental understanding of the interaction between the fuel and the surface, both the surface and the fuel must be well-defined. As part of the wider project focused on understanding carbonaceous deposits, TEM cross-sections of a fresh and fouled injector taken, as shown in Figure 3.6. These analyses by Dr. James Gilchrist revealed that the surface of fouled injectors was composed of iron-containing species with a sub-surface layer of chromium-containing species. As the composition of the surface oxide is shown to be dynamic, the focus of this work, and specifically this chapter, is to gain an understanding of the effect of engine conditions on the surface of the steel. BP reported average engine temperatures to range from room temperature to 400°C and hence, the surface composition of Fe-13Cr substrates was characterised over this temperature range. SIMS depth profiles were used to identify species in the surface oxide following heat treatment.

3.4.1 Characterisation of Fe-13Cr Surface at Room Temperature

Characterisation of the as-received Fe-13Cr substrate showed an oxide that reached diffusely and inhomogeneously into the sample. As the pre-treatment and thermal history of the Fe-13Cr

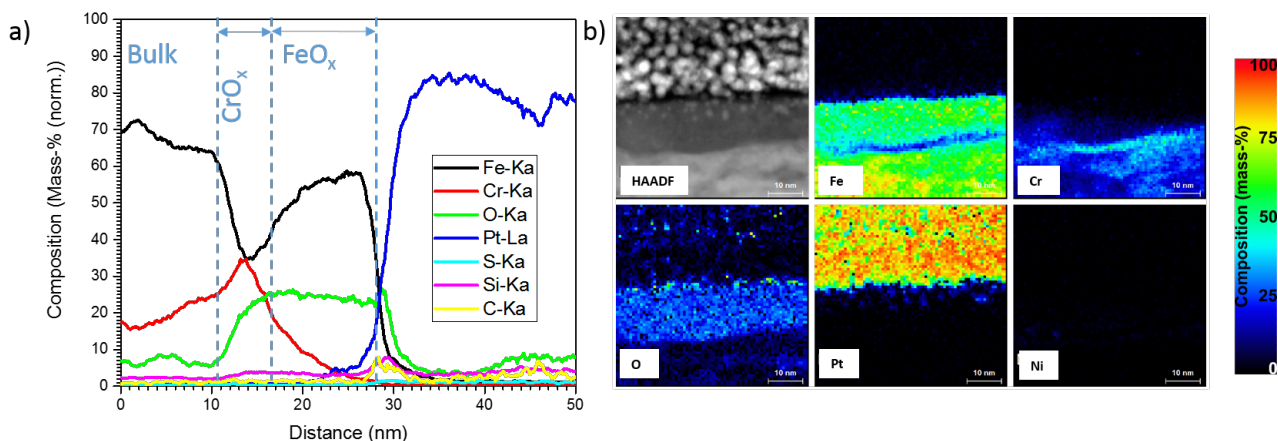


Figure 3.6: a) Line profile and b) mapping of a cross-section of a fouled diesel injector. These data were measured, analysed and presented by Dr. James Gilchrist. Experiments were conducted on the ChemiSTEM at the University of Manchester in collaboration with Professor Grace Burke.

substrates used in this work was also unknown, the oxide layer was removed through polishing (Section 2.2.2), to achieve a uniform and well-defined starting surface. The root mean squared (RMS) roughness was found to decrease from 205 nm to 4 nm.

The oxide subsequently formed at room temperature on the polished Fe-13Cr substrate sample was characterised by SIMS. A wide range of iron and chromium-containing species are observed, as shown in Figure 3.7, and will be discussed further in Section 3.4.4. Many of the trace alloying elements presented in Table 2.1 including manganese, silicon, carbon, nickel, copper, nitrogen, niobium, molybdenum, aluminium, vanadium, cobalt, phosphorus and sulfur are found to be present at or near the surface. The distribution of some of these species will be discussed further in Section 3.4.7.

Energy dispersive X-ray spectroscopy (EDX) analysis of the Fe-13Cr substrate at room temperature showed the lateral distribution of iron and chromium on the substrate to be inhomogeneous (Figure 3.8a and b). Localised chromium-rich and iron-deficient regions are observed across the sample; the presence of chromium grains is a possible explanation, with chromium-rich iron-deficient regions measuring approximately 1 μm . The speciation of the chromium is discussed in Section 3.4.6. Chromium is also observed at lower concentrations homogeneously across the substrate.

A dynamic SIMS measurement through the oxide layer was used to produce the iron and

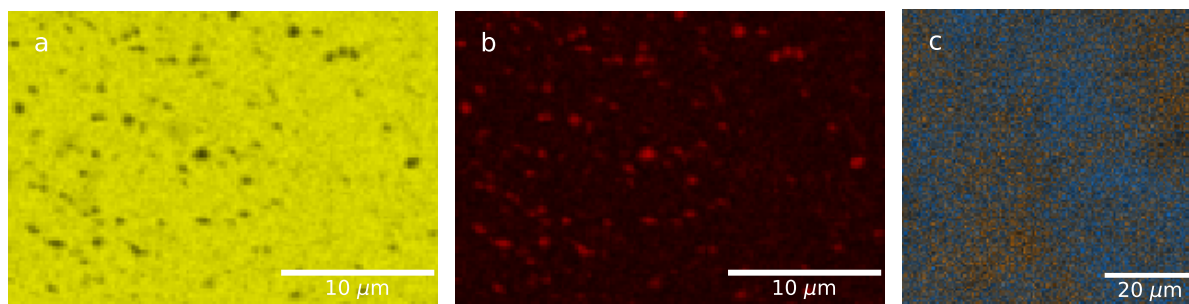


Figure 3.8: EDX images showing the distribution of a) iron and b) chromium on 13 Cr at room temperature. c) An overlay of SIMS maps showing the sum of all iron species in blue and all chromium species in orange on the 13 Cr substrate at room temperature. The EDX images in a) and b) were taken by Dr. Catriona McGilvery.

3.4.2 Limitations of SIMS Analysis

This section will briefly introduce several considerations required in the interpretation of SIMS data. These primarily relate to the matrix effect, which is discussed in Section 2.4.3.3, meaning that the measured intensity cannot be directly correlated to concentration. This has implications in both comparing different species as well as changes in intensity of one species if the chemical environment that those ions are coming from has also changed. In Figure 3.9 the measured intensities are plotted for demonstration, however for the remainder of this chapter, the ion intensities are normalised.

On the IONTOF TOF-SIMS V instrument, which was used in this work, it is not possible to simultaneously detect positive and negative species, although this feature is available on newer instruments. Due to the preferential ionisation of oxygen-containing species to form anions and metals to form cations, the optimum measurement conditions for attaining information on both the oxide and the alloy cannot be attained concurrently. In this work, the negative spectra and associated depth profiles have been used to optimally measure oxygen-containing species; Fe^- and Fe_2^- have been used as an indicator of the bulk alloy, although the most reliable and robust signal for determining the alloy would be from the metal cation, Fe^+ .

3.4.3 Characterisation of Fe-13Cr Oxide Layer at Room Temperature

SIMS depth profiles were used to investigate the composition of the oxide layer on Fe-13Cr steel, providing information on how different species change as a function of depth. FeO^- and CrO^- were chosen due to their high counts and the clear demonstration of trends. Figure 3.9 shows a depth profile for FeO^- and CrO^- through the oxide layer of Fe-13Cr at room temperature. The measured intensity of these ions does not necessarily directly correlate with the concentration of these species on the surface, as discussed in Section 3.4.2. Therefore, comparisons between the concentrations of FeO^- and CrO^- can not be drawn, however their own relative concentrations provide useful insights into their distribution in the surface oxide, based on the assumption that the chemical environment of these species does not change.

The FeO^- depth profile in Figure 3.9a shows a relatively sharp drop at the oxide-alloy interface at a sputter time of around 35 s, demonstrating that at room temperature the oxide layer is well-defined. The maximum concentration of CrO^- is localised in the lower section of the oxide layer near to the oxide-alloy interface, demonstrating a variation in the oxide composition with depth. An iron oxide surface, with a sub-surface chromium-containing mixed oxide is expected at room temperature, due to iron's mobility at lower temperatures and the stability of iron oxides in air. The maximum FeO^- concentration, highlighted by the black line labelled position 1, is observed at a sputter time of approximately 10 s.

Figure 3.9b shows a map of the surface after a sputter time of 10 s; the surface here is predominantly iron oxide (blue), however some pixels of chromium oxide are present (as shown in orange), suggesting chromium-enriched grains are present in the outer oxide layer. An image at position 2, where the chromium oxide concentration is at a maximum, is shown in Figure 3.9c. There are significantly more chromium oxide pixels identified here, as well as a low level of chromium coverage, suggesting that this inner oxide consists of a mixed iron-chromium oxide containing some chromium grains. A possible cause for the dip in the concentration of FeO^- at approximately 20 s is a change in the sputtering yield, as the composition or structure of the oxide changes with the addition of chromium atoms into the oxide lattice. The gradual

increase in chromium concentration suggests the composition of the oxides changes gradually and two distinct layers are not formed, in contrast to reports in the literature as summarised in Table 3.3.

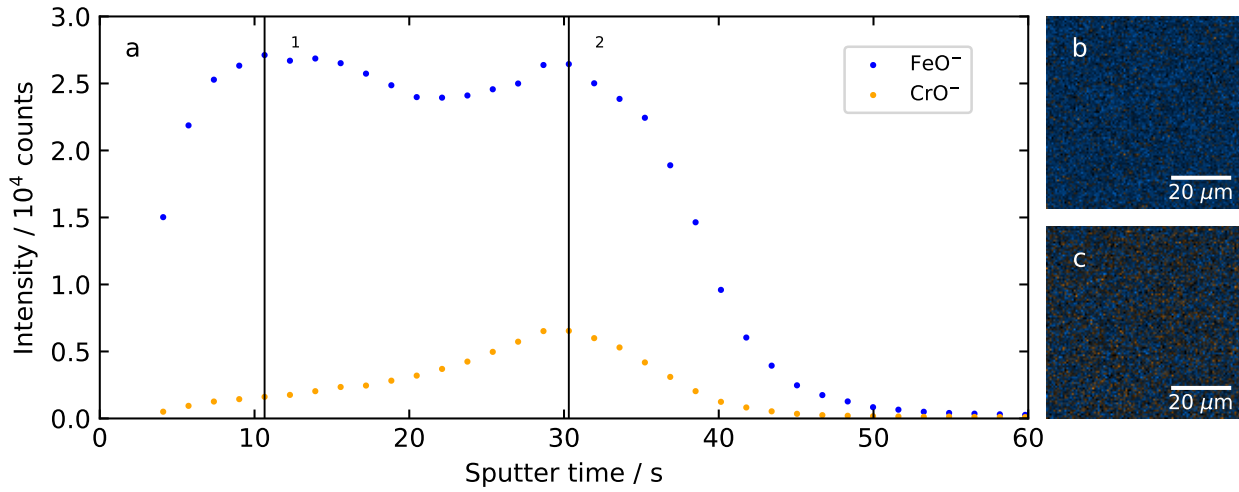


Figure 3.9: a) SIMS depth profile of a Fe-13Cr substrate at room temperature. SIMS maps of the surface at b) position 1 and c) position 2 for the iron-rich and chromium-rich regions respectively. FeO^- and CrO^- are shown in blue and orange respectively.

3.4.3.1 Correlating Sputter Time to Depth

To rigorously correlate the sputter time to the depth, standard measurements are required of each measured chemical environment to determine the sputter rates, which could then be applied to the different parts of the sample to accurately determine distances. However, as the oxide structure and composition of iron and/or chromium in the oxide layer is unknown and shown to change gradually as a function of depth, accurate use of a sputter rate, determined for each chemical environment, would be very challenging for these samples. Therefore, the rough assumption that the sputter rate is consistent through both the oxide and the bulk material was used for these system.

To determine the sputter rate, the topology of the sample surface and the crater produced from the SIMS depth profile was measured by white light interferometry as shown in Figure 3.10a. Ten line profiles were attained for each crater and the difference between the average surface height and the average crater depth was determined, as shown in Figure 3.10b. It is also worth noting, that the surface may sputter preferentially in some regions compared to others due to the

varying hardness associated with different grain structures; this is demonstrated in Figure 3.10c, by the differences in texture and height at the bottom of the crater.

Table 3.4 shows the calculated sputter rates. The lower sputter rate on samples treated at higher temperatures suggests that the assumption of a constant sputter rate though the oxide and the alloy is not valid. In spite of this, these calculated values were shown to be in relatively good agreement with the thicknesses of oxide layers measured on lamellars by TEM by Dr Catriona McGilvery, presented in Section 3.4.6.

Table 3.4: Sputter rates calculated from the crater depth and the sputter time

Treatment ($^{\circ}\text{C}$)	Sputter time (s)	Average crater depth (nm)	Sputter rate (nm s^{-1})
RT	1508	-	-
100	2522	280	0.11
200	2517	200	0.08
300	2537	200	0.08
400	2014	140	0.07

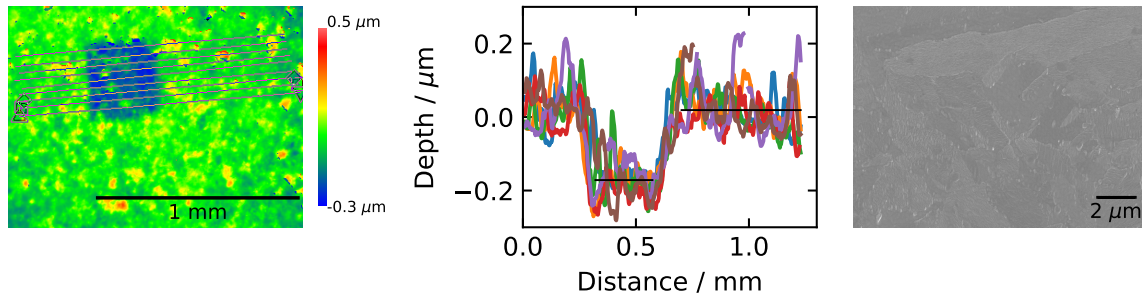


Figure 3.10: a) Example of a white light interferometry image of a crater; b) the line profiles across the crater shown by the lines in (a) and c) SEM image of the bottom of the crater.

3.4.4 Effect of Temperature on the Thickness of the Oxide Layer

A thin oxide is formed on the alloy surface at room temperature, discussed in Section 3.4.3, with a mixed sub-surface layer of chromium and iron oxide towards the oxide-alloy interface is shown in Figure 3.9. Figure 3.11 shows depth profiles of FeO^- and CrO^- at room temperature, 100 $^{\circ}\text{C}$,

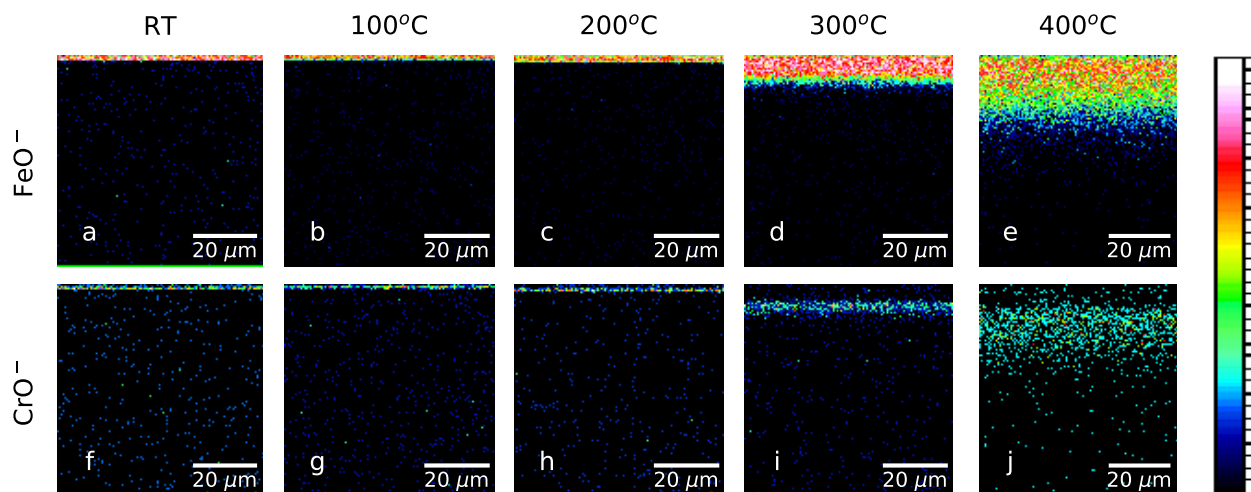


Figure 3.11: Depth profiles of Fe-13Cr of FeO^- and CrO^- respectively following treatment at a,f) RT; b,g) 100°C; c,h) 200°C; d,i) 300°C and e,j) 400°C under a vacuum of 0.3 mbar. The scale bar corresponds to the normalised intensity of a-e) FeO^- and f-j) CrO^- per pixel.

200°C, 300°C and 400°C. Each image has been normalised to the maximum counts observed within that image. At higher temperatures, the oxide layer increases in thickness and the depth of the chromium-rich oxide increases to maintain its position at the oxide-alloy interface. The large increase in iron oxide thickness at 300°C is attributed to the increased mobility of iron ions at these temperatures.¹⁸ At 400°C the iron oxide layer extends further into the bulk producing a thick iron oxide surface, suggesting a significant increase in iron mobility occurs at this temperature. At 400°C there is not a sharp interface between the oxide and the alloy as observed at lower temperatures. The chromium layer is also more diffuse at 400°C extending into the alloy and significantly increasing in thickness; chromium is known to be mobile above 700°C, however these results suggest an increase in chromium mobility occurs between 300°C and 400°C supporting findings from Lampimäki *et al.* that chromium mobility increased around 350°C.¹⁹

Through correlating the sputter time and the depth, the oxide thickness at room temperature was found to be around 5 nm which is consistent with reports of a 1–4 nm thick oxide forming on steels.¹ At higher temperatures, the oxide increases in thickness to 23 nm at 300°C and 70 nm at 400°C, which show similarities to observations on another steel (Fe-20Cr-18Ni) under similar conditions.¹⁹ Figure 3.12 presents depth profiles for FeO^- and CrO^- , produced by summing the species measured over the analysis area as a function of depth. The CrO^- trace is relatively

sharp for the room temperature and 100°C substrates shown in Figure 3.12a and d respectively. The images in Figure 3.12c and f at position 2, show a relatively high ratio of chromium oxide to iron oxide in this chromium-rich sub-surface layer. At higher temperatures the chromium layer becomes thicker and more diffuse resulting in a thicker chromium-containing oxide. However, the local concentration of chromium in this layer, with a maximum marked by position 2, is lower, as shown by the images for position 2 in Figure 3.12i, l, o. As a result of the overall thickening of the oxide layer, the chromium-containing layer moves increasingly further from the surface to maintain its place at the oxide-alloy interface. A consequence of this shift, is the reduction of chromium species near the surface at higher temperatures; images at position one, corresponding to the maximum concentration of iron, shown in Figure 3.12 demonstrate that with increasing temperature, there is a decrease in the concentration of chromium producing a surface that is predominantly iron-rich.

3.4.5 Detailed Analysis of Iron and Chromium Oxides at 300°C

Here a range of iron and chromium containing species, including FeO^- and CrO^- , are evaluated as a function of depth to gain a fuller understanding of the oxide layer. The oxide layer produced at 300°C was chosen due to its well-defined profile and its relevance to engine conditions. All identified species containing iron or chromium are discussed, with the exception of species where the signal is indistinguishable from the noise. The ion intensities of these species have been normalised to highlight the relative positions of different species as meaningful conclusions on relative concentrations cannot be drawn.

Figure 3.13 demonstrates the gradual change in the oxide composition as a function of depth. FeO_2^- and FeO_3^- have the highest oxygen to iron ratio and decrease sharply in intensity over the first 4 nm of the oxide, subsequently decreasing further in intensity with distance from the surface. Sputtered species such as FeO^- and Fe_2O_2^- (and also Fe^-) increase sharply in intensity in the first nanometer and remain consistent in intensity through the oxide layer. The intensity of the iron-rich species Fe_2O^- , Fe_3O_2^- and FeCl_2^- increases sharply 4 nm into the substrate. Species associated with the bulk, for example Fe_2^- and Fe_3^- have a low concentration through the oxide that begins to increase at 12 nm, increasing to a constant level at 18 nm that remains

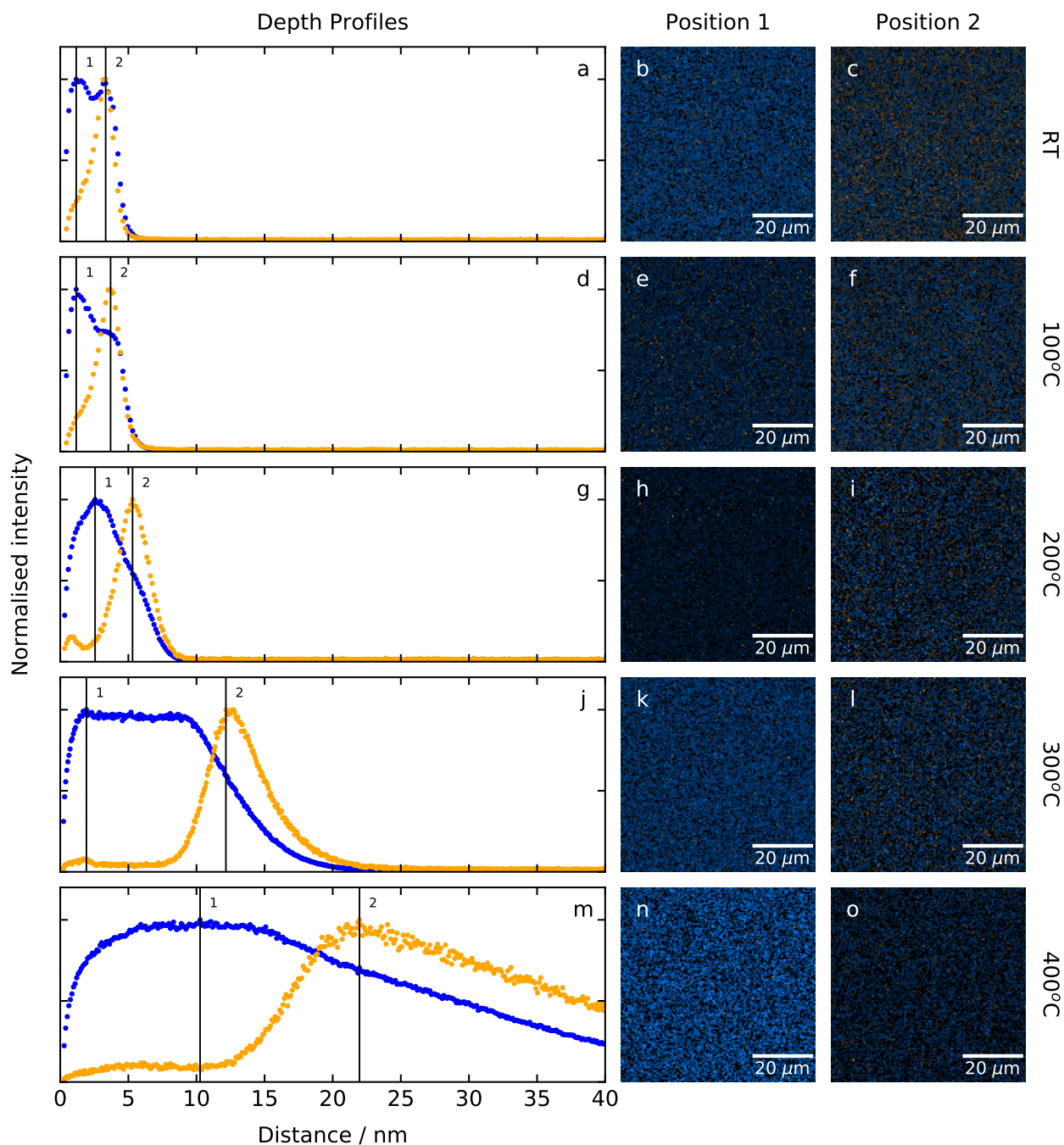


Figure 3.12: Depth profiles of Fe-13Cr following treatment at a-c) RT; d-e) 100°C; f-h) 200°C; i-j) 300°C and k-l) 400°C under a vacuum of 0.3 mbar. FeO⁻ is shown in blue while CrO⁻ is shown in orange. Positions 1 and 2 refer to the maximum in FeO⁻ and CrO⁻ respectively; images of position 1 and 2 are shown in column 2 and 3 respectively.

consistent through the bulk. Interestingly, the species Fe⁻, which was expected to correlate to the bulk, correlates instead to the oxide layer. Iron hydroxide is found at the surface, which decreases in concentration over the first 3 nm of the surface, before reaching a local maxima at 12 nm at the bottom of the oxide layer. The trends in iron-oxygen species outlined here, support

the presence of an oxide gradient across the iron surface, as suggested by Kofstad in 1989.⁷

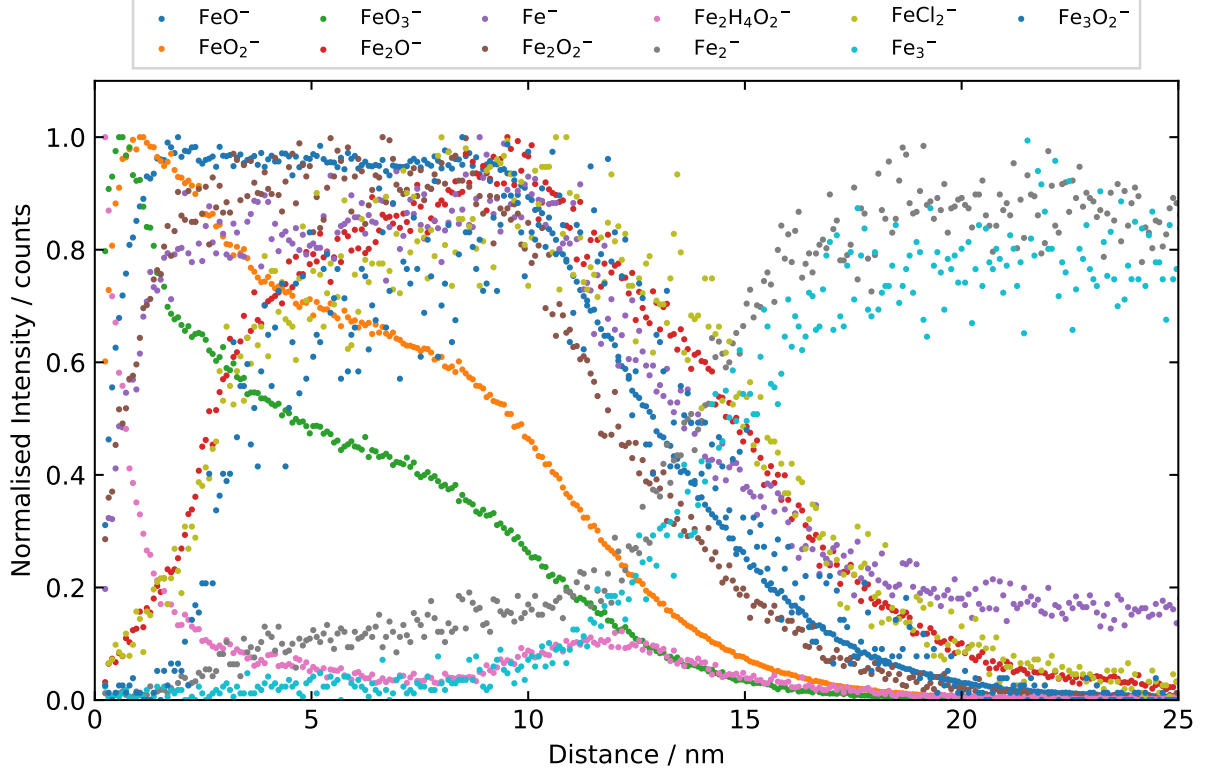


Figure 3.13: Depth profiles of iron species in Fe-13Cr following heating at 300°C under a vacuum of 0.3 mbar.

On the contrary, the chromium containing species do not tend to show any oxide gradient, with all oxidised species appearing at a similar depth of approximately 12 nm. An increase in Fe_2^- and Fe_3^- , species associated with the alloy, was also observed at this depth, further supporting the presence of the chromium-rich layer at the oxide-alloy interface. As above, all chromium species identified in the mass spectra, where the signal is distinguishable from the noise, are presented in Figure 3.14. The maximum concentration of each of the species studied (CrO^- , Cr^- , CCr^- , C_2O^- , Cr_2O_4^- and Cr_2O_5^-) are all found at 12 nm. The level of Cr^- in the alloy (at distances > 20 nm) is greater than the levels of Cr^- observed through the oxide layer (at distances less < 5 nm).

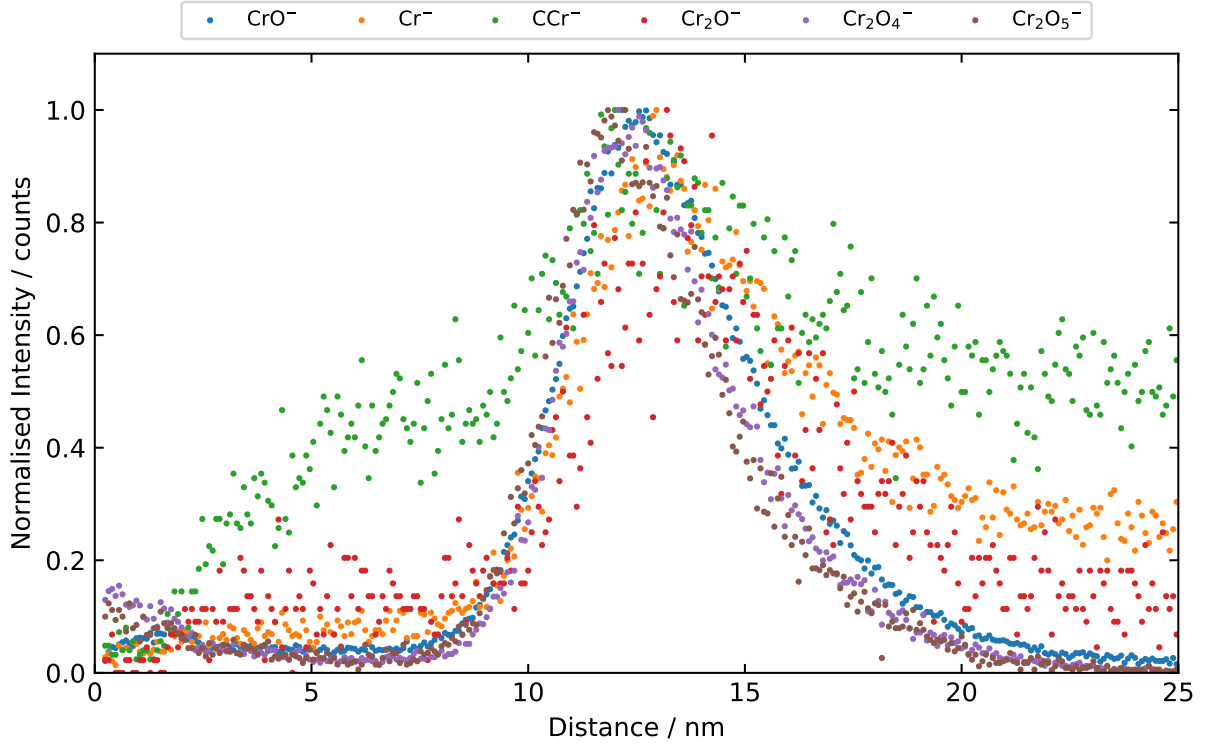


Figure 3.14: Depth profiles of chromium species in Fe-13Cr following heating at 300°C under a vacuum of 0.3 mbar.

3.4.6 Comparison to TEM analysis of Fe-13Cr substrates

Transmission electron microscopy was measured on lamellas cut out of the Fe-13Cr steel. These data were measured and processed by Dr. Catriona McGilvery and are presented in Figure 3.15. Samples of Fe-13Cr that has been heated to 200°C and 300°C were compared to the room temperature sample. Elemental maps of the distribution of chromium, iron and oxygen are presented in Figure 3.15d-f, which are taken from the areas annotated by a rectangle in images 3.15a-c. Figure 3.15d for the oxide at room temperature shows a high concentration of iron in the bulk alloy on the right-hand side of the image. A slight increase in the oxygen content at the expected position is observed, however oxygen extends both into the platinum surface coating and into the bulk of the alloy. Chromium appears to extend from the oxide surface into the alloy bulk. The line profile for the room temperature sample in Figure 3.15g provides no clear insights into the distribution of elements with chromium, iron and oxygen shown in red, blue and green respectively. However, the SIMS measurements of the oxide film provided valuable insights into the layering of the oxides at room temperature.

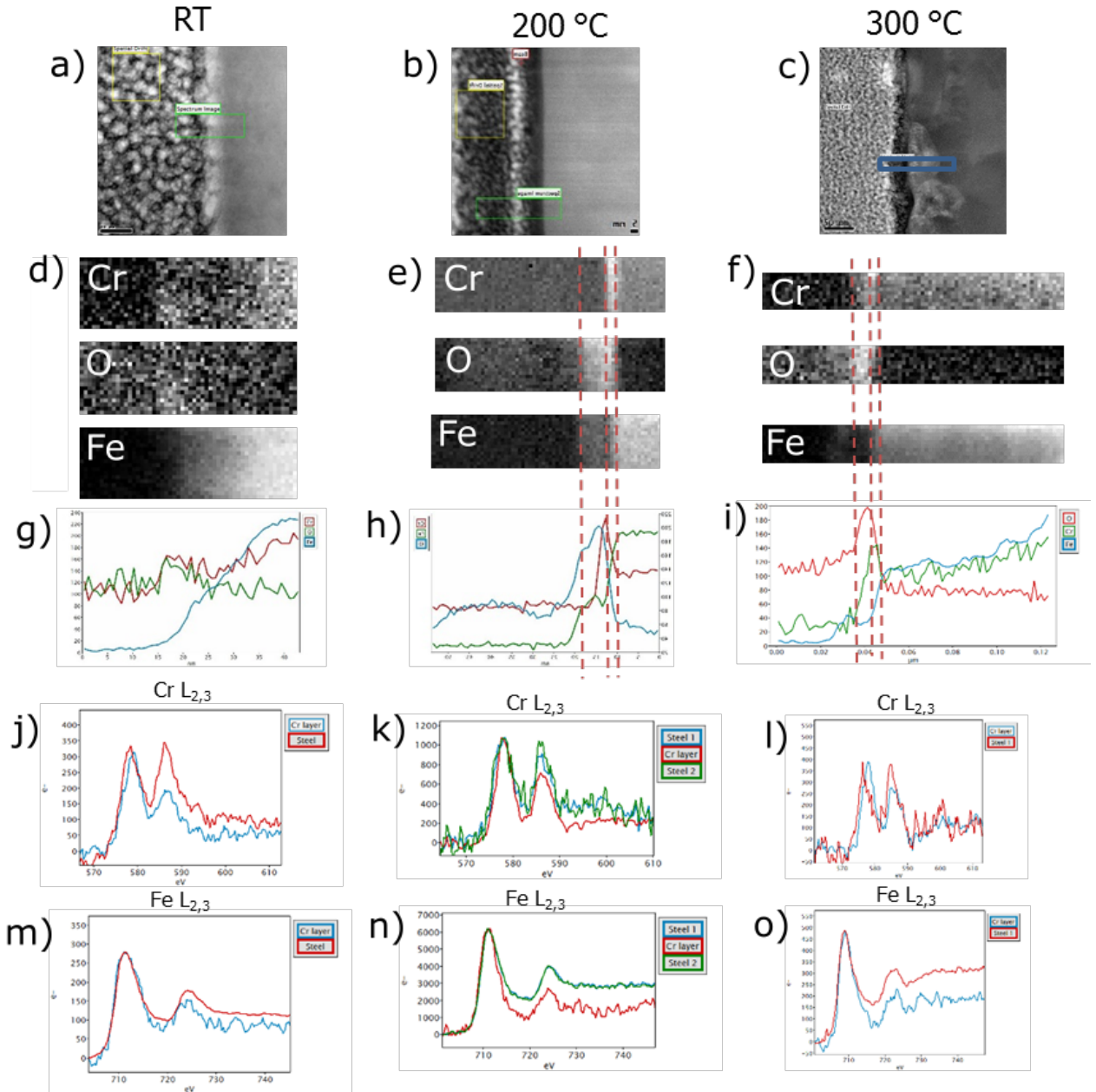


Figure 3.15: Fe-13Cr steel treated at room temperature, 200°C under a vacuum of 0.3 mbar and 300°C under a vacuum of 0.3 mbar are presented respectively for a-c) TEM images of the oxide layer; d-f) elemental maps showing chromium, oxygen and iron across the lamella; g-i) Line profiles for oxygen, chromium and iron: Electron Energy Loss Spectroscopy (EELS) profiles at varying positions are presented for chromium (j-l) and iron (m-o). Dr. Catriona McGilvery conducted the analysis, processing and presentation of these data.

On the substrate that had been heated to 200°C, presented in Figure 3.15e, there is a clearly defined oxide layer, with a chromium-rich inner layer towards the bulk, at the oxide-alloy interface. The thickness of the oxide layer, just less than 10 nm, also correlates well to the thickness approximated by measuring the SIMS crater depth. Iron is most prevalent in the

alloy, however it is also present through the whole oxide layer. The line profile in Figure 3.15h suggests that the concentration of iron (shown in green) increases through the oxide (oxygen is shown in blue) before it reaches its bulk concentration. The chromium concentration (shown in red) rises sharply part way through the oxide layer, reaching a maximum before dropping down to its concentration present in the alloy. At 300°C, similar trends are observed in Figure 3.15f in the oxide layer with an inner chromium-rich layer. The line profiles in Figure 3.15i show an oxide layer (oxygen is shown in red), with a sub-surface chromium layer (shown in green); the iron signal (shown in blue) is observed to increase across the oxide and into the bulk.

Electron energy loss spectroscopy (EELS) was measured at various points on the lamella presented in Figure 3.15j-o, providing information on the oxidation state of species that is not available from SIMS measurements. However in the absence of suitable references, from this work we can conclude, as expected, that the chemical environments of both iron and chromium differ between the chromium-rich layer and the alloy.

3.4.7 Presence of Other Alloying Elements on the Surface at Room Temperature

Several alloying elements, presented in Table 2.1, are observed on the surface of the steel. As in Figure 3.8c, the sum of all species containing that element was used to produce the surface maps shown in Figure 3.16. Each image is normalised to the pixel with the maximum intensity in that image. The maps for silicon (Figure 3.16a) and sulfur (Figure 3.16b) show a relatively even distribution of these elements across the measured area. Manganese however is more inhomogeneously distributed across the analysis area, as shown in Figure 3.16c, with regions of high concentration and regions where no manganese-containing species are detected. Manganese is widely reported to form manganese sulfide inclusions in steel, therefore explaining the inhomogeneous distribution of manganese observed.³² Copper-, molybdenum- and nickel-containing species are localised in certain areas and not homogeneous across the sample. The inhomogeneity observed with copper-containing species may be a result of the formation of a separate copper phase as discussed in Section 3.4.8. The concentration of molybdenum is

0.03 at.% in Fe-13Cr steel and the oxide layer appears to reflect its low concentration. The appearance of localised nickel-rich regions is unexpected as nickel is widely reported to form a sub-surface metallic layer.

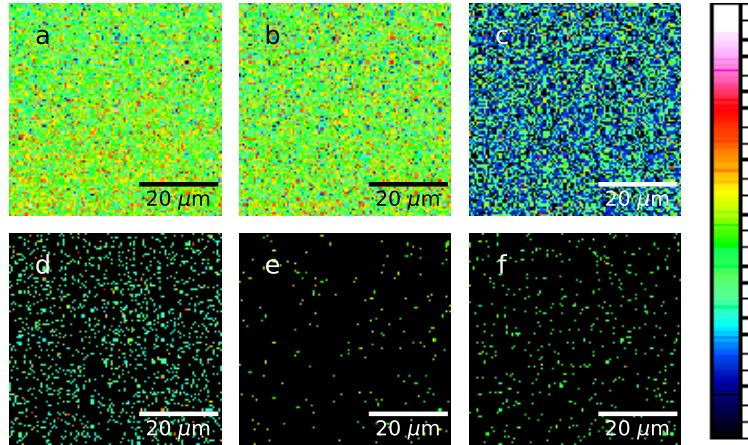


Figure 3.16: Surface images of a) silicon; b) sulfur; c) manganese; d) copper; e) molybdenum; f) nickel obtained using static SIMS on the room temperature Fe-13Cr substrate. The scale bar corresponds to normalised intensity of ion counts per image.

3.4.8 Trends in the Oxides of Alloying Elements at 300°C

This section evaluates the distribution of these alloying elements through the oxide layer. As above, the oxide formed at 300°C is presented due to the clear trends observed at this temperature, as shown in Figure 3.17. The location of manganese in the oxide layer can be attributed to the fast diffusion to the surface and its subsequent oxidation due to the thermodynamic stability of manganese oxides, as shown in 3.1. Cooper *et al.* observed a manganese-chromium spinel (MnCr_2O_4) at the surface, however in this work, we observe the manganese oxide species in a sub-surface layer.⁶ The manganese oxide is located at the same position as the chromium oxide, suggesting that a mixed chromium-manganese oxide may still be observed here. A possible explanation for the discrepancy in the position of this mixed chromium-manganese oxide between this work, where it is at the oxide-alloy interface, and that of Cooper, where it is at the surface, can be attributed to the temperature at which the steels were oxidised. At 800°C chromium, and presumably manganese, are highly mobile, which, combined with their thermodynamic

stability leads to a surface oxide constituted of these species, however at 300°C chromium has limited mobility whilst iron is mobile, leading to an iron oxide surface.

Nickel is widely reported to form a metallic layer at the oxide-alloy interface due to nickel's relative nobility and slow rate of diffusion. In Figure 3.16, nickel was shown to have an inhomogeneous lateral distribution. The observation of nickel species Ni^- and Ni_2O_4^- at the oxide-alloy interface shifted slightly towards the alloy are consistent with these findings, however the presence of NiO^- and Ni_2O_4^- is unexpected. Due to the reactive nature of ion bombardment in SIMS, observation of oxidised nickel ions does not necessarily mean that nickel oxide was present in the sample, nonetheless these are unexpected results. To verify the oxidation state of nickel on the sample further studies are required.

Silicon oxides (SiO_2 and Si_5O) are also identified by SIMS at the alloy-bulk interface, in the same position at the chromium-rich layer. Della Rovere *et al.* studied the passive films formed on shape memory stainless steels (SMSS) which contain approximately 5 wt % of silicon. They reported that the incorporation of silicon in a 'chromium oxyhydroxide' resulted in a highly protective film. Si(IV) cations are believed to be incorporated into an iron-chromium mixed spinel. The authors suggest that the incorporation of two Si(IV) cations, replacing two iron cations, will suppress the formation of additional cation interstitial and/or will increase the number of oxygen ions, decreasing the number of oxygen ion vacancies and making the film more protective.³³ Therefore, here silicon is proposed to be incorporated into the sub-surface chromium-rich layer. Copper on the other hand is observed in the outermost oxide, decreasing in intensity before the maxima in the chromium concentration. A possible explanation for the localisation of copper oxide at the surface is the insolubility of copper in ferrite (solubility 0.2%), tending to precipitate it into its ϵ -phase.³⁴

3.4.9 Trends in Other Species of the Alloying Elements at 300°C

The distribution of different species, that were summed to make the elemental maps in Figure 3.16, through the oxide layer at 300°C are discussed in this section. At room temperature, silicon is observed to form a homogeneous layer over the surface (Figure 3.16a). This silicon may be a result of the 0.3 at.% silicon as an alloying element in the steel and/or may be a contaminant

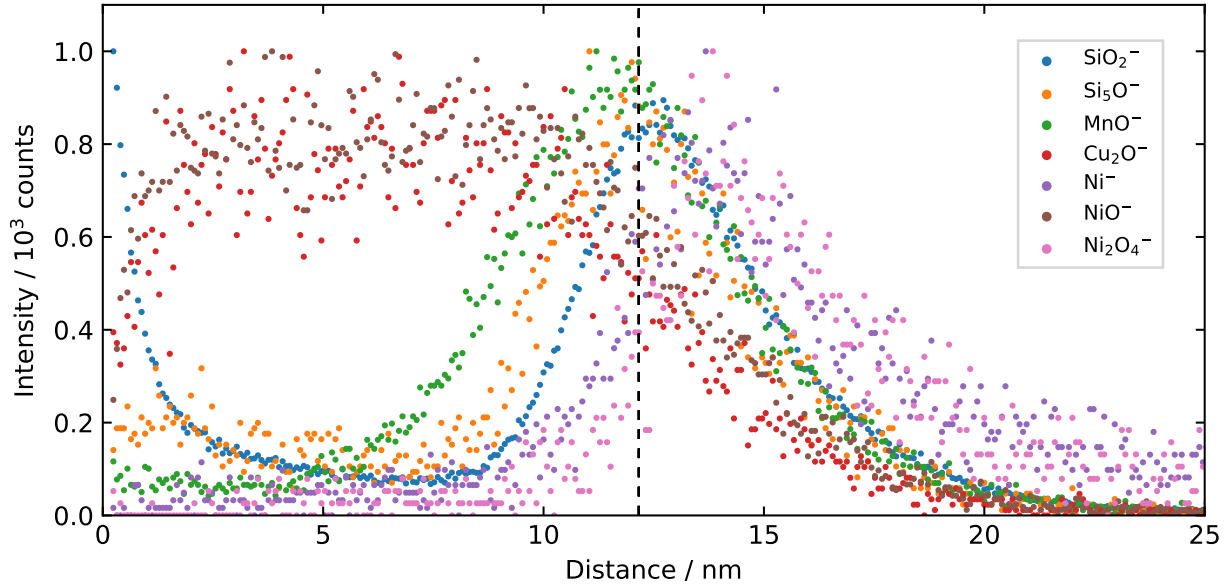


Figure 3.17: SIMS depth profiles of silicon, nickel and manganese oxide species in Fe-13Cr following heating at 300°C under a vacuum of 0.3 mbar. The dotted line represents the depth at which the maximum chromium intensity within the inner chromium-rich oxide was observed.

from the polishing of the steel surface with silicon carbide paper that may not have been effectively removed following cleaning. Similarly to the silicon oxides discussed in Section 3.4.8, following heating to 300°C, other silicon-containing species are observed in a sub-surface layer at the same position as the chromium-rich layer as shown in Figure 3.18a. From other studies on chromium-iron spinel structures, as discussed in Section 3.4.8, silicon cations are believed to replace iron cations in the matrix resulting in the addition of oxygen anions to the lattice resulting in reduced dissolution through this layer.³³ The location of silicon at the oxide-alloy interface, with iron and chromium implies that a similar structure may be observed here. The slight increase in silicon containing species at the surface may be a result of surface contamination diffusing into the steel following the heat treatment.

At room temperature, sulfur-containing species are also distributed homogeneously across the surface (Figure 3.16b). However following heating, all the sulphur-containing species do not follow the same trends. Si₂CS⁻ is observed in the chromium-rich oxide layer alongside silicon oxide species as shown in Figure 3.18b. Sulfur oxide species (SO⁻) are also observed to have an intensity maximum at the inner oxide position. The species containing manganese and sulfur, MnH₂S⁻, is found to be localised in the oxide layer, decreasing in intensity with distance from

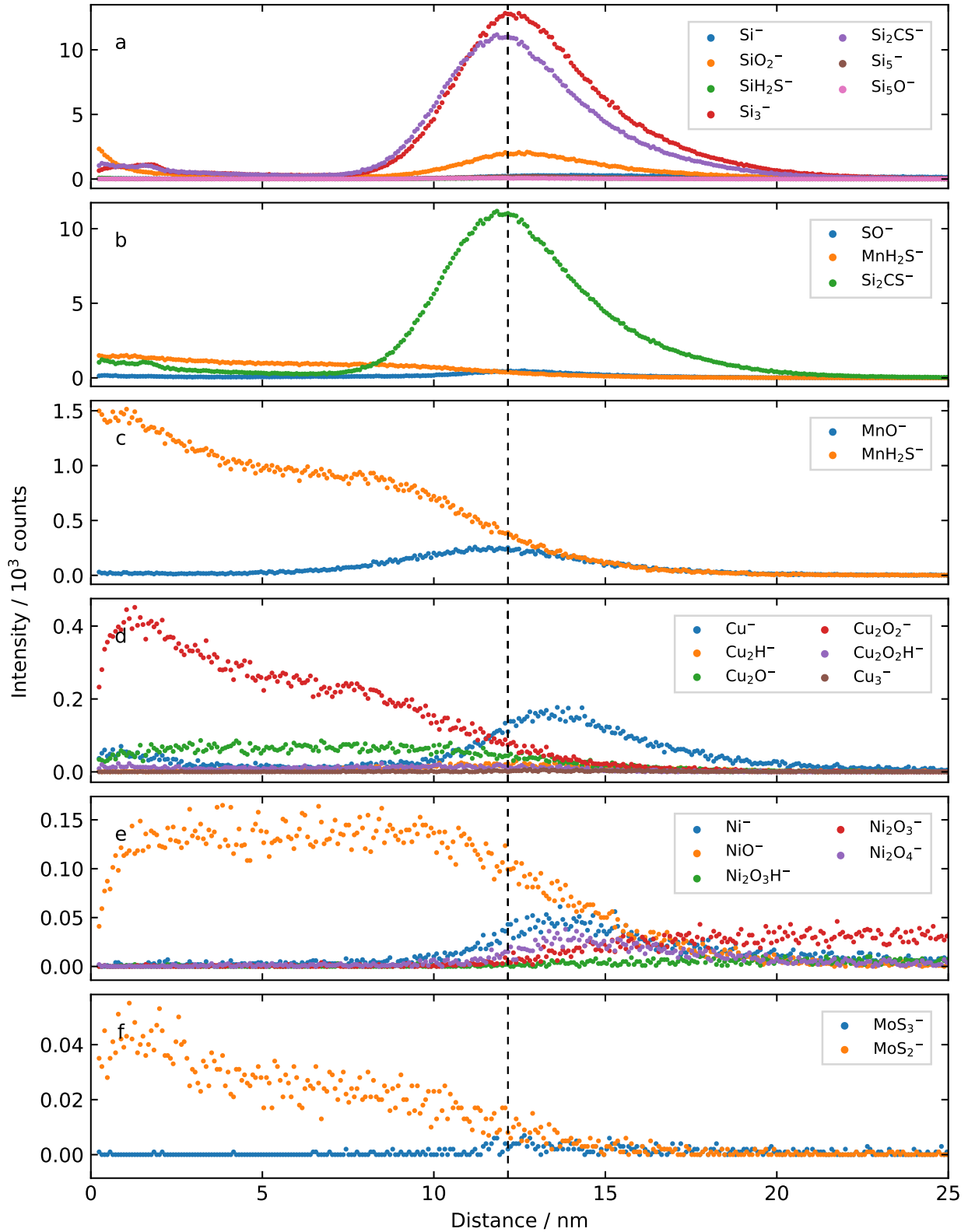


Figure 3.18: SIMS depth profiles of Fe-13Cr at 300°C under a vacuum of 0.3 mbar for alloying elements a) silicon; b) sulfur; c) manganese; d) copper; e) nickel and f) molybdenum. The dotted line represents the depth at which the maximum chromium intensity within the inner chromium-rich oxide was observed.

the surface. This profile can be seen more clearly in Figure 3.18c. Manganese sulfide inclusions have been widely studied in the field of corrosion due to the promotion of pitting around this areas.³² Manganese oxide (MnO^-) is localised in the inner oxide, as discussed in Section 3.4.8.

At room temperature copper was observed in localised regions on the surface as shown in Figure 3.16d. Following heating, different copper-containing species were observed through the oxide layer as shown in Figure 3.18d. Copper oxide species (Cu_2O_2^- and Cu_2O^-) are observed through the oxide layer. Similarly to iron, the species that are more oxygen-rich have their maximum closer to the surface (Cu_2O_2^-), whereas the maximum for less oxygen-rich species (Cu_2O^-) is further into the oxide providing further evidence for an oxygen gradient. Metallic copper (Cu^-) is localised beneath the chromium-rich layer suggesting that, similarly to reports of nickel, copper forms an enriched layer beneath the oxide. As mentioned in Section 3.4.2, to clearly observe these metallic layers, trends in the positive SIMS spectra would need to be evaluated.

Metallic nickel (Ni^-) is observed at the same position as the Cu^- layer, suggesting that in Fe-13Cr steel a metallic nickel sub-layer is observed. A maximum for Ni_2O_4 is also located at this position, suggesting some level of oxygen is present in this layer. There are some surprising observations with nickel-containing species, for example the presence of NiO^- through the oxide layer, as nickel is relatively unreactive and has low diffusion rates.

Molybdenum-containing species are localised at specific lateral positions at room temperature as shown in Figure 3.16e. Following heating to 300°C, as shown in Figure 3.18f, MoS_2^- is observed to decrease in intensity across the oxide. A slight increase in the intensity of MoS_3^- ions is observed at the position of the inner oxide, perhaps due to the increased sulfur levels at this depth.

3.4.10 Summary of Results

The characterisation of Fe-13Cr steel using SIMS, and supported by TEM, showed the surface of the Fe-13Cr steel to be predominantly iron oxide at all the temperatures studied. A chromium-rich mixed oxide sub-layer was observed at the oxide-alloy interface. The oxide layer was found to increase in thickness at higher temperatures, reaching a thickness of 70 nm at 400°C. The

growth of the outer iron oxide resulted in the distance from the surface of the chromium-rich layer increasing with increasing temperature to maintain its position at the oxide-alloy interface. The other alloying elements, with atomic percentages in the bulk steel of less than 0.5 at.%, identified at the surface will not be discussed any further and their potential role in deposition will not be discussed. As mentioned above, concordant studies by Dr. James Gilchrist on the surface chemistry of fouled injector deposits, using TEM analysis, found an iron oxide surface layer with a chromium-containing sub-layer. A convincing correlation was found between the surface composition of Fe-13Cr substrates at engine relevant temperatures (RT and 400°C) and the surface of fouled injectors; the surfaces were found to be predominantly iron, suggesting that iron oxide surfaces are an appropriate model surface for studying injector deposition. Therefore, iron will be used as a model surface henceforth.

3.5 Characterising Model Iron Surfaces

Characterisation of the surface and near-surface of Fe-13Cr steel by SIMS provided convincing evidence that the surface composition of the steel at engine relevant temperatures is iron oxide. However, the structure and oxidation state of this iron oxide is unknown, expected to depend heavily upon the gases or liquid present at these high temperatures. Therefore, several iron oxide surfaces will be used as model surfaces in Chapter 4 to investigate whether the state of the iron surface influences deposition. These surfaces include the oxide formed on the 99.9 % iron substrate following a) polishing, b) polishing and annealing and c) polishing and oxidising referred to as the polished, annealed and oxidised substrates respectively; see Section 2.2.4 for experimental details. XPS was used to gain chemical information on the oxidation of iron, providing surface-sensitive information. A SIMS depth profile is used to investigate the surface and near-surface composition, whilst SEM images on the surface provide insights into how oxidation affects the morphology of the surface.

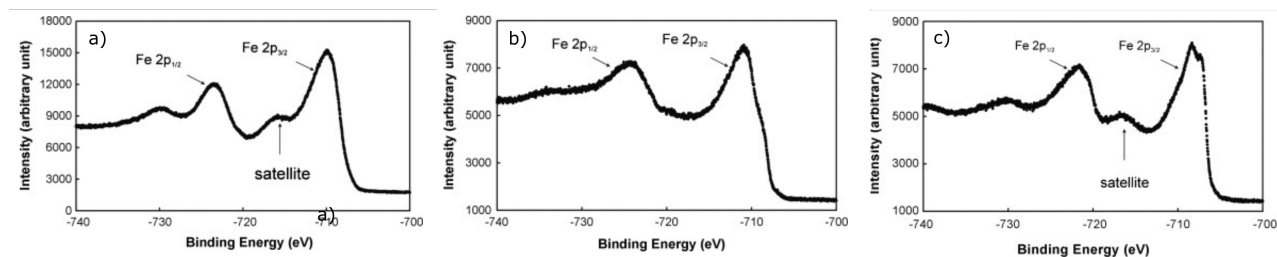


Figure 3.19: XPS iron traces for a) wüstite $\text{Fe}_{0.96}\text{O}$; b) Fe_2O_3 ; c) Fe_3O_4 . Reprinted with permission from Yamashita and Hayes [35].

3.5.1 Chemical Characterisation of the Iron Surface

XPS analysis of the polished, annealed and oxidised samples provides an insight into the chemical state of iron in the first few nanometers of the surface. In the literature various approaches are taken to interpreting, including peak-fitting, the iron trace, however there is not one widely accepted approach due to the complexity of the electronic structure of iron. Therefore in this work, characteristic features and fingerprinting is used to identify the oxidation state. Yamashita and Hayes produced standards of wüstite, magnetite and hematite, which they measured with XPS;³⁵ these iron traces are shown in Figure 3.19.

The XPS traces attained for the polished, annealed and oxidised samples are shown in Figure 3.20. A key feature on the polished substrate is the presence of the sharp peak at 706.7 eV which corresponds to metallic iron/iron(0) as annotated in Figure 3.20a. The peaks at approximately 711 eV and 728 eV correspond to an iron oxide and specifically the $2p_{3/2}$ and $2p_{1/2}$ states respectively. Upon exposure of the metallic iron surface to air following polishing, a native oxide, 1-4 nm in thickness, is expected to form on the metallic iron surface. The appearance of both the metallic iron signal and peaks attributed to iron oxide on the polished surface is a result of the information depth of XPS being greater than the thickness of the native oxide, sampling photoelectrons from the metal below.

The XPS trace of the annealed sample, shown in Figure 3.20b, is characterised by the the shoulder at 708.5 eV and the relative absence of satellites between the iron doublet. Through comparison to the standards in Figure 3.19, the annealed surface is identified to have a composition of Fe_3O_4 and a structure corresponding to magnetite or iron (II)(III) oxide. The oxidised substrate, shown in Figure 3.20c, demonstrates similarities to the Fe_2O_3 trace

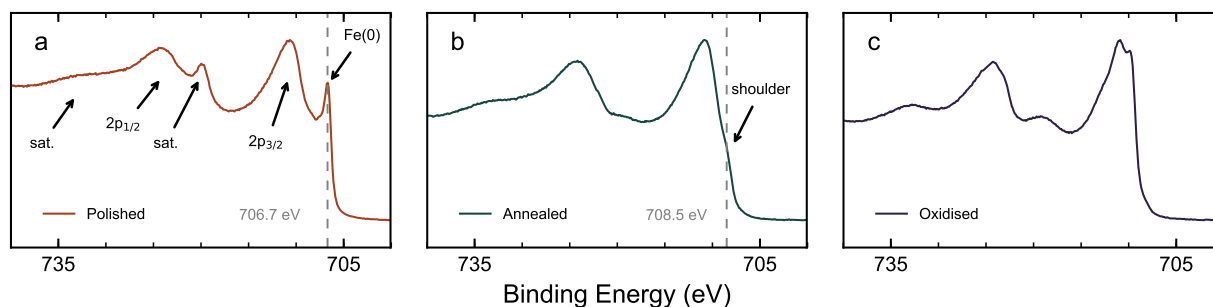


Figure 3.20: XPS traces for the a) polished; b) annealed; c) oxidised 99.9 % iron substrate.

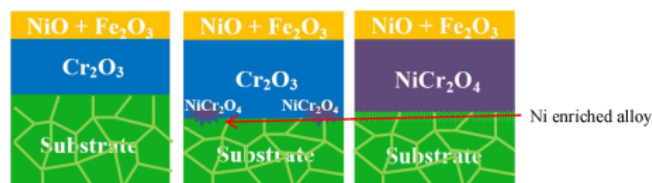


Figure 3.21: Schematic from Wu *et al.* of oxide segregation showing uniform oxide on the polycrystalline nickel alloy. Reprinted with permission from.³⁶

in Figure 3.19 with a double peak at 710.0 eV and 711.2 eV and a satellite at 719.0 eV. The sample measured in [35] was hematite (α - Fe_2O_3), however XPS traces for maghemite (γ - Fe_2O_3), another iron (III) oxide, is not available for comparison, therefore the oxidised sample will be referred to as iron (III) oxide.

3.5.2 Iron Substrate Morphology

Imaging of these iron surfaces by SEM provides some further insights into the process of oxidation. The polished surface appears relatively homogeneous, as shown in the left column in Figure 3.22, with the exception of some scratches from polishing and some deformation at the surface, presumably as a result of polishing as shown in Figure 3.22j. The literature on polycrystalline metals widely presents the surface oxide as a uniform film that is unaffected by the microstructure of the steel, an example of this is shown in Figure 3.21.³⁶ The homogeneity observed on the iron surface at all magnifications, supports this model.

However, in contrast, the oxide film forming on the oxidised substrate is not a uniform layer on the surface, as shown in the right column in Figure 3.22. The oxide growth on this substrate resemble electron backscatter diffraction (EBSD) images, which are used to investigate the

microstructure metals.³⁷ These images demonstrate that the rate and extent of oxide growth is dependent on the orientation of the iron crystal on which it grows. Evidence for enhanced oxygen and iron diffusion at grain boundaries is provided by the thick lines of oxide surrounding regions with different textures. Furthermore, the thick oxide growing in straight lines, presumably along scratch marks, provided further evidence for surface deformations providing fast diffusion pathways leading to increased oxidation.

The annealed sample, shown in the middle column in Figure 3.22 appears to be an intermediate between a uniform oxide surface and a polycrystalline surface oxide. In Figure 3.22b, the surface of the steel appears inhomogeneous, however the grain structure of this steel is not clearly defined by the oxide growth. In Figure 3.22h enhanced oxide growth along grain boundaries and scratch lines can be observed. These observations suggest that the surface of the annealed sample, which is heated under vacuum, is less oxidised than the oxidised sample, which is heated in air; an observation which is supported by the identification of different oxidation states by XPS.

3.5.3 Characterisation of the Near-Surface

Depth profiles were taken through the iron oxide layers on the polished, oxidised and annealed substrates to develop further understanding of these oxides and how they compare to the oxide films on Fe-13Cr. The oxygen (O^-) and hydroxide (OH^-) traces provide a relatively clear indication of the oxide thickness; the O^- trace remains constant across the oxide, while the signal for OH^- changes across the oxide layer. The signal for OH^- is at a maximum at the surface, dropping in the first nanometer of the substrate to reach an intermediate level in the oxide film, before dropping further to its bulk level. Using the sputter rate determined on the Fe-13Cr sample at 300°C (which may not necessarily apply here) the film on the polished substrate was predicted to be approximately 6 nm as shown in Figure 3.23. The iron film on the polished sample displayed similarities to the oxide film on 13Cr at room temperature, with an oxygen gradient through the oxide layer; FeO_3^- and FeO_2^- are observed at the surface, with FeO^- through the oxide, decreasing in oxygen content to Fe_2O^- and Fe_3O^- at the oxide-alloy interface. Despite the use of a 99.9 % iron substrate, chromium is still observed to form a

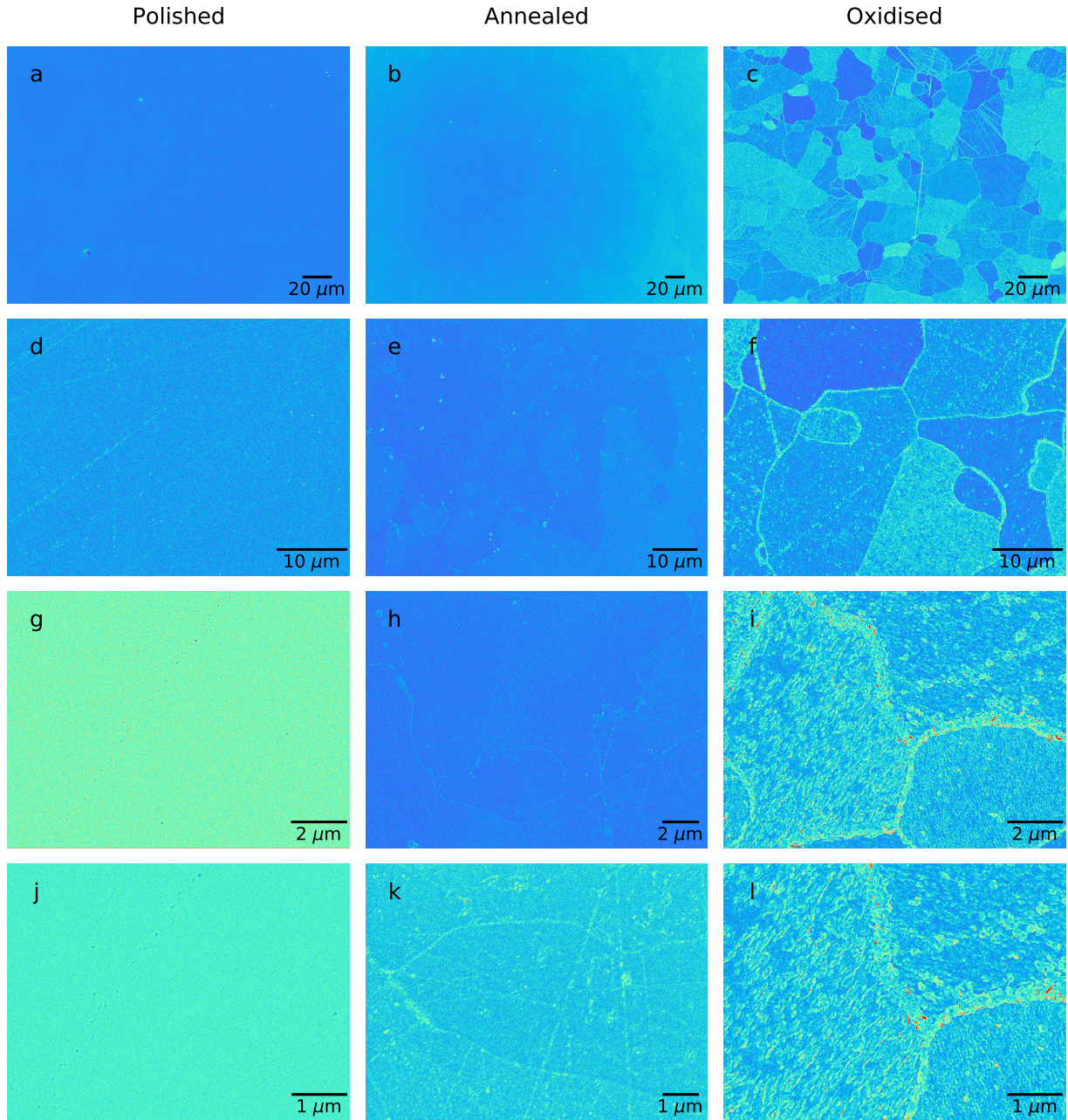


Figure 3.22: SEM images of the polished, annealed and oxidised surface on the 99.9 % iron substrates respectively for magnifications of a-c) 1×; d-f) 5×; g-h) 20× and i-j) 40×. These images have been false-coloured to improve the contrast.

chromium-rich layer at the oxide-alloy interface. This region is also shown to contain FeCl_2^- . The concentration of metallic iron increases with the onset of this layer, reaching its signal associated with the alloy near the bottom of this layer, shown here by Fe_2^- .

The oxide layers on the annealed (Figure 3.23b) and oxidised (Figure 3.23c) sample extends to significant depths into the sample; even at a depth of 125 nm on the annealed surface

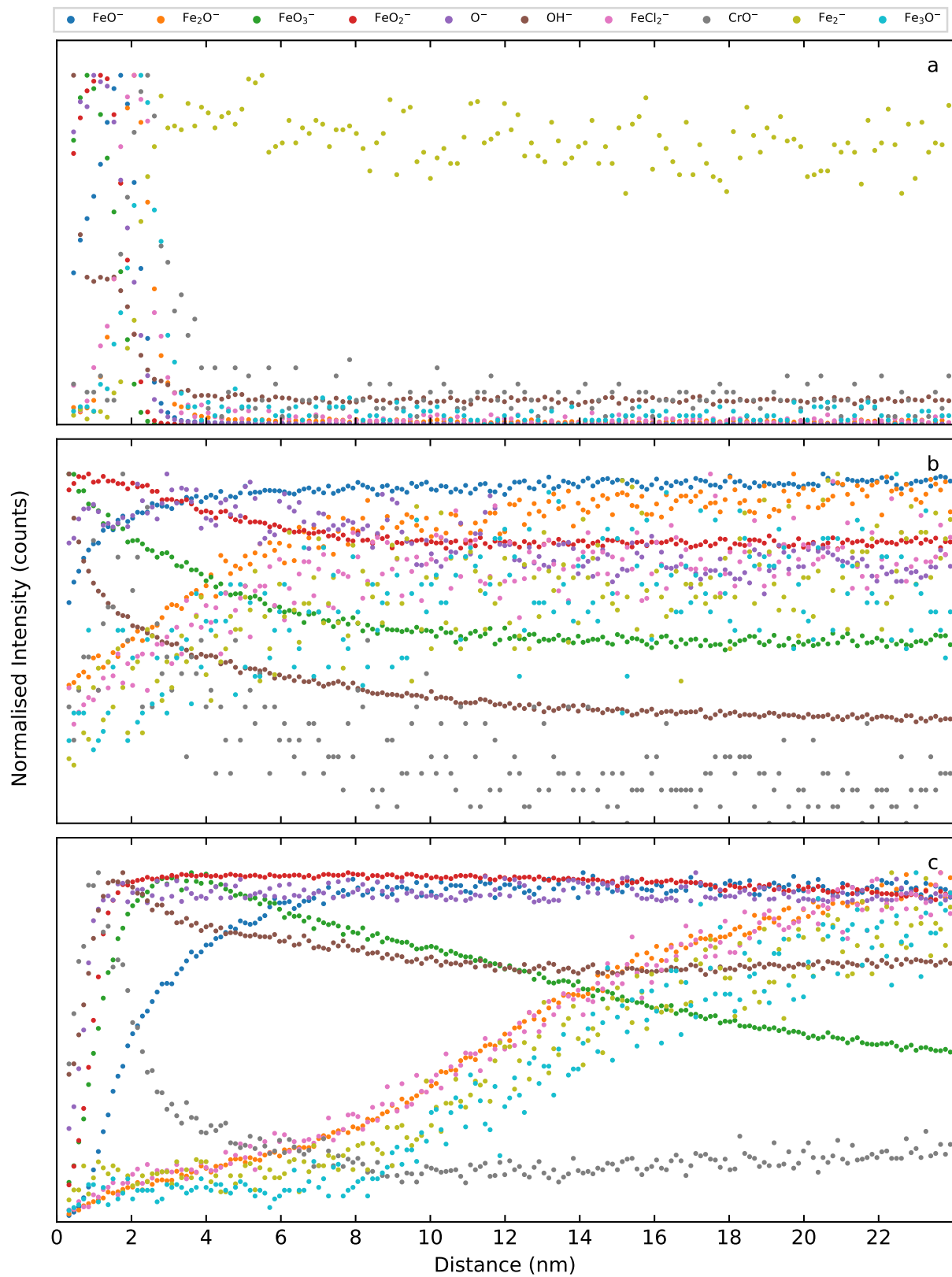


Figure 3.23: SIMS depth profiles on the a) polished; b) annealed and c) oxidised 99.9 % iron substrate showing the profile of iron and chromium containing species over the depth.

changes in the ion signal associated with the oxide-alloy interface are not observed (not shown). The significant increase in oxide thickness on iron substrates compared to Fe-13Cr heated to 300°C is attributed to the absence of the chromium-rich layer that moderates the diffusion of iron ions toward the surface and oxygen ions into the sample. Here we compare the depth profiles for various species between the annealed and the oxidised surfaces to gain an insight into these oxides. The high level of O^- that remains near its maximum level over the depth measured provides evidence for the oxide layer extending well beyond the depth presented here. A thin layer of contamination on the oxidised sample is responsible for the maximum signals associated with the oxide appearing sub-surface; a possible explanation for this is enhanced surface contamination on the sample that is oxidised in air. For subsequent comparisons, the region where O^- and OH^- reach a maximum will be considered the start of the oxide surface.

The surface of the oxidised substrate is shown by XPS to be more oxidised than the annealed substrate. The SIMS depth profiles presented in Figure 3.23b, c demonstrate high levels of oxidation throughout the oxide layer for both the annealed and oxidised samples. The highly oxidised iron species FeO_3^- is observed to decrease on both substrates with depth. On the annealed substrate, this decrease is relatively rapid before reaching a constant intensity at a depth of approximately 10 nm, whilst the FeO_3^- signal on the oxidised substrate maintains its maximum concentration for a couple of nanometers before slowly decreasing through the measured depth of the film. FeO_2^- is shown to maintain a signal at almost its maximum level throughout the measured depth on the oxidised sample, whilst its intensity on the annealed substrate decreases. The signal from FeO^- increases below the surface (reach a plateau at approximately 2 nm and 6 nm respectively for the annealed and oxidised substrates) due to the sputtering of highly oxidised species from the surface and maintains a constant level through the depth measured. CrO^- , which was observed on Fe-13Cr to maintain its position at the oxide-alloy interface is found to maintain this position on the polished sample as shown in Figure 3.23a. However, on the annealed and oxidised substrates, CrO^- reaches a maximum within the first 2 nm of the surface, demonstrating that in these 99.9 % iron substrates heated to 300°C, the chromium-rich layer, located near the surface, is not sufficiently thick to prevent the diffusion of oxygen and iron. The increase in the signal to their maximum intensity for Fe_2O^- ,

FeCl_2^- , Fe_2^- and Fe_3O^- tends to occur part way through the oxide layer, as observed for the polished substrate in Figure 3.23a. These species reach their maximum value at approximately 6 nm and 20 nm on the annealed film and oxidised substrates respectively, suggesting that the oxide layer on the oxidised substrate is significantly thicker than on the annealed substrate. On both substrates, these species maintain their maximum intensity for the depth measured. On the polished substrate, Fe_2^- is associated with the alloy, rising in intensity at the base of the oxide and maintaining a high level into the bulk. On the annealed and oxidised samples, Fe_2^- is observed to increase with the species whose maximum intensity is located part way through the oxide layer (Fe_2O^- , FeCl_2^- , Fe_2^- and Fe_3O^-).

3.5.4 Summary of Results

Three model iron surfaces were produced to investigate the effect of the iron surface on deposition. The polished surface was found to have a native oxide of approximately 6 nm, with metallic iron observed beneath the oxide layer by XPS. The annealed and oxidised substrate were identified to be Fe_3O_4 and Fe_2O_3 by XPS, or magnetite and iron (III) oxide (the phase $-\alpha$ or γ - is undetermined) respectively. The polished surface was observed to be mostly homogeneous, with some scratches and surface deformities, attributed to the grinding and polishing of the surface. On the oxidised surface extensive iron oxide growth is observed along these scratches, as well as at grain boundaries; this is attributed to the improved diffusion of elements in these regions, leading to increased oxidation. Inconsistent iron oxide growth is observed on the oxidised sample which is attributed to the preferential growth of oxides on some faces of ferrite crystals. Enhanced iron oxide growth is also observed on the annealed surface along grain boundaries and scratch marks. There is some contrast between oxide growth on some regions of this substrate, however it is more subtle than the contrast apparent on the oxidised substrate. SIMS depth profiles through the oxide thickness demonstrates that a very thick oxide forms on the annealed and oxidised substrates extending to depths of greater than 125 nm, as the thickness of the oxide layer is no longer limited by the chromium content of the substrate. An oxygen gradient is observed over measured depth of the oxide, with more oxygen-rich iron species sputtered from the substrate nearer the surface and more iron-rich species sputtered from further into the

substrate.

3.6 Conclusions

Despite expectation, elemental studies by Dr. James Gilchrist of fouled injectors revealed an iron surface layer with a sub-surface chromium layer. In this Chapter Fe-13Cr substrates were studied at engine relevant temperatures, revealing a surface iron oxide with a chromium-rich sub-layer in good correlation with the characterisation work on injectors. As a result of these studies, iron was chosen as a model surface to investigate deposition. Three iron surfaces were prepared for use as model engine surfaces for deposition studies. These include a surface with a thin native oxide, referred to as the polished surface, an iron (III) oxide surface and a iron(II)(III) oxide surface believed to be magnetite. The oxide on the polished surface was shown to be very homogeneous, however the oxide on the oxidised surface seemed to grow based on the orientation of the iron crystal beneath it on the polycrystalline iron surface. The annealed surface, was shown to behave in the same way to a lesser degree.

References

- (1) Rees, E.; McPhail, D.; Ryan, M.; Kelly, J.; Dowsett, M. Low energy SIMS characterisation of ultra thin oxides on ferrous alloys. *Applied Surface Science* **2003**, *203-204*, 660–664.
- (2) Ostwald, C.; Grabke, H. J. Initial oxidation and chromium diffusion. I. Effects of surface working on 9-20% Cr steels. *Corrosion Science* **2004**, *46*, 1113–1127.
- (3) Holloway, P. H. Chemisorption and oxide formation on metals: Oxygen-nickel reaction. *Journal of Vacuum Science and Technology* **1981**, *18*, 653.
- (4) Hofmann, S Formation and diffusion properties of oxide films on metals and on nitride coatings studied with Auger electron spectroscopy and X-ray photoelectron spectroscopy. *Thin Solid Films* **1990**, *193-194*, 648–664.
- (5) Bradford, S. A., *Corrosion Control*, 1st ed.; Springer US: Boston, MA, 1993.
- (6) Cooper, L.; Benhaddad, S.; Wood, A.; Ivey, D. The effect of surface treatment on the oxidation of ferritic stainless steels used for solid oxide fuel cell interconnects. *Journal of Power Sources* **2008**, *184*, 220–228.
- (7) Kofstad, P., *High Temperature Corrosion*; 4, 1989; Vol. 24, pp 378–378.
- (8) Caplan, D.; Sproule, G. I. Effect of oxide grain structure on the high-temperature oxidation of Cr. *Oxidation of Metals* **1975**, *9*, 459–472.
- (9) Van Staden, M.; Roux, J. The controlled oxidation of the high chromium steel alloys Fe–40Cr and Fe–40Cr–3Ru. *Applied Surface Science* **1990**, *44*, 263–269.
- (10) Wang, Z.; Lu, K.; Wilde, G.; Divinski, S. Interfacial diffusion in Cu with a gradient nanostructured surface layer. *Acta Materialia* **2010**, *58*, 2376–2386.
- (11) Xia, Z. X.; Zhang, C.; Huang, X. F.; Liu, W. B.; Yang, Z. G. Improve oxidation resistance at high temperature by nanocrystalline surface layer., en *Scientific reports* **2015**, *5*, 13027.
- (12) Doyle, C. S.; Seal, C. K.; James, B. J. Evolution of steel surface composition with heating in vacuum and in air. *Applied Surface Science* **2011**, *257*, 10005–10017.

- (13) Li, X.; Wei, Y.; Lu, L.; Lu, K.; Gao, H. Dislocation nucleation governed softening and maximum strength in nano-twinned metals. *Nature* **2010**, *464*, 877–880.
- (14) Wang, J.; Farrell, J. Investigating the role of atomic hydrogen on chloroethene reactions with iron using tafel analysis and electrochemical impedance spectroscopy. *Environ. Sci. Technol* **2003**, *37*, 3891–3896.
- (15) Kizilyalli, M.; Corish, J.; Metselaar, R. Definitions of terms for diffusion in the solid state. *Pure and Applied Chemistry* **1999**, *71*, 1307–1325.
- (16) Thiel, P. A.; Madey, T. E. The interaction of water with solid surfaces: Fundamental aspects. *Surface Science Reports* **1987**, *7*, 211–385.
- (17) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS tables of chemical thermodynamic properties. Selected values for inorganic and C1 and C2 organic substrates in SI units. *Journal of Physical and Chemical Reference Data* **1982**, *11*.
- (18) Hakiki, N.; Montemor, M.; Ferreira, M.; da Cunha Belo, M. Semiconducting properties of thermally grown oxide films on AISI 304 stainless steel. *Corrosion Science* **2000**, *42*, 687–702.
- (19) Lampimäki, M.; Lahtonen, K.; Jussila, P.; Hirsimäki, M.; Valden, M. Morphology and composition of nanoscale surface oxides on Fe-20Cr-18Ni{111} austenitic stainless steel. *Journal of Electron Spectroscopy and Related Phenomena* **2007**, *154*, 69–78.
- (20) Greeff, A.; Louw, C.; Swart, H. The oxidation of industrial FeCrMo steel. *Corrosion Science* **2000**, *42*, 1725–1740.
- (21) Betz, G. Composition-vs-depth profiles obtained with Auger electron spectroscopy of air-oxidized stainless-steel surfaces. *Journal of Applied Physics* **1974**, *45*, 5312.
- (22) Harrington, D. A.; Wieckowski, A.; Rosasco, S. D.; Schardt, B. C.; Salaita, G. N.; Hubbard, A. T.; Lumsden, J. B. Films formed on well-defined stainless steel single-crystal surfaces in oxygen and water: studies of the (111) plane by LEED, Auger and XPS. *Corrosion Science* **1985**, *25*, 849–869.

- (23) Cho, B.; Choi, E.; Chung, S.; Kim, K.; Kang, T.; Park, C.; Kim, B. A novel Cr_2O_3 thin film on stainless steel with high sorption resistance. *Surface Science* **1999**, *439*, 799–802.
- (24) Mandrino, D.; Godec, M.; Torkar, M.; Jenko, M. Study of oxide protective layers on stainless steel by AES, EDS and XPS. *Surface and Interface Analysis* **2008**, *40*, 285–289.
- (25) Kurokawa, H. Oxidation behavior of Fe-16Cr alloy interconnect for SOFC under hydrogen potential gradient. *Solid State Ionics* **2004**, *168*, 13–21.
- (26) Vander Wal, R. L.; Hall, L. J. Carbon nanotube synthesis upon stainless steel meshes. *Carbon* **2003**, *41*, 659–672.
- (27) Tedmon, C. S. The effect of oxide volatilization on the oxidation kinetics of Cr and Fe-Cr alloys., en *Journal of The Electrochemical Society* **1966**, *113*, 766.
- (28) Ketteler, G.; Weiss, W.; Ranke, W.; Schlögl, R. Bulk and surface phases of iron oxides in an oxygen and water atmosphere at low pressure., en *Physical Chemistry Chemical Physics* **2001**, *3*, 1114–1122.
- (29) De Smit, E.; Weckhuysen, B. M. The renaissance of iron-based Fischer-Tropsch synthesis: On the multifaceted catalyst deactivation behaviour. *Chemical Society Reviews* **2008**, *37*, 2758.
- (30) Greeff, A.; Louw, C.; Terblans, J.; Swart, H. The influence of sulphur segregation on the oxidation of industrial FeCrMo steel. *Corrosion Science* **2000**, *42*, 991–1004.
- (31) Olefjord, I.; Elfstrom, B. The composition of the surface during passivation of stainless steels. *Corrosion* **1982**, *38*, 46–52.
- (32) Eklund, G. S. Initiation of pitting at sulfide inclusions in stainless steel. *Journal of the Electrochemical Society* **1974**, *121*, 467–473.
- (33) Della Rovere, C.; Alano, J.; Silva, R.; Nascente, P.; Otubo, J.; Kuri, S. Characterization of passive films on shape memory stainless steels. *Corrosion Science* **2012**, *57*, 154–161.
- (34) Banas, J.; Mazurkiewicz, A. The effect of copper on passivity and corrosion behaviour of ferritic and ferriticaustenitic stainless steels. *Materials Science and Engineering: A* **2000**, *277*, 183–191.

- (35) Yamashita, T.; Hayes, P. Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide materials. *Applied Surface Science* **2008**, *254*, 2441–2449.
- (36) Wu, X.; Voyshnis, S.; Seyeux, A.; Chumlyakov, Y.; Marcus, P. ToF-SIMS study of oxide films thermally grown on nickel-base alloys. *Corrosion Science* **2018**, *141*, 175–181.
- (37) Schwartz, A. J.; Kumar, M.; Adams, B. L.; Field, D. P., *Electron Backscatter Diffraction in Materials Science*, 2nd ed., 2009.

Chapter 4

Simulating Carbonaceous Deposit Growth

4.1 Overview

Deposits forming within injector components have adverse effects on engine performance, fuel economy and emissions. An understanding of the deposition mechanism is key in engineering fuel formulations and engine parts to prevent deposition. Carbonaceous deposits are formed from the thermal degradation of the fuel in a variety of hydrocarbon stream systems. These deposits have posed a long-standing challenge to the oil and gas industry, however a mechanistic understanding of deposition remains incomplete. This work aims to develop a mechanistic understanding of deposition by using a model system. N-hexadecane was chosen as a model diesel compound. Chapter 3 focused on characterising the engine steel Fe-13Cr, identifying iron as a model surface. The oxidation state and structure of the iron surface experienced by fuel within the injector is unknown, and therefore three different iron substrates were used to gain insights into the deposition mechanism. A polished substrate with a native oxide was compared to an iron(III) oxide and an iron (II)(III) oxide, which were characterised in Chapter 3. Using a combination of advanced characterisation techniques to characterise these model systems, the potential of iron surfaces to promote hexadecane oxidation is investigated.

In this chapter, the deposits forming on these iron substrates are investigated at different

soak times. The soak time refers to the time the substrate and hexadecane are left in contact following heating. This parameter aims to capture the effect of fuel, that has experienced thermal stress, remaining in contact with engine surfaces, following cooling (0.5 hours), a system that is left overnight (24 hours) and over the weekend (72 hours).

4.2 Aims and Experimental Details

1. Determine the effect of a metallic and non-metallic substrate on oxidation and deposition of hexadecane (Section 4.4.1)

- *Substrate:* a) 99.9 % iron substrate and b) silicon.
- *Sample preparation:* a) Polished (Section 2.2.2) and heat treated (Section 2.2.4); b) Cleaned (Section 2.2.1).
- *Characterisation:* XPS (Section 2.4.5.4 and Section 2.4.5.5); SEM (Section 2.4.8.3); ESI-MS (Section 2.4.2 and Section 2.4.2.1).

2. Investigate the interaction between iron and hexadecane (Section 4.4.2 – 4.4.6)

- *Substrate:* 99.9 % iron substrate.
- *Sample preparation:* Polished (Section 2.2.2) and heat treated to produce the oxidised and annealed substrates (Section 2.2.4).
- *Characterisation:* XPS (Section 2.4.5.4 and Section 2.4.5.5); SEM (Section 2.4.8.3); SIMS (Section 2.4.3.8 and Section 2.4.3.7); ESI-MS (Section 2.4.2 and Section 2.4.2.1).

4.3 Literature Review

The processes involved in the radical oxidation of hydrocarbons, the formation of oxidation products and the aggregation or nucleation of these species to form carbonaceous deposits are discussed in this chapter, with a particular focus on the role of iron. Much of the fundamental studies on the role of iron in fuel oxidation were carried out in the 1950s–1960s at industrial laboratories, with a focus on jet fuels. These studies are widely cited in peer-reviewed academic

publications, however the primary sources, including conference proceedings and industrial reports, are frequently unavailable. In subsequent decades, fundamental studies on the interaction between iron and hydrocarbons are particularly scarce in the open literature. Recent applied studies of injector deposits, which focus on characterising deposits (discussed in Chapter 1), do not further any mechanistic understanding. Therefore, recent studies of analogous systems will be discussed to provide mechanistic insights into the interaction of hydrocarbons and iron surfaces for applications in fuel systems.

4.3.1 Deposition

The stability of a fuel refers to its ability to resist ‘appreciable deterioration’ under certain conditions, for example where fuel is stored for extended periods of time (storage stability) or exposed to elevated temperatures (thermal stability).¹ Fuel degradation occurs via oxidation producing a variety of soluble and insoluble oxidation products (including particulate matter), referred to as gums. Soluble gums can oxidise or grow further forming high mass (200+ m/z) and heteroatom-rich species that are no longer soluble in a hydrocarbon matrix.^{1,2} Through both nucleation and aggregation processes, insoluble oxidation products will form sediment or surface deposits under storage conditions or thermal conditions respectively. These processes are shown in Figure 4.1.¹

Insoluble gums are identified as precursors to deposition; the processes through which deposits form are outlined here. Watkinson *et al.* published a schematic summarising mechanisms for chemical fouling (modified and shown in Figure 4.2) for an array of hydrocarbon stream systems under a variety of different conditions.³ As well as understanding the chemical reactions leading to the formation the deposit precursors, which is discussed in Section 4.3.2, a sense of how these precursors form deposits is key in understanding deposition. These processes include:

- The formation of aggregates from oxidation products in solution and subsequent deposition.
- The deposition of oxidised molecules onto the surface.
- The generation of oxidised products at the surface.

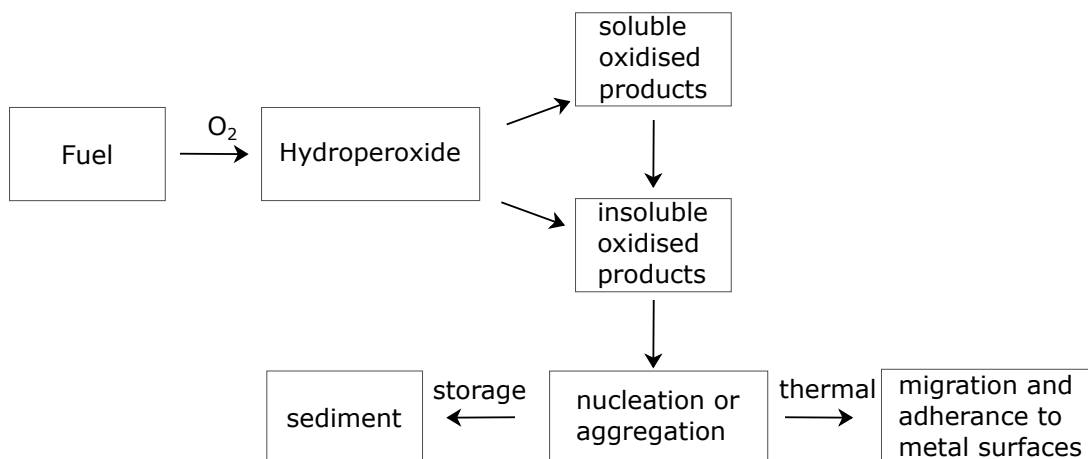


Figure 4.1: Schematic of the overall process of fuel stability. Modified from [1].

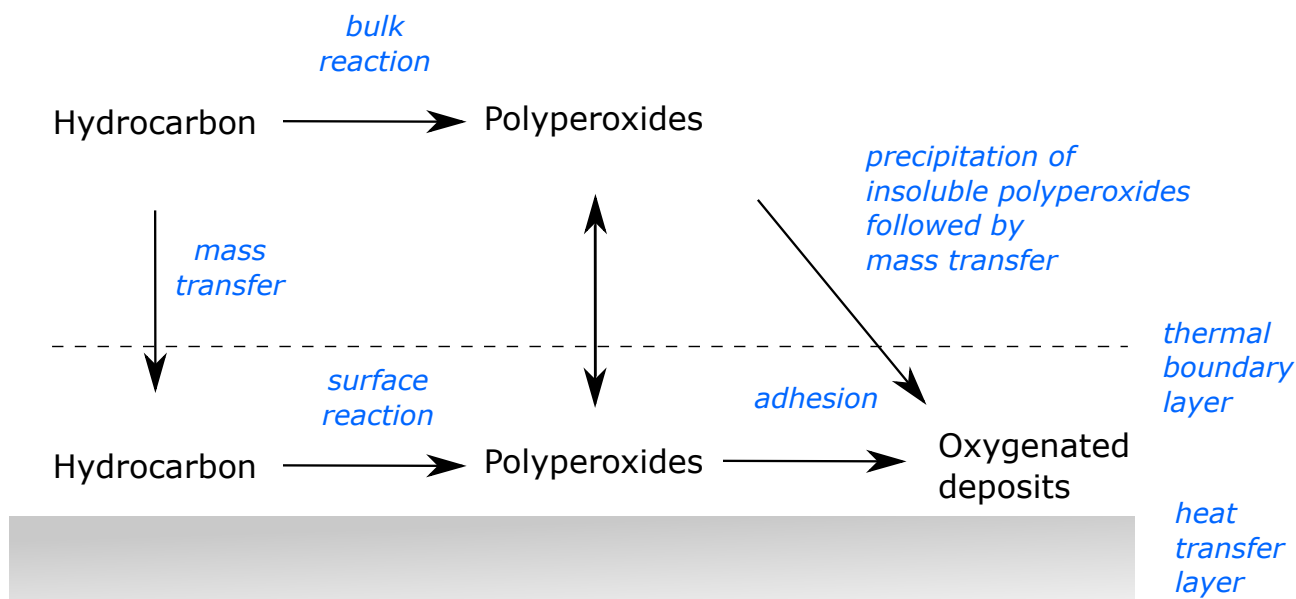


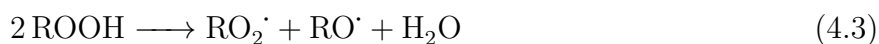
Figure 4.2: Schematic of the chemical fouling mechanism for hydrocarbons. Modified from [3].

4.3.2 Hydrocarbon Oxidation

The oxidation of hydrocarbons with dissolved oxygen is a free radical mechanism which proceeds via hydroperoxide intermediates (RO-OH) to produce a vast array of branched and oxidised products. This process is also referred to as autoxidation.

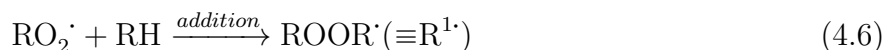
The initiation process for autoxidation is shown in Equation 4.1 to 4.3. Ultraviolet light, heat and metal contaminants are identified as possible radical initiators in the degradation of the fuel. Under engine relevant conditions, both heat and metal contaminants are likely sources of radical initiators. Depending on the conditions, initiation may occur through thermal decomposition or reactions with molecular oxygen.⁴

Initiation



Through propagation (Equation 4.4 to 4.7) and termination (Equation 4.8 to 4.10) reactions, numerous species are generated, leading to an increase in oxygen content, branching and polymerisation. Equation 4.1 to Equation 4.10 are widely referred to as the ‘basic autoxidation scheme’ (BAS).

Propagation



Termination



4.3.3 The Effect of Other Heteroatoms on Oxidation

The potential deleterious effect of nitrogen and sulfur heteroatoms on diesel stability is reviewed by both Hazlett and Batts.^{1,5} The nitrogen compound's identity determines its effects on the fuel, with some compounds found to be inert, whilst other compounds are found to promote both the degradation of the diesel and the formation of sediments/deposits. Similarly, some sulfur-containing species can promote the formation of oxidation products and hence deposits and sediment, through catalysing the oxidation of hydrocarbons while other sulphur compounds are reported to have anti-oxidant properties.^{6,7} The faceted role of heteroatoms in hydrocarbon oxidation will not be discussed further.

4.3.4 Oxidation of Hexadecane

The oxidation behaviour of n-hexadecane is well understood following extensive studies by Jensen *et al.* between 1976 and 1994 whilst working at Ford Motor Company.^{8,9} These studies: detailed the kinetics and mechanisms of reactions of peroxy radicals,¹⁰ described the formation of scission and cleavage products;^{8,11} determined the rate constant for hydrogen extraction; identified oxidation products^{9,12,13} and investigated the effect of oxygen pressure.¹⁴ All these studies were conducted between 120°C and 180°C, making them particularly relevant to engine conditions, as well as demonstrating that significant hydrocarbon oxidation will occur at relatively low temperatures.

In more recent experimental and computational studies (2001), Ristori *et al.* identified 242 oxidation products forming through 1801 chemical reactions in the oxidation of n-hexadecane.⁴

This study was conducted at high temperatures (1000 K to 1250 K), reducing its relevance to engine conditions, as thermal decomposition processes will contribute to hexadecane degradation at these temperatures,⁴ however this study served to demonstrate the complexity of the 'two-component' model system used in this work.

4.3.5 Oxidation Products of Hexadecane

In a study at 180°C lasting 12 hours, Blaine and Savage identified more than 300 species in the gas chromatography (GC) analysis of n-hexadecane. They studied the oxidation products formed in the autoxidation of n-hexadecane at temperatures ranging from 140°C to 180°C, using proton nuclear magnetic resonance (NMR), ¹³C NMR, gas chromatography mass spectrometry (GC-MS) and titrations to identify the reaction products and functional groups.¹⁵ The increase in viscosity observed upon heating is attributed to the oxidation of n-hexadecane forming high molecular weight polymeric products and solid deposits. Solid deposits were not observed in this work, however the concentration of oxidation products, by functional group, was studied in detail at temperatures of 140°C, 160°C and 180°C as a function of time, as shown in Figure 4.3.

Blaine and Savage measured how the concentration of different functional groups varied with temperature, observing the trends outlined below across the temperature range measured. Hydroperoxides (R-O-O-H) are the first product observed and therefore believed to form directly from hydrocarbons. Hydroperoxides are proposed to decompose and further oxidise, forming carboxylic acids, ketones and alcohols, due to the concurrent decrease in hydroperoxide concentration and increase in concentration of these secondary reaction products, as shown in Figure 4.3. Alcohols and ketones are postulated to form through bimolecular termination reactions with peroxy radicals R-O-O· whilst alkoxy radicals RO· can also form alcohols through hydrogen abstraction. Ketones are also proposed to form through intramolecular abstraction. The concentration of carboxylic acids are found to increase throughout the reaction, while the concentrations of alcohols and ketones decrease. Esters are observed as the last oxidation products in low concentrations; esters are believed to form from other oxidation products and not directly from hydroperoxides. Aldehydes are not observed in detectable levels, perhaps due to their rapid oxidation to carboxylic acids. These findings were summarised by Blaine and

Savage in Figure 4.4. More recent studies of oxidation products on n-hexadecane and diesel support these findings.^{4,16}

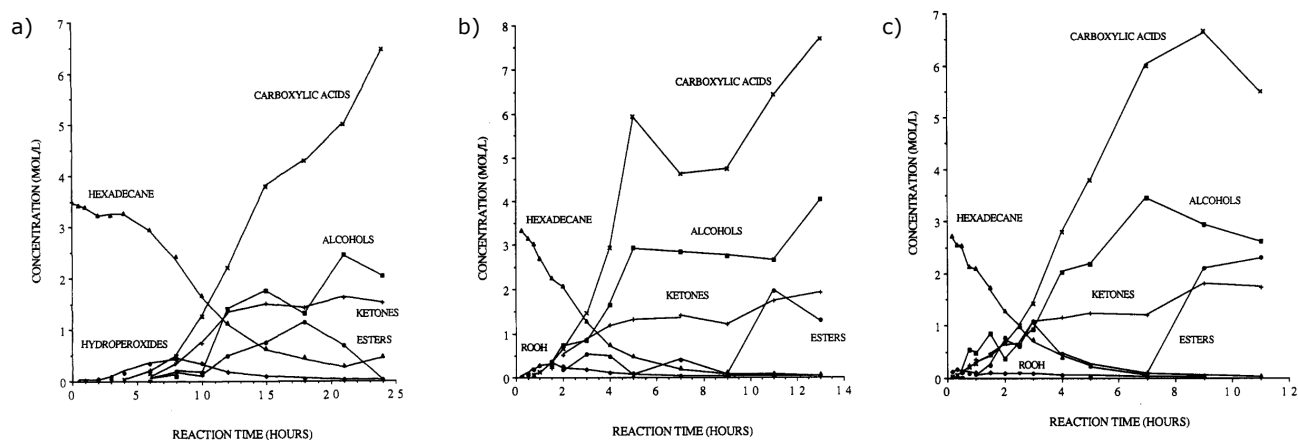


Figure 4.3: Concentrations of oxidation products following autoxidation at a) 140°C; b) 160°C; c) 180°C. Summary of findings from [15].

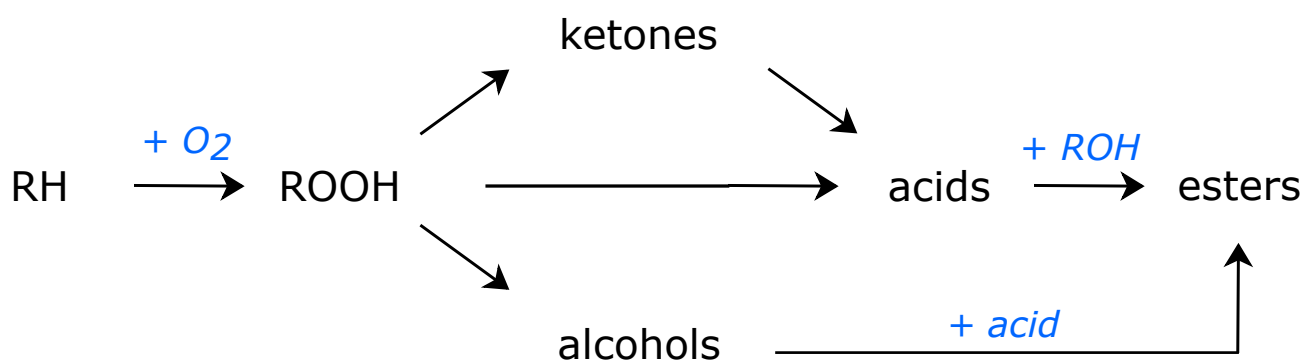


Figure 4.4: Schematic of the oxidation process. Modified from [15].

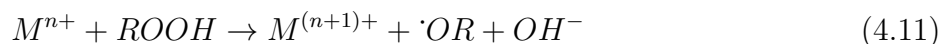
4.3.6 Homogeneous Catalysis of Autoxidation by Trace Metals

An acceleration of the oxidation process, and an associated reduction in fuel stability, has been observed in the presence of dissolved trace metals, including copper, lead and iron. Extensive studies were carried out from 1977 to 1990 on the thermal and oxidation properties of jet fuels in the presence of metal contaminants, particularly copper. From these studies the presence of copper in fuel was found to: increase the oxidation rate,¹⁷ increase the usage of dissolved oxygen at a given temperature¹⁸ and hydroperoxides were observed at lower temperatures.¹⁹ As a result of these findings, and the low concentrations of dissolved metals in the fuel, these metal contaminants were proposed to play a catalytic role in fuel autoxidation, leading to

the formation of insoluble gums.^{5,20} These catalytic mechanisms were outlined for copper contaminants, however concentrations of iron as low as 25 ppb are found to alter the properties of autoxidation, suggesting that iron also acts through a catalytic mechanism.²¹

4.3.7 Proposed Catalytic Behaviour of Iron

From the observations of the effect of iron on the properties of autoxidation, iron (as well as other trace metals) is proposed to promote oxidation through two catalytic mechanisms. The first pathway proposes that iron acts as an initiator in free radical oxidation. In addition, dissolved metals are proposed to further contribute to the oxidation of fuel through catalysing the breakdown of peroxides. In 1957, Walling proposed that dissolved multi-valent metal ions can catalyse the degradation of hydroperoxide species through the following equations.²²



4.3.8 Potential of Metals to Promote Heterogeneous Catalysis

In addition to homogeneous catalysis, the potential for heterogeneous catalysis of hydrocarbon autoxidation was reported in several studies in the 1960s, referenced by Taylor.²³ These studies demonstrated that metal and metal oxides surfaces, as well as solid suspended metal oxides, increase the rate of hydrocarbon oxidation with oxygen in the liquid phase. These findings are supported by more recent studies.²⁴ From investigations into the catalysis of jet fuel by Fe_2O_3 , Pickard and Jones proposed that iron oxide surfaces promote the dissociation of adsorbed hydroperoxides into an alkoxy and hydroxy radical.²⁵ These radicals can abstract hydrogen from other species, leading to the production of water, alcohols and alkyl radicals.²⁵ They also noted the level of deposits did not rise as expected in the doped fuel, which they attributed to the capacity of iron oxide surfaces to capture insoluble gums.²⁵

Dissolved iron contaminants, nanoparticles and solid suspensions have been conclusively

demonstrated to have adverse effects on the thermal and oxidation properties of the fuel, yet, there is strikingly few published investigations into the effect of iron surfaces, which are used throughout hydrocarbon stream systems, on the properties of the fuel. In 1990, a study by Stavinoha *et al.* at Belvoir Fuels and Lubricants Research Facility investigated the levels of deposition forming on tubes made from different materials; the levels of deposition were found to increase from gold to aluminium to copper to magnesium and 316 steel where equal levels of deposition were observed and finally to copper tubes.²⁶ Ervin *et al.* compared a steel surface with silico-treated steel surface; they observed a delay in fuel oxidation and decreased deposition with the treated tubing.²⁷ These studies provide convincing evidence that the surface can play a role in both oxidation and deposition but does not consider potential oxidation or deposition mechanisms.

Other studies considered the effect of surface coverage by deposits on the oxidation and deposition rate. An early study by Taylor reported surface fouling to have a limited, if any, effect on oxidation and deposition rates.²⁰ Due to an observed decrease in oxidation rate with deposition, Jones and Balster suggested deposition had a passivating effect on the surface, blocking ‘active sites’ and therefore eliminating any potential for heterogeneous catalysis.²⁸ Lacey *et al.* reported a similar sentiment in their more recent studies of internal diesel injector deposits, where they proposed that iron is ‘unlikely’ to participate in oxidation and/or deposition due to its burial under micrometer-thick deposits.²⁹ Whilst the deactivation of the surface following deposition is a feasible mechanism, robust analysis is required to elucidate the potential of iron surfaces to promote oxidation and deposition and evaluate key parameters.

4.3.9 Studies on Model Systems

Venkatarman and Eser used a model system of hexadecane and a stainless steel tube reactor to reproduce deposits they had characterised from inside fouled injectors. They reported a good correlation between injector deposits and deposits produced in the laboratory from the thermal stressing of the model diesel compound, hexadecane in a flow reactor at 160°C and 31 bar.³⁰ Both these deposits were found to contain polyaromatic hydrocarbons with oxygen moieties, therefore, deposits formed from hexadecane under these conditions are shown to provide a

valuable model for injector deposits.³⁰

4.4 Results and Discussion

4.4.1 The role of iron

To gain an insight into the role of iron in hexadecane oxidation and deposition, non-metallic silicon substrates were compared to iron substrates, which were identified as a model engine surface in Chapter 3. The substrate is found to affect the amount, morphology and chemical composition of deposits. Several deposit morphologies are observed on polished iron substrates, including a film, islands and aggregates; at soak time of 72 hours these morphologies are clearly distinguishable and therefore presented in Figure 4.5a-b. At 0.5 hours soak time, these morphologies are observed in their initial stages as shown in (Figure 4.5c). On the silicon substrate only aggregates are observed (Figure 4.5d). These findings demonstrate deposition on iron occurs through both surface nucleated growth and the deposition of aggregates, however on the silicon substrate, surface nucleated growth is not observed.

Chemical characterisation of the substrates before and after deposition demonstrates that the silicon surface acts a passive substrate, whilst the iron surface plays an active role. XPS characterisation of the silicon substrate shows the silicon substrate did not change during deposition (Figure 4.5e), with the observed 3 % decrease in the atomic percentage of silicon attributed to deposits forming on the surface. Iron however, undergoes a transition upon exposure to hexadecane at elevated temperatures, shown in Figure 4.5f by the loss of the sharp peak associated with metallic iron at 706.7 eV. This transition is believed to be real, rather than an artefact of a decrease in XPS probing depth due to increased deposition at the surface, as only an 8 % decrease in the atomic percentage of iron is observed. The XPS probing depth is commonly quoted as approximately 10 nm and the native oxide thickness on the untreated polished substrate is determined to be approximately 5 nm in Section 3.5.3. These findings support the active role of iron in deposition of hexadecane.

Chemical characterisation of the deposit demonstrates the effect of the substrate on the oxidation and deposition of hexadecane. On the silicon substrate, the atomic percentage of

carbon increases from 5 % (attributed to adventitious carbon) to 10 % following deposition. The XPS lineshapes of oxygen and carbon remain essentially unchanged (Figure 4.5g,i), suggesting that the substrate does not promote hexadecane oxidation or deposition. On the contrary, more deposition is observed on the iron substrate, with the atomic concentration of carbon increasing from 22 % (attributed to adventitious carbon) to 33 % following deposition. Furthermore, an increase in the carbon oxidation state is shown in Figure 4.5h, with an associated increase in the oxygen trace shown in Figure 4.5j. From the results presented in Figure 4.5, iron surfaces can be concluded to play an active role in deposition.

Hexadecane oxidation is also promoted by iron substrates, compared to silicon substrates. The solutions from which the deposits formed are analysed by positive/negative ion ESI-MS and plotted using the Kendrick mass defect (KMD), as shown in Figure 4.6. Plotting the mass spectra using the KMD highlights homologous series; using the KMD for CH_2 , homologous series increase in (i)-(iii) CH_2 and (iv) oxygen atoms will be observed along horizontal and diagonal lines respectively. Examples of homologous series are annotated in Figure 4.6g-h. Processes associated with the autoxidation of hydrocarbons, including branching, increasing oxygen content and ‘polymerisation’, are present in these plots in the form of horizontal lines, diagonal lines and the repetition of diagonal lines respectively. Each data point in these plots corresponds to an oxygen-containing species, including isotope ions, broadly presumed here to be an oxidation products of hexadecane. Saturated and unsaturated hydrocarbons containing 1–11 oxygen and/or 48 carbon atoms per molecule have been observed, demonstrating high levels of branching, oxidation and polymerisation.

Utilising the polarities of ESI-MS the obtained positive and negative ions reveal broad insights into the levels of oxidation in solution. Positive ion ESI-MS largely ionises basic/neutral compounds, such as carbonyls and esters whilst negative ion ESI-MS predominantly favours the ionisation of acids. Aldehydes are commonly not observed oxidation products due to their rapid oxidation to carboxylic acids, while esters are reported to form in low concentrations at longer times. Ketones form as primary oxidation products from the hydroperoxides and therefore the positive plots will be used as a representation of the early stages of oxidation. Carboxylic acids have been shown to form as both primary oxidation products from hydroperoxides and

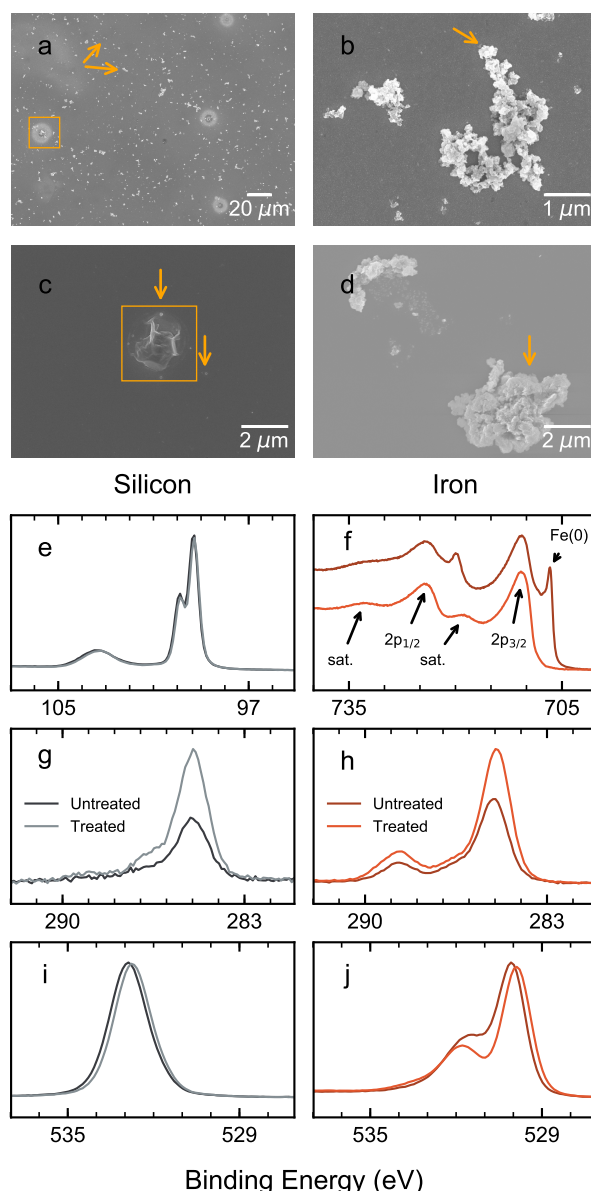


Figure 4.5: a/b) Examples of deposit morphologies forming on polished iron after a 72 hour soak time including: islands (shown in orange boxes); aggregates (highlighted by orange arrows) and film deposits. SEM images of deposits forming on polished iron substrates after 0.5 hours soaking are shown for c) iron and d) silicon substrates. Chemical characterisation by XPS are shown on silicon (grey) and iron (orange) for the: (e) silicon; (f) iron; (g) - (h) carbon and (i) - (j) oxygen traces. These data are normalised to the total substrate, carbon and oxygen areas for each sample.

secondary oxidation products from the reaction of primary oxidation products. Alcohols are primary oxidation products. Both carboxylic acids and alcohols will ionise to form negative ions, however the negative plots in this work are used to illustrate extensive hydrocarbon oxidation.

Heat is widely accepted to act as a free radical initiator in the autoxidation of hydrocarbons.

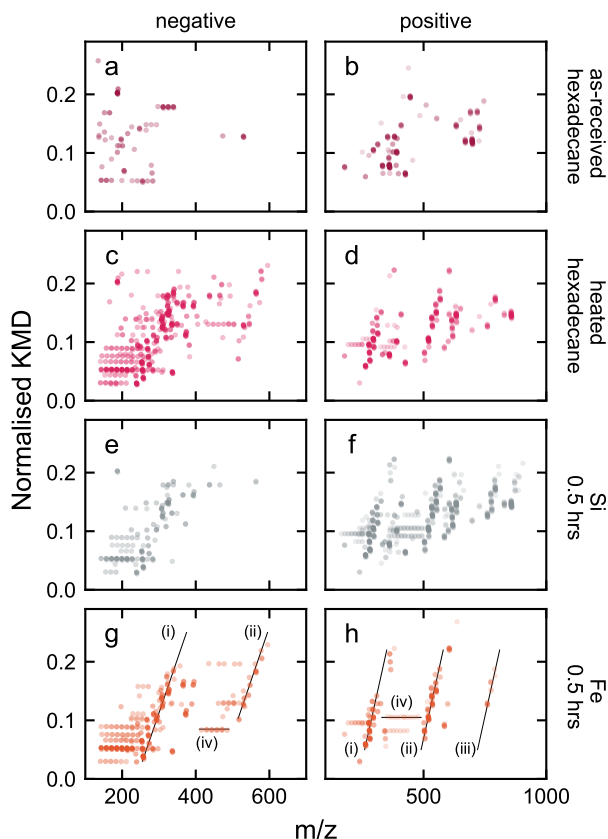


Figure 4.6: Mass spectrometry of the solutions following deposition are presented in Kendrick mass defect (KMD) plots. Negative and positive ion ESI-MS are shown respectively for: a/b) as-received hexadecane; c/d) heated hexadecane; hexadecane heated with e/f) silicon and g/h) polished iron substrates. Homologous series for (i)-(iii) oxygen and (iv) CH_2 series are annotated. The colour scale is the relative abundance normalised to the total intensity on compared scans plotted on a logarithmic scale.

Significantly more oxidised species are observed following heating, shown in Figure 4.6c-d, than in the as-received bottle of hexadecane shown in Figure 4.6a-b. The decrease in the number of species detected using negative ion ESI-MS in solution (Figure 4.6e,g), upon the addition of a passive silicon substrate, is attributed to the deposition of these oxidised species onto the surface as aggregates. Analysis of the species detected using negative ion ESI-MS in solution, following deposition on iron, (Figure 4.6g), reveal both a decrease in the number of species with masses below 400 m/z compared to heated hexadecane (Figure 4.6c) yet an increase in the number of oxygen-containing species compared to the silicon substrate and the appearance of homologous series at high masses (Figure 4.6g). These observations demonstrate the interplay between the promotion of hexadecane oxidation by iron and the affinity of oxidised species for iron surfaces. The increase in oxidised species in solution as well as the increase in oxidation in

the deposit provide compelling evidence that iron surfaces, similarly to dissolved iron, can have harmful effects on fuel stability.

As mentioned above, the species detected using positive ion ESI-MS, shown in Figure 4.6, are believed to have ketone functionality and are interpreted here to represent the early stages of oxidation. The decrease in the number of species detected using positive ion ESI-MS found in solution with the iron substrate compared to the silicon substrate can be attributed to either, the enhanced deposition of these species onto the iron surface, or, the further oxidation of ketones to carboxylic acids promoted by the presence of iron. The decrease in the number of species detected using positive ion ESI-MS (ketones) in the solution heated with an iron substrate, compared to a silicon substrate, and corresponding increase in the number of species detected using negative ion ESI-MS (carboxylic acids) support the hypothesis of further hexadecane oxidation. A reason for the increase in the number of species detected using positive ion ESI-MS when the solution is heated with silicon, as opposed to heated without silicon, is unclear (Figure 4.6f).

These findings provide evidence for the potential of iron surfaces to promote the oxidation of hexadecane and its deposition.

4.4.2 The Effect of The Iron Surface Finish

Three iron substrates with differing surface chemistry were used to gain mechanistic insights into the role of iron in oxidation and deposition. These substrates were characterised in Chapter 3, but will be briefly introduced here. On the polished substrate a native oxide approximately 5 nm in thickness forms on the surface, therefore, metallic iron is found in the XPS spectra, as shown by the sharp peak at 706.7 eV in Figure 4.7a. The annealed substrate is assigned as iron(II)(III) oxide due to the shoulder at 708.8 eV and the absence of a satellite between the iron doublet, as shown in Figure 4.7b.³¹ The oxidised substrate is assigned as iron (III) oxide due to its double peak at 710.0 and 711.2 eV and a satellite at 719.0 eV, as shown in Figure 4.7c.

Following exposure to hexadecane at elevated temperatures, a chemical change occurred on the polished and the annealed sample, shown in Figure 4.7 by the loss of the metallic iron and shoulder respectively. The resulting chemistry appears to be the same on both substrates

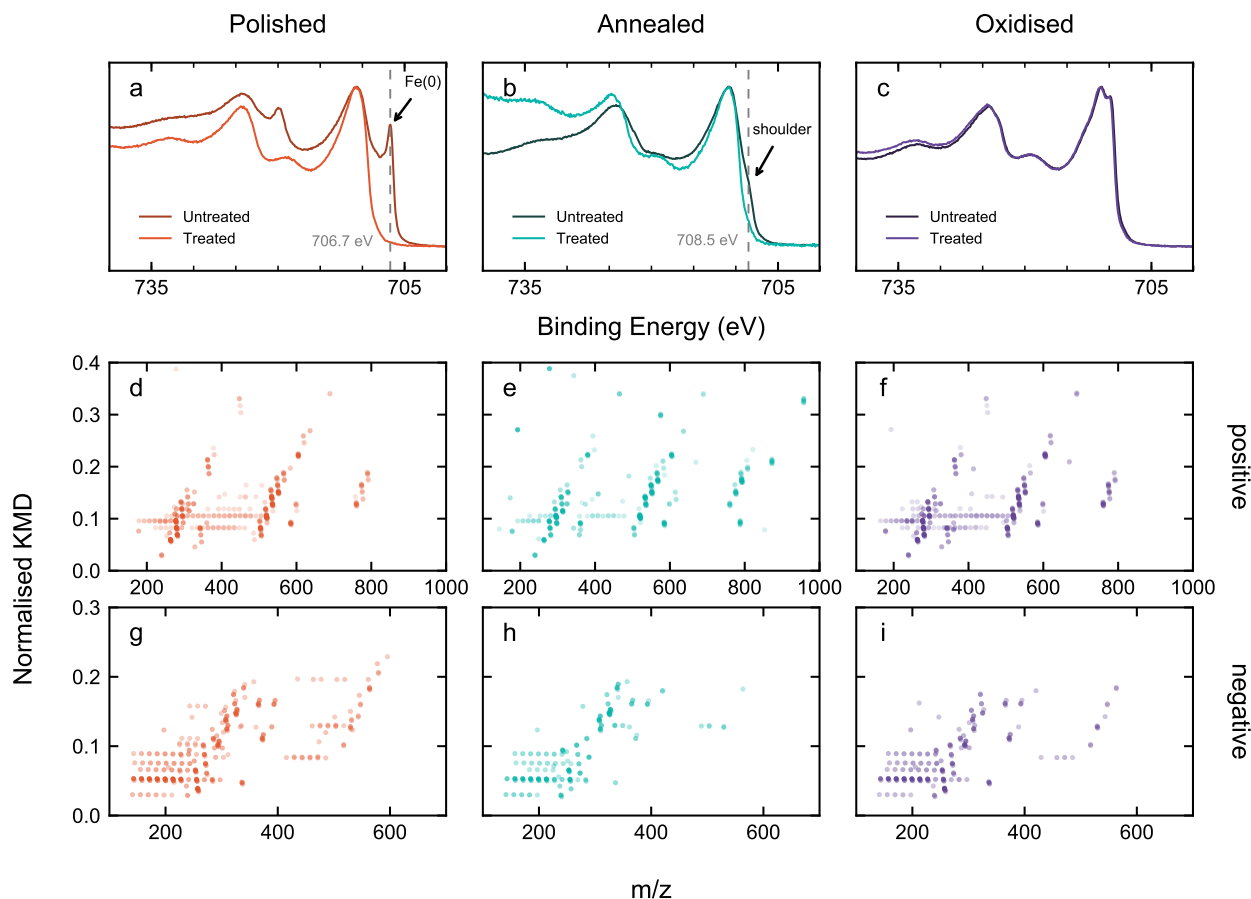


Figure 4.7: XPS iron traces are shown for the a) polished; b) annealed and c) oxidised substrates before and after exposure to hexadecane at elevated temperatures at 0.5 hour soak times. Positive and negative Kendrick Mass Defect (KMD) plots are shown respectively for a solution heated with: d/g) the polished substrate (orange); e/h) the annealed substrate (turquoise); f/i) the oxidised substrate (pink) and soaked for 0.5 hours produced from positive/negative ion ESI-MS. The colour scale is the relative abundance normalised to the maximum intensity of the most intense peak in all compared scans, plotted on a logarithmic scale.

and is proposed to be iron(III) oxide hydroxide.³² This transition accounts for an increase in iron oxidation state from iron(0) and iron(II)(III), on the polished and annealed substrate, to iron(III) following deposition. The iron (III) surface did not change following exposure to hexadecane at elevated temperatures.

The surface chemistry of the substrate was found to affect the degree of hexadecane oxidation. High mass, oxygen-rich species that were not observed with the silicon substrate are observed with all iron substrates, demonstrating that iron can promote hexadecane oxidation regardless of its oxidation state. The largest number of oxidised species are observed with the polished substrate; CH₂- and oxygen- homologous series at high masses (500 and 600 m/z) correspond to

alkenes containing O_3 , O_4 or O_3N along horizontal lines and the species $C_{38}H_{59}O_x$ where $x = 0-5$ and $C_{38}H_{57}O_x$ where $x = 1-4$ along vertical lines, as shown in Figure 4.7g. The increased levels of hexadecane oxidation with the polished sample suggests that the availability of metallic iron near the surface is key promoting oxidation. The lowest number of oxidised species are observed with the annealed surface, as shown in Figure 4.7e/h. A similar number of positively ionising species (Figure 4.7f) are found with the oxidised substrate compared to the polished substrate, yet fewer species detected using negative ion ESI-MS are observed (Figure 4.7i) suggesting less hexadecane oxidation.

In addition to hexadecane oxidation, the surface chemistry is found to influence the morphology and amount of deposits and their chemical states. The SEM images in Figure 4.8 are shown for a 24 hour soak time as the deposit morphologies are more obvious at this time point, however the chemical characterisation is presented for a 0.5 hour soak. On the polished sample, a film, islands and aggregates are observed (Figure 4.8a), as discussed in Section 4.4.1. These deposits contain the largest fraction of oxidised material as shown in Figure 4.8e. Aside from some small aggregates, it is difficult to identify any deposition on the annealed sample (Figure 4.8b), however XPS characterisation of this substrate after 0.5 hours demonstrates that the most deposition is observed on this substrate (Figure 4.8d), which is relatively, the least oxidised (Figure 4.8e). Therefore a thick, predominantly aliphatic, carbonaceous layer is proposed to form on the iron(II)(III) substrate following deposition. The oxidised substrate is inhomogeneous and therefore, distinguishing between deposition and surface variations is challenging. The least deposition was observed on the oxidised substrate (Figure 4.8d), which was also the least oxidised overall (Figure 4.8d)

To further investigate the chemistry of the deposit, and track the levels of oxidation within the deposit under different conditions, each XPS carbon trace was fit with the peaks identified in Figure 4.8f. The absence of the $\pi-\pi^*$ satellite in these traces suggest that polyaromatic hydrocarbons deposits, which are found in fouled injectors, are not reproduced in this model system. These states have largely attributed to C-C, C-O, C=O, O-C=O and metal carbonate bonds. A small shift to higher binding energies was observed for the peak attributed to C-O and C=O under some conditions.

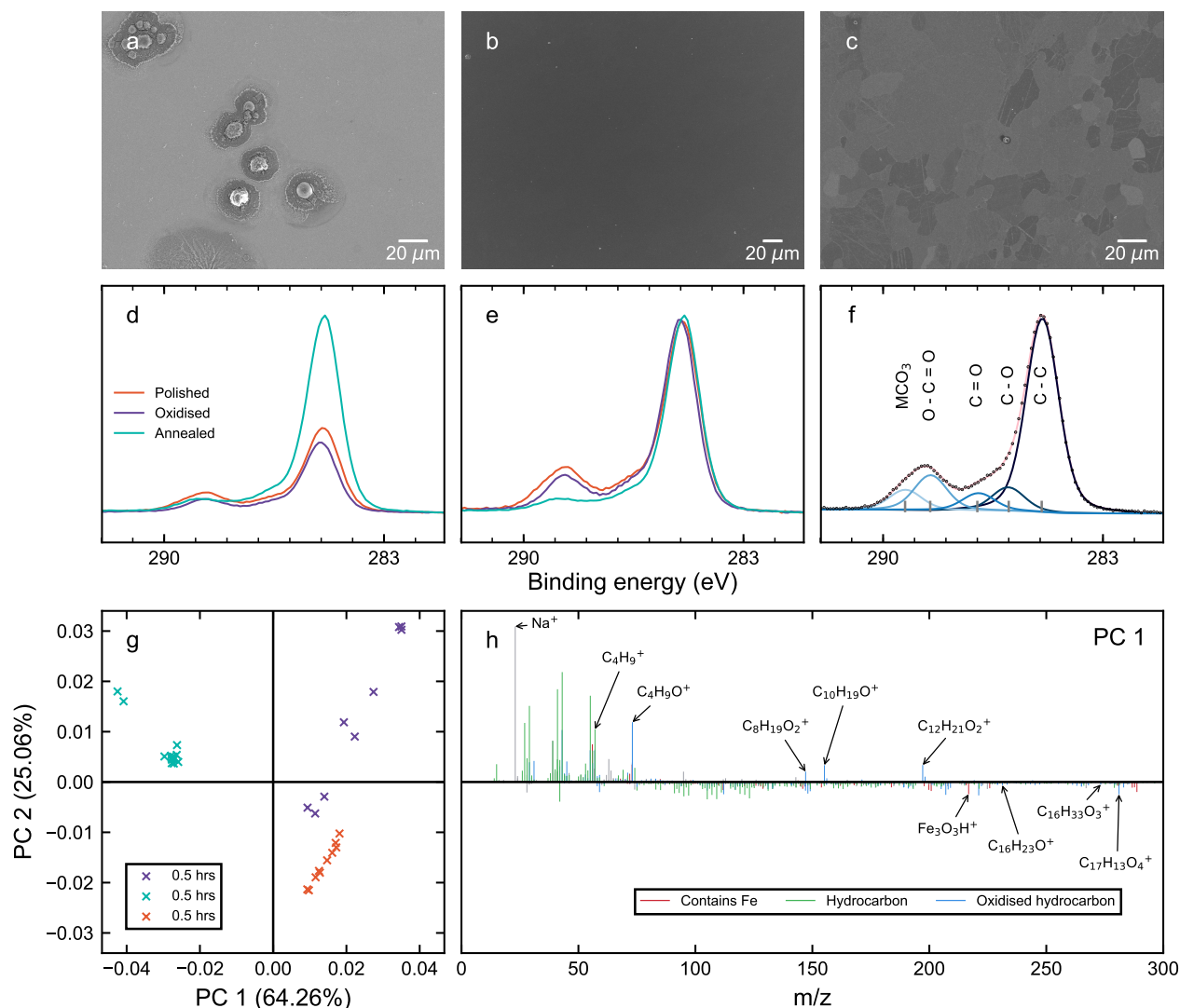


Figure 4.8: SEM images of deposits after 24 hours on a) polished; b) annealed and c) oxidised iron substrates. XPS carbon traces of deposits after 0.5 hours are shown d) normalised to the total counts of iron, carbon and oxygen; e) normalised to the C-C bond and f) on a polished substrate with fits showing the chemical state. The g) scores plot and h) loadings plot (PC1) from principal component analysis of static SIMS on the deposit on polished, annealed and oxidised substrates.

The surfaces of these substrates were studied using SIMS following deposition and a soak time of 0.5 hours. Principal component analysis (PCA) was used to highlight the major differences in deposit composition between samples, with each data point in Figure 4.8g representing a surface scan of that substrate. The scores plot in Figure 4.8g, also provides an insight into the homogeneity of deposition. The small distribution of the points for the annealed sample (with the exception of 2 measurements) supports the formation of a uniform layer on the annealed substrate. As expected from the SEM image in Figure 4.8c, the deposit on the oxidised substrate

is the most inhomogeneous.

Principal component 1 (PC1) identifies the largest differences in sample composition to be between the annealed substrate and the other two substrates, as shown in the scores plot in Figure 4.8g. The loadings plot in Figure 4.8h accounts for these differences; on the polished and oxidised substrates, a number of aliphatic (shown in green) and oxidised species (shown in blue) are observed at masses less than 70 m/z. In contrast, on the annealed substrate masses up to 300 m/z are shown in Figure 4.8h, with peaks associated with hexadecane, hexadecene, oxidised hexadecane/ene ($C_{16}H_{...}O_x$) and hydrocarbon fragments with masses above 70 m/z are identified. An explanation for these observations is that highly oxidised deposits, expected on the polished and oxidised sample, will fragment upon impact of the primary ion beam leading to the detection of relatively low-mass species. However on the annealed substrate, where the deposits are less oxidised and primarily aliphatic in character, less fragmentation will occur as a result of the experimental technique and therefore higher mass species are observed. The reduced solution oxidation, lower levels of oxidation within the deposit and increased deposition on the annealed substrate, suggest that the interaction between hexadecane and the annealed surface, containing both iron(II) and iron(III) species is different from the interactions of the oxidised and polished substrates.

4.4.3 Mechanism on Different Substrates

The loss of the iron(0) peak following exposure to hexadecane at 200°C, alongside the extensive hexadecane oxidation observed in the solution and in the deposit, suggest that iron(0) plays an active role in the oxidation of carbon species. The iron substrate is believed to be oxidised from a surface where iron(0) is accessible to a surface containing iron(III) which is identified as iron(III) oxide hydroxide.³² The transfer of electrons from the iron substrate to the solution, initiating free radical oxidation, is supported by both these findings, as well as the widely reported role of iron in the initiation of autoxidation. The oxidation of an iron substrate from iron(0) to iron(III) and concurrent transfer of electrons from the surface to an aqueous species has been observed in other systems. Examples of these systems include the passivation of iron by chromate solutions³³ and the use of iron as a reducing agent for chlorinated solvents, where

the mechanism is reported to occur through direct electron transfer at neutral pHs and hydrogen atom transfer at low pHs.^{34,35} Whilst the presence of carboxylic acids is widely reported, the pH of these solutions is unknown.

A similar electron transfer process, albeit with less electrons, is proposed for the annealed substrate where a transition from iron(II) to iron(III) is observed. In a study by Kendelewicz *et al.*, magnetite (111) was oxidised to form iron(III) oxides and hydroxides through redox reactions with chromates. Using XAS, Pinakidou *et al.* found a surface layer of maghaemite (γ -Fe₂O₃) to form following electron transfer from the magnetite surface. The lower levels of hexadecane oxidation observed both in the solution and in the deposit with iron(II) compared to iron(0), provides further support for electron transfer from the metal substrate to initiate hydrocarbon oxidation.

The transition to iron(III) and the respective electron transfer initiating oxidation is not possible on the oxidised (iron(III) oxide) substrate, however enhanced hydrocarbon oxidation is observed compared to the silicon substrate. Therefore, an alternative mechanism is required to explain the behaviour of iron(III) oxide; the catalytic breakdown of peroxides by metal contaminants is another widely cited yet vague phenomenon in the catalytic oxidation of hydrocarbons.^{22,25}

The breakdown of peroxides is compared here to Fenton catalysis, whereby hydrogen peroxides are broken down by iron at room temperature for water treatment. Fenton catalysis has been extensively studied in recent years, with both iron(II) and iron(III) shown to catalyse the breakdown of hydrogen peroxides, through Fenton (analogous to Equation 4.11) and Fenton-like (analogous to Equation 4.12) reactions respectively. Iron(II) is shown to be more active than iron(III) in both homogeneous and heterogeneous (magnetite versus hematite) catalysis.³⁶⁻³⁸

The catalytic breakdown of peroxides by iron(III) provides a feasible explanation for the increased hydrocarbon oxidation on the oxidised substrate, despite no changes in the iron oxidation state. The potential of the annealed substrate to both initiate hydrocarbon oxidation and catalyse the breakdown of hydroperoxides may explain the high amounts of deposition observed on this substrate, however an explanation for the predominantly aliphatic deposits remains uncertain. Surface area, crystallinity and pH are highlighted as important factors to

consider in Fenton catalysis, and therefore, may provide some useful insights in this system.^{36,37}

The dissolution of iron, especially at low pHs, is shown to facilitate both heterogeneous and homogeneous catalysis. Zhao *et al.* recently proposed that the iron surface chemistry determines the type of catalysis that will occur; heterogeneous catalysis occurs on iron(III) oxide hydroxide surfaces, homogeneous catalysis occurs due to the dissolution of hematite and both heterogeneous and homogeneous catalysis is observed on magnetite surfaces.³⁹ This study may provide valuable insights in understanding the oxidation and deposition behaviour of these systems, however the type of catalysis, the dissolution of iron and its speciation was not investigated in this work. The trends observed following deposition at 0.5 hours soak times are presented in Figure 4.12.

4.4.4 The Effect of Soak Time

Figure 4.12 illustrates the trends in oxidation and deposition discussed in this section. When substrates are left in hexadecane that has been thermally stressed at room temperature, further hexadecane oxidation and deposition is found to occur. Following heating, all the substrates have a similar surface chemistry, containing iron(III). At soak times of 0.5 hours, the substrate chemistry prior to heating determines the amount of deposition and the hexadecane oxidation in the solution and in the deposit. At 24 hours, changes in the levels of deposition and oxidation are attributed to the the overall system oxidation which is a consequence of the original substrate chemistry.

The deposition at 24 hours soak times is proposed to be a consequence of the initial surface chemistry. The extensive solution oxidation observed at 0.5 hours with the polished sample results in increased deposition at 24 hours (Figure 4.9a), in which the deposit is more oxidised (Figure 4.9b). The decrease in oxidised species in solution, due to their deposition onto the surface, as aggregates or a film, suggests that further hexadecane oxidation does not occur at this time point. Similar trends are observed with the oxidised substrate; some hexadecane oxidation occurs at soak times of 0.5 hours producing species that are believed to deposit at 24 hours. The carbon atomic percentage stays constant (Figure 4.9a) despite the deposition of oxidised species (Figure 4.9b), suggesting deposition is accompanied by the loss of predominantly

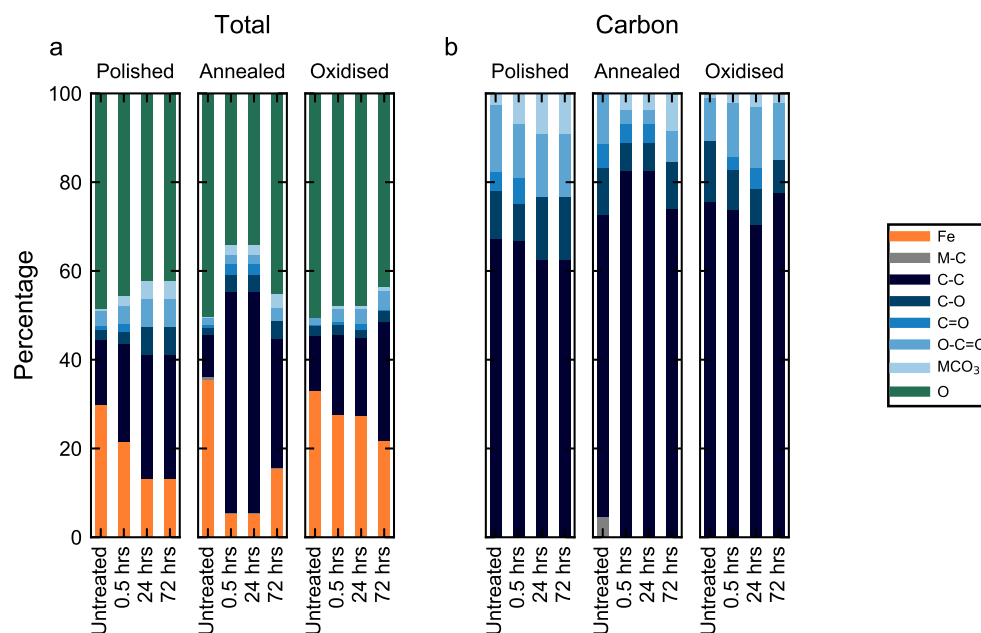


Figure 4.9: Atomic quantifications from XPS spectroscopy based on the fits presented in Figure 4.8f for the untreated and treated (0.5, 24 and 72 hour soaks) polished, annealed and oxidised surfaces are presented. a) Provides the overall atomic quantification; b) provides the atomic percentages of carbon oxidation states.

aliphatic species from the deposit. A thick uniform deposit is proposed to form on the annealed sample at 0.5 hours, which appears unchanged at 24 hours, as shown in Figure 4.9a/b. However, the cause of increased solution oxidation on the annealed substrate, despite extensive surface coverage, is unclear, suggesting that perhaps, analogous to Fenton catalysis, homogeneously catalysed hexadecane oxidation may occur.

Following heating, iron(III) oxide and/or hydroxide is present on the surface of each substrate. At 72 hours further hexadecane oxidation is observed, demonstrating iron(III) has the capacity to catalyse hydrocarbon oxidation at room temperature. Oxidation and deposition are observed to varying extents on each substrates; this difference is attributed to the surface coverage of the deposit and hence the availability of iron to the solution.

The least deposition is observed on the oxidised substrate at 24 hours (Figure 4.9a) meaning iron on the oxidised substrate is the most available. Therefore, the greatest levels of oxidation and deposition are expected on the oxidised substrate at 72 hours. An increase in the solution oxidation is observed as well as an increase in deposition at the surface (Figure 4.9a). The depositing species are thought to be largely aliphatic as the proportion of aliphatic to oxidised

carbon species increases in Figure 4.9b. On the polished surface, which is shown to be less exposed than the oxidised surface (Figure 4.9a), no changes are observed in the amount of deposition or deposit oxidation at the surface (Figure 4.9a/b), however an increase in hexadecane oxidation is observed.

Due to the extensive deposit formed on the annealed surface, the iron(III) surface is expected facilitate limited oxidation and deposition. At 72 hours, the carboxylic acid concentration in solution increases, whilst the carbonyl concentration in solution decreases, suggesting that the oxidation of carbonyl species is occurring in solution. The atomic percentage of carboxylic acid in the deposit increases, as shown in Figure 4.9a, despite no overall change in the amount of oxidised carbon in the deposit. These observations demonstrate that further oxidation, albeit limited, is occurring in this system. There is a significant decrease in the amount of deposition at the surface; the increase in solution polarity caused by increased hexadecane oxidation is believed to facilitate the dissolution of predominantly aliphatic carbon species from the surface, which were previously insoluble in the hydrocarbon matrix. A relative increase in the concentration of oxidised carbon in the deposit is shown in Figure 4.9b.

At 24 hours, the original surface chemistry is found to still have an effect on oxidation and deposition. At 72 hours, the iron(III) surfaces are believed to promote further oxidation. The degree of oxidation is postulated to depend on the availability of iron(III) at the surface, which has been observed to promote further oxidation at room temperature. The activity of iron(III) is believed to be the most active for the oxidised, followed by the polished and then the annealed substrate. Further hexadecane oxidation leads to increased deposition on the oxidised substrate. No change is observed in the amount or nature of the deposit on the polished substrate despite increased hexadecane oxidation. On the annealed substrate a decrease in the amount of deposition is observed at 72 hours, attributed to the re-dissolution of the deposit due to increased solubility of the deposit in the oxidised solution. Zhao *et al.* proposed haematite (iron(III)) surfaces to promote oxidation through homogeneous catalysis, suggesting that the dissolution of iron plays a more important role than heterogeneous catalysis on this surface.³⁹ Magnetite surfaces are also reported to promote oxidation through homogeneous catalysis, which may provide an explanation for the continued solution oxidation at 24 hours

on the annealed surface in spite of the extensive deposition that covers this surface.³⁹ The dissolution of iron, its speciation and its subsequent potential for homogeneous catalysis is not studied here. However, the finding - that the iron(III) surface, produced by all starting surface chemistries, upon exposure to hexadecane at elevated temperatures, can promote oxidation at room temperature - has significant consequences for engine deposition.

4.4.5 Variations in Deposit Composition With Soak Time

As in Figure 4.8g/h, the scores plot from principal component analysis provide an insight into the degree of homogeneity across the surface through the comparison of ten SIMS surface analyses per sample. In Figure 4.10a for the polished substrate, the surface homogeneity is consistent with the deposition model: following heating, a homogeneous film forms on the substrate, however following the formation of islands after soaking for 24 hours, a decrease in the surface homogeneity is observed. On the annealed surface, where a uniform carbonaceous layer is hypothesised, the surface chemistry is the most inhomogeneous at 0.5 hours. The deposit homogeneity is found to increase after 24 hours on the annealed substrate, despite the atomic percentages of carbon and oxidised carbon appearing unchanged (Figure 4.9). The dissolution of the deposit at 72 hours leads to the most homogeneous deposit that is observed on the annealed substrate. Overall, the least homogeneous deposits are observed on the oxidised sample. The untreated oxidised substrate presents an inhomogeneous surface, as shown in Figure 4.8c, which leads to inhomogeneous deposition.

The loadings plots provide the mass spectra that account for the differences shown in the scores plot. On the polished surface, principal component 1 (PC1) corresponds to the difference between the deposit chemistry at 24 and 72 hours (not shown), compared to 0.5 hours and the untreated surface. Unfortunately, salt contamination, observed in the 24 and 72 hour deposits, significantly contributes to the differences between these samples. On the 0.5 hour, similarly to Figure 4.8, and the untreated sample, only low masses (< 90 m/z) are observed; these deposits are attributed to an oxidised deposit film and adventitious carbon layer respectively. At longer soak times, oxidised hexadecane is observed, consistent with the increase in aliphatic material observed in Figure 4.9. The next biggest variance (PC2) corresponds to the untreated surface

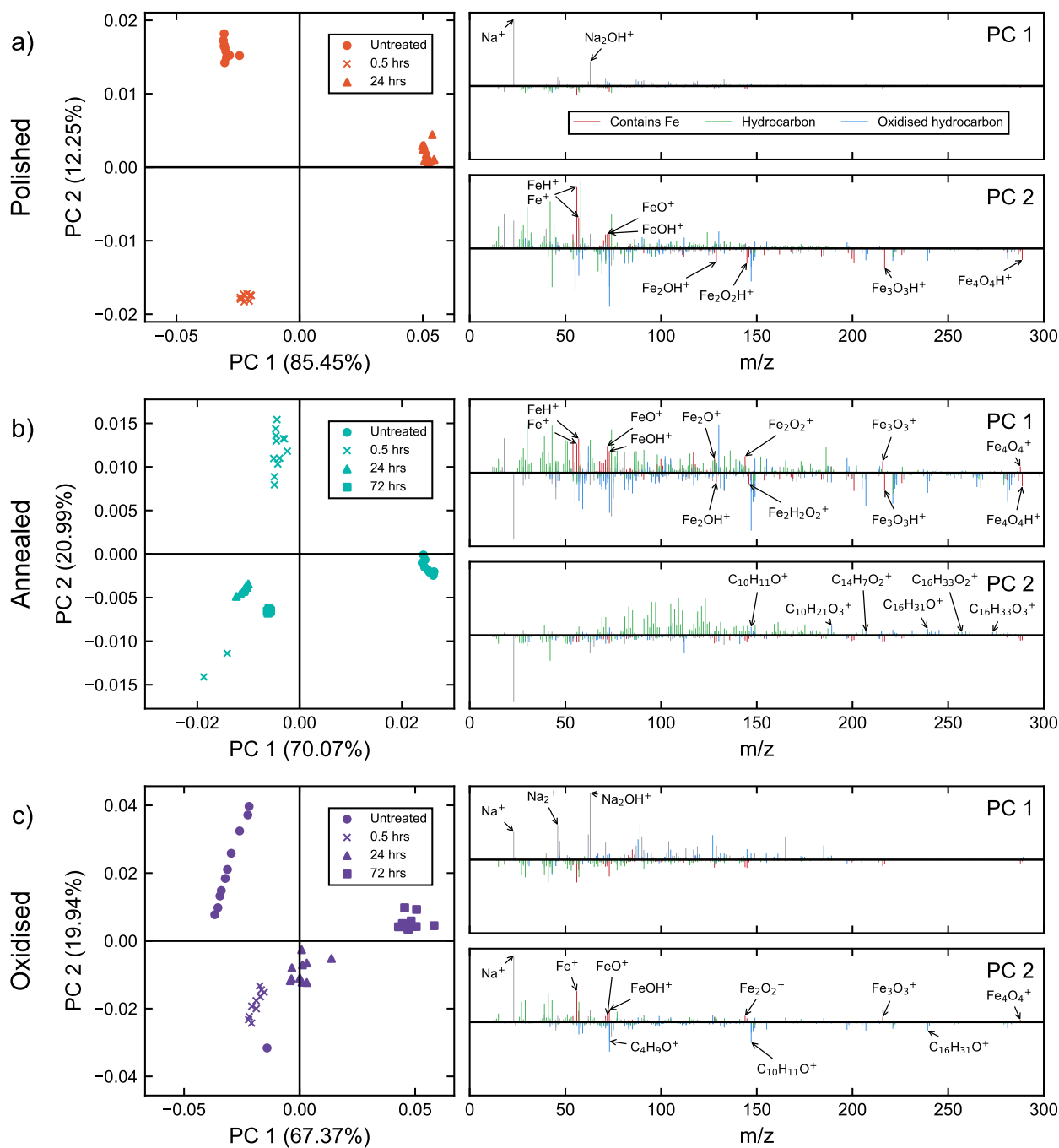


Figure 4.10: Principal component analysis of static SIMS analysis of the untreated surface and deposits at 0.5, 24 and 72 hour soak times on the a) polished, b) annealed and c) oxidised substrates. The scores plots are shown on the left, with the corresponding loadings for principal components 1 and 2 on the right.

and the deposit at 0.5 hours, with the 24 and 72 hour samples as intermediates. The oxidised species (blue) in the deposit extend to higher masses than those attributed to adventitious film on the untreated sample. Furthermore, $\text{Fe}_x\text{O}_x\text{H}^+$ species are observed on the treated

substrates, further supporting the formation of an iron hydroxide species following treatment with hexadecane at 200°C.

PC1 on the annealed substrate shows the difference between the untreated and the treated samples. On the treated samples, relatively long oxidised hydrocarbon species (blue) are observed, with chain lengths of up to C₂₆. A notable difference between these spectra is the observation of Fe_xO_x⁺ and Fe_xO_xH⁺ species on the untreated and treated substrates respectively, where x = 2–4, as annotated in Figure 4.10b. This observation provides further support for a chemical change occurring at the annealed surface and for the identification of the XPS iron trace (Figure 4.7b) as iron hydroxide. The next greatest variance (PC2) on the annealed sample is between the deposit at 0.5 hours and the other samples. At 0.5 hours, the deposit composition is predominantly hydrocarbon (green), with long oxidised chains (some species are annotated in Figure 4.7b), supporting limited oxidation on this substrate as demonstrated in Figure 4.9b.

On the oxidised sample, PC1 corresponds to the difference between: a) the deposit at 72 hours and b) the untreated substrate and deposit at 0.5 hours. Unfortunately, salt contamination observed in the deposits at 72 hour significantly contributes to the differences between these samples. The fragments corresponding to the untreated substrate and the deposit at 0.5 hours are predominantly hydrocarbon (green) and also include iron species (red); the exposure of the iron surface is supported by the low levels of deposition observed on the oxidised substrate, as shown in Figure 4.9a. PC2 highlights the differences between the untreated sample and deposit at 0.5 hours. Oxidised hydrocarbon species are observed in the deposit at 0.5 hours, whilst iron species and less-oxidised adventitious carbon is found on the untreated substrate.

4.4.6 Effect of Storage Stability on Thermal Oxidation

The level of oxidation in the hexadecane reagent, also known as storage stability, is found to cause inconsistencies in the amount and chemistry of deposition. The deposition from two different bottles of hexadecane on polished iron substrates was investigated to consider the relationship between oxidation, solubility and deposition. The hexadecane reagent that has been used for all the work presented previously is referred to as bottle 1. Bottle 1 (Figure 4.11a) is found to be more oxidised than bottle 2 (Figure 4.11b), demonstrated by the extended

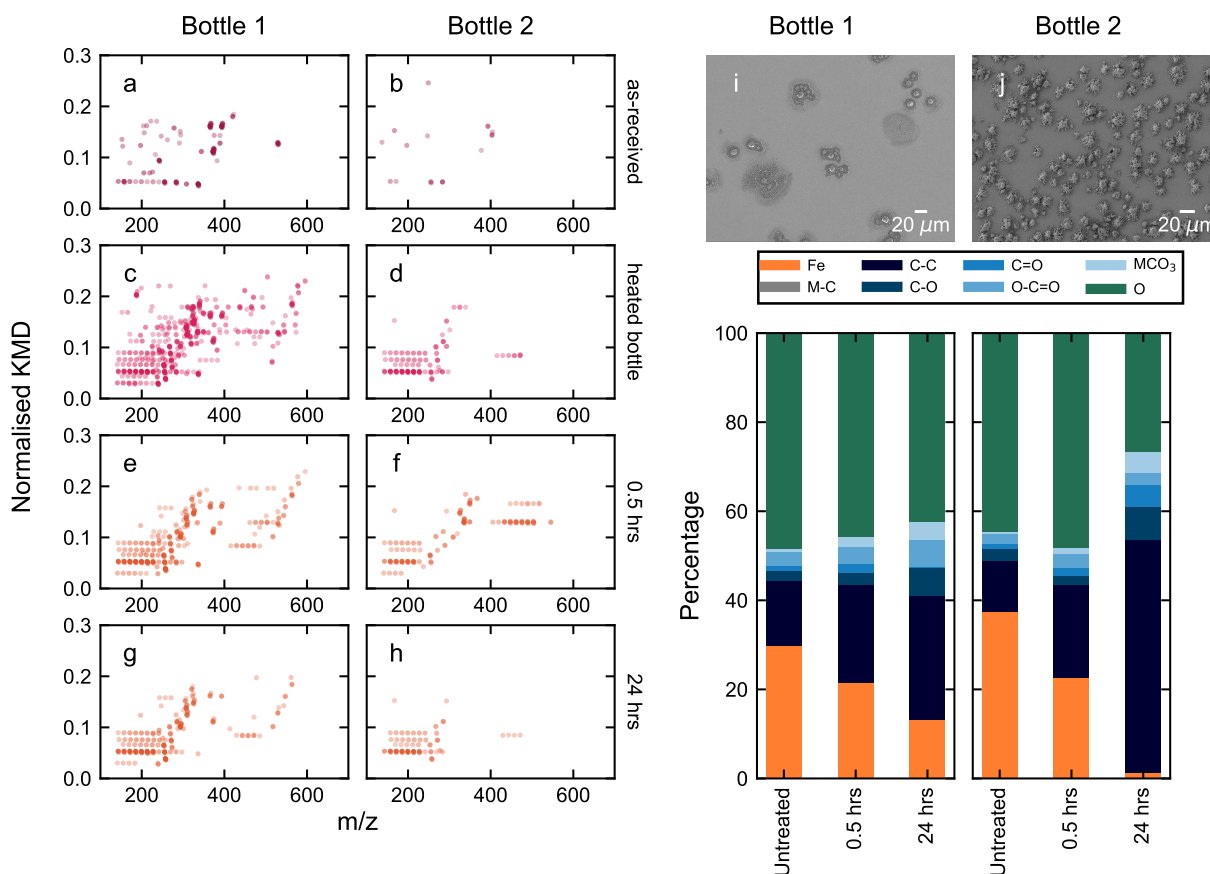


Figure 4.11: Negative Kendrick mass defect plots for hexadecane from bottle 1 and bottle 2 respectively for: (a) - (b) as-received hexadecane; (c) - (d) hexadecane following heating; the solution following deposition on a polished iron substrate for a (e) - (f) 0.5 hour and (g) - (h) 24 hour soak time. SEM images of the deposit forming from (i) bottle 1 and (j) bottle 2 after a 24 hour soak. k) Atomic percentages measured by XPS for the deposit formed on polished substrate from bottle 1 and 2.

homologous series attributed to the carboxylic acid species $C_nH_{2n-2}O_2^-$ in Figure 4.11a.

Upon heating, significantly more oxidation is observed in bottle 1 (Figure 4.11c) than in bottle 2 (Figure 4.11d), illustrating that the storage stability - in this case a more oxidised starting solution - has adverse effects on the thermal stability, generating a significantly more oxidised solution upon heating. The addition of a polished iron substrate (Figure 4.11e/f) results in a decrease in oxygen-containing species in solution as these species deposit onto the surface; a phenomenon which is exaggerated at longer soak times (Figure 4.11g/h). However at 24 hours, more deposition is observed from bottle 2; this is postulated to be a consequence of the reduced solubility of oxidised species in a predominantly hydrocarbon matrix, encouraging the deposition of these species. Significantly more deposition is observed from bottle 2 at 24

hours, as shown by SEM in Figure 4.11i/j and quantified using XPS in Figure 4.11k.

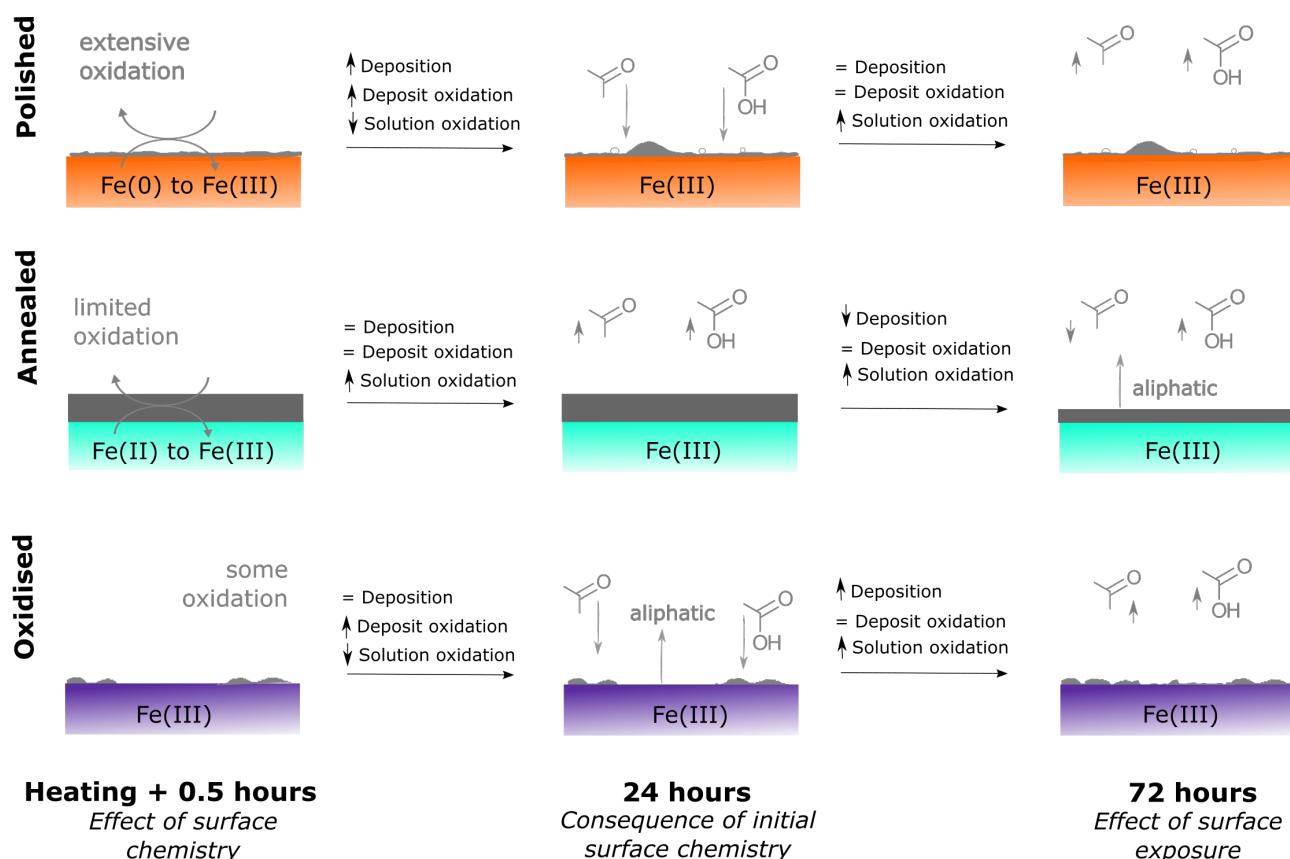


Figure 4.12: Schematic of the proposed mechanism detailing changes in hexadecane oxidation, deposition oxidation and the amount of deposition at varying soak times on the polished, annealed and oxidised substrates.

4.5 Conclusions

A schematic for the proposed mechanism is given in Figure 4.12. Compared to inert substrates, such as silicon, iron substrates were found to promote hexadecane oxidation. Surface-nucleated deposit growth (films and island-structures) was observed on the iron substrates as well as aggregates which were observed on all surfaces. Three iron substrates were studied; a polished surface, where iron(0) is believed to be accessible, an annealed surface and an oxidised surface, which were identified as iron(II)(III) oxide and iron (III) oxide respectively. Upon exposure to hexadecane at 200° C, the iron species in the polished and annealed substrates are believed to transition to iron(III). The XPS trace demonstrates characteristics similar to the iron(III) oxide hydroxide, which is supported by the identification of iron hydroxides in the SIMS spectra.

Iron(0) is believed to facilitate the extensive hydrocarbon oxidation, observed with the polished substrate, through the transfer of electrons to the solution, which can initiate the radical oxidation process. Iron(II) is also believed to initiate oxidation through electron transfer to the solution. Iron(II) on the annealed surface may also catalyse the breakdown of peroxides in a mechanism analogous to Fenton catalysis. The most deposition is observed on the annealed sample, with the absolute percentages of oxidised hydrocarbon species displaying similar values to the polished sample. Extensive deposition of aliphatic carbon occurs on the annealed surface, perhaps as a consequence of limited solution oxidation encouraging deposition of oxidised species that are not soluble in a predominantly hydrocarbon matrix. No changes in the chemical state of iron are observed on the oxidised sample however, enhanced oxidation and deposition occurs compared an inert substrate. Through analogies to Fenton-like catalysis, the iron(III) oxide is believed to catalyse the breakdown of peroxides.

Following heating, all the surfaces have similar surface chemistries which is believed to contain iron(III). The initial surface chemistry determined the degree of oxidation in the system and was found to influence the deposition at 24 hours. On the polished substrate, the species generated through the extensive oxidation of hexadecane deposit onto the surface at 24 hours resulting in island and film growth. Oxidised species are also found to deposit onto the oxidised substrate; lesser oxidised species are proposed to re-dissolve maintaining the atomic percentage of carbon at the surface. On the annealed substrate at 24 hours, no changes are observed in the level of oxidation in the deposit or the amount of deposit, however an increase in the hexadecane oxidation occurs.

At 72 hours, further deposition and oxidation is observed, demonstrating that an iron(III) surface at room temperature can accelerate the degradation of hexadecane and increase deposition. Whether this occurs through homogeneous or heterogeneous catalysis is not studied here, however, the activity of the iron was attributed to its availability on the substrate, with increased activity on surfaces covered by less deposition. The most exposed surface is on the oxidised substrate and increases in deposition and hexadecane oxidation are observed with this substrate. On the polished sample there is no change in deposition but an increase in solution oxidation. The annealed sample contains the most deposit and therefore the smallest effect of the iron is

expected on this surface. The carbonyl species in solution are further oxidised to carboxylic acids; the increased polarity of the solution is believed to facilitate the re-dissolution of the deposit.

References

- (1) Batts, B. D.; Fathoni, A. Z. A literature review on fuel stability studies with particular emphasis on diesel oil. *Energy & Fuels* **1991**, *5*, 2–21.
- (2) Taylor, W. F.; Frankenfeld, J. W. In, *2nd International Conference on Long-Term Storage Stabilities of Liquid Fuels*: Southwest Research Institute, San Antonio, TX, **1986**.
- (3) Watkinson, A.; Wilson, D. Chemical reaction fouling: A review. *Experimental Thermal and Fluid Science* **1997**, *14*, 361–374.
- (4) Ristori, A.; Dagaut, P.; Cathonnet, M. The oxidation of n-hexadecane: experimental and detailed kinetic modeling. *Combustion and Flame* **2001**, *125*, 1128–1137.
- (5) Hazlett, R. N., *Thermal Oxidation Stability of Aviation Turbine Fuels*; ASTM Publication Code Number 31-001092-12: Philadelphia, PA, **1991**.
- (6) Kauffman, R. E. In, *ASME 1995 International Gas Turbine, Aeroengine Congress, and Exposition*: **1995**; Vol. 3: Coal, Biomass and Alternative Fuels; Combustion and Fuels; Oil and Gas Applications; Cycle Innovations.
- (7) Frankenfeld, J.; Taylor, W. Fundamental synthetic fuel stability study. Final report, May 1, 1979 – June 30, 1981. *U.S. Department of Energy Office of Scientific and Technical Information* **1982**.
- (8) Jensen, R.; Korcek, S; Mahoney, L.; Zinbo, M Liquid-phase autoxidation of organic compounds at elevated temperatures. 2. Kinetics and mechanisms of the formation of cleavage products in n-hexadecane autoxidation. *Journal of the American Chemical Society* **1981**, *103*, 1742–1749.
- (9) Jensen, R.; Korcek, S; Mahoney, L.; Zinbo, M Liquid-phase autoxidation of organic compounds at elevated temperatures. 1. The stirred flow reactor technique and analysis of primary products from n-hexadecane autoxidation at 120–180°C. *Journal of the American Chemical Society* **1979**, *101*, 7574–7584.
- (10) Korcek, S.; Jensen, R. K.; Mahoney, L.; Zinbo, M. In, *Abstracts of papers of the American Chemical Society*: **1976**; Vol. 172, p 17.

- (11) Korcek, S.; Jensen, R. K.; Mahoney, L.; Zinbo, M. In, Abstracts of papers of the American Chemical Society: **1976**; Vol. 172, p 18.
- (12) Zinbo, M; Jensen, R.; Korcek, S Gas-liquid chromatography of oxygenated compounds related to the autoxidation of n-hexadecane. *Analytical Letters* **1977**, *10*, 119–132.
- (13) Jensen, R.; Zinbo, M; Korcek, S HPLC Determination of hydroperoxidic products formed in the autoxidation of n-hexadecane at elevated temperatures. *Journal of chromatographic science* **1983**, *21*, 394–397.
- (14) Korcek, S; Jensen, R.; Zinbo, M; Mahoney, L. Effects of oxygen pressure on liquid-phase autoxidation of hexadecane at 160–190°C. *American Chemical Society, Division of Petroleum Chemistry, Preprints;(USA)* **1987**, *32*.
- (15) Blaine, S.; Savage, P. E. Reaction pathways in lubricant degradation. 2. n-hexadecane autoxidation. *Industrial & Engineering Chemistry Research* **1991**, *30*, 2185–2191.
- (16) Chen, C.-I.; Hsu, S. M. A chemical kinetics model to predict lubricant performance in a diesel engine. Part I: Simulation methodology. *Tribology Letters* **2003**, *14*, 83–90.
- (17) Kendall, D. R.; Mills, J. S. Thermal stability of aviation kerosines: techniques to characterize their oxidation properties. *Industrial & Engineering Chemistry Product Research and Development* **1986**, *25*, 360–366.
- (18) Morris, R. E.; Turner, N. H. Influences exerted by metal deactivator on the thermal stability of aviation fuel in the presence of copper. *Fuel Science and Technology International* **1990**, *8*, 327.
- (19) Marteney, P. J. Thermal Stability of JP-5 in Long Duration Tests. *American Chemical Society, Division of Petroleum Chemistry, Preprints* **1989**, *34*, 809.
- (20) Taylor, W. F. Catalysis in liquid-phase autoxidation: I. Effect of polymeric surfaces. *Journal of Catalysis* **1970**, *16*, 20–26.
- (21) Schenk, L. W.; Johnston, R. K.; Monita, C. M. Investigation of the Effects of Trace Metals on the Thermal Stability of JP-7 Fuels. Report AFAPL-TR-71-98. *Southwest Research*

Institute on contract with Air Force Aero Propulsion Laboratory, Wright-Patterson Air Force Base, OH **1971**.

- (22) Walling, C. Free Radicals in Solution. *John Wiley and Sons* **1957**, 427.
- (23) Taylor, W. F. Kinetics of deposit formation from hydrocarbons. III. Heterogeneous and homogeneous metal effects. *Journal of Applied Chemistry* **1968**, *18*, 251–254.
- (24) Shi, F.; Tse, M. K.; Pohl, M.-M.; Radnik, J.; Brückner, A.; Zhang, S.; Beller, M. Nano-iron oxide-catalyzed selective oxidations of alcohols and olefins with hydrogen peroxide. *Journal of Molecular Catalysis A: Chemical* **2008**, *292*, 28–35.
- (25) Pickard, J. M.; Jones, E. G. Catalysis of Jet-A Fuel Autoxidation by Fe_2O_3 . *Energy Fuels* **1997**, *11*, 1232–1236.
- (26) Stavinoha, L. L.; Naegeli, D. W.; McInnis, L. The role of surface composition in fuel deposition. *American Chemical Society, Division of Fuel Chemistry, Preprints* **1990**, *35*, 1315.
- (27) Ervin, J. S.; T. A. Ward; Jarrod, T. F. W.; Bento Surface Deposition within Treated and Untreated Stainless Steel Tubes Resulting from Thermal-Oxidative and Pyrolytic Degradation of Jet Fuel. *Energy Fuels* **2003**, *17*, 577–586.
- (28) Jones, E. G.; J. Balster, W. Surface Fouling in Aviation Fuel: Short- vs Long-Term Isothermal Tests. *Energy and Fuels* **1995**, *9*, 610–615.
- (29) Lacey, P.; Gail, S.; Kientz, J. M.; Milovanovic, N.; Gris, C. Internal Fuel Injector Deposits. *SAE International Journal of Fuels and Lubricants* **2011**, *5*, 2011–01–1925.
- (30) Venkataraman, R.; Eser, S. Characterization of deposits formed on diesel injectors in field test and from thermal oxidative degradation of n-hexadecane in a laboratory reactor. *Chemistry Central Journal* **2008**, *2*, 25.
- (31) Yamashita, T.; Hayes, P. Analysis of XPS spectra of Fe^{2+} and Fe^{3+} ions in oxide materials. *Applied Surface Science* **2008**, *254*, 2441–2449.

- (32) Grosvenor, A. P.; Kobe, B. A.; Biesinger, M. C.; McIntyre, N. S. Investigation of multiplet splitting of Fe 2p XPS spectra and bonding in iron compounds. *Surf. Interface Anal* **2004**, *36*, 1564–1574.
- (33) McCafferty, E.; Bennett, M.; Murday, J. An XPS study of passive film formation on iron in chromate solutions. *Corrosion Science* **1988**, *28*, 559–576.
- (34) Wang, J.; Farrell, J. Investigating the role of atomic hydrogen on chloroethene reactions with iron using tafel analysis and electrochemical impedance spectroscopy. *Environ. Sci. Technol* **2003**, *37*, 3891–3896.
- (35) Bandstra, J. Z. and Miehr, R. and Johnson, R. L. and Tratnyek, P. G. Reduction of 2,4,6-trinitrotoluene by iron metal: kinetic controls on product distributions in batch experiments. **2004**, *39*, 230–238.
- (36) Matta, R.; Hanna, K.; Chiron, S. Fenton-like oxidation of 2,4,6-trinitrotoluene using different iron minerals. *Science of The Total Environment* **2007**, *385*, 242–251.
- (37) Garrido-Ramírez, E.; Theng, B.; Mora, M. Clays and oxide minerals as catalysts and nanocatalysts in Fenton-like reactions A review. *Applied Clay Science* **2010**, *47*, 182–192.
- (38) Kwan, W. P.; Voelker, B. M. Rates of hydroxyl radical generation and organic compound oxidation in mineral-catalyzed Fenton-like systems. *Environmental Science and Technology* **2003**, *37*, 1150–1158.
- (39) Zhao, L.; Lin, Z.-R.; Ma, X.-H.; Dong, Y.-H. Catalytic activity of different iron oxides: Insight from pollutant degradation and hydroxyl radical formation in heterogeneous Fenton-like systems. *Chemical Engineering Journal* **2018**, *352*, 343–351.

Chapter 5

Investigating the Reactive Interface

5.1 Overview

In Chapter 4, Fe(0) and Fe(II) species were found to oxidise to Fe(III), whilst also promoting the oxidation and deposition of hexadecane. The resultant surface was identified in Chapter 4 to be iron (III) (oxy)-hydroxide, however other preliminary experiments have suggested that iron carbide species may form. This Chapter focuses on further characterising the structural and chemical changes occurring at the interface during exposure to hexadecane at 200°C using synchrotron radiation. *In situ* experiments have facilitated the measurement of changes at the iron surface as a function of time and temperature. Through defining these transitions, this work aims to facilitate the development of engine surfaces and fuel additives that will maintain optimum engine performance for the lifetime of the vehicle.

5.2 Aims and Experimental Details

1. Determine the structure of iron substrates and thin films (Section 5.4.1 – 5.4.7)

- *Substrate:* a) 99.9 % iron substrate b) 150 nm thin films.
- *Sample preparation:* a) Polished (Section 2.2.2) and b) Grown (Section 2.2.5.3) and oxidised (Section 2.2.6).
- *Cell Design:* Figure 2.3c.

- *Rig design*: Figure 2.4b.
 - *Characterisation*: WAXS (Section 2.4.7.2).
2. **Determine the effect of hexadecane on the composition of iron oxides (Section 5.4.8)**
- *Substrate*: 99.9 % iron substrate.
 - *Sample preparation*: Polished (Section 2.2.2) and heat treated (Section 2.2.4).
 - *Characterisation*: Raman spectroscopy.
3. **Determine the effect of hexadecane on the identity of iron species at the surface (Section 5.4.9)**
- *Substrate*: 10 nm iron thin film on a silicon nitride grid.
 - *Sample preparation*: Grown (Section 2.2.5.3).
 - *Characterisation*: TEM.
4. **Determine the effect of hexadecane on the chemical environment of iron species at the surface (Section 5.4.10 – 5.4.11)**
- *Substrate*: 10 nm, 50 nm and 100 nm iron thin films.
 - *Sample preparation*: Grown (Section 2.2.5.3).
 - *Cell Design*: Figure 2.3b.
 - *Rig design*: Figure 2.4a.
 - *Characterisation*: XAS (Section 2.4.6.4).

5.3 Literature Review

As demonstrated in Chapter 3, iron surfaces are dynamic complex systems whose structure and composition is highly dependent on their chemical and physical environment. As there are limited studies on the reactions of iron surfaces in hydrocarbon stream systems, this Chapter

will review other hydrocarbon-iron systems where a variety of iron oxides, hydroxides and carbides are observed. The structures of metallic iron, iron oxides and iron carbides are briefly introduced. Numerous techniques have been used in the literature to investigate the oxidation state, coordination and phase of iron surfaces; this work focuses on the use of wide angle X-ray scattering (WAXS) and X-ray absorption fine structure (XAFS) spectroscopy to characterise the structure and chemical environment of the iron surface respectively. Insights into this interface can be gained from the transitions occurring in and reactions occurring on iron surfaces in analogous systems, for example Fischer-Tropsch catalysis.

5.3.1 The Structure of Metallic Iron

Ferrite (α -Fe) and austenite (γ -Fe) iron have body centred cubic (bcc) and face centred cubic (fcc) crystal structures respectively. Ferrite (soft iron) is observed to form at temperatures below 723°C, whilst austenite (hard iron) forms at higher temperatures.¹

5.3.2 The Structure of Iron Oxides and Hydroxides

‘Iron oxides’ can be used to refer to the wider category of sixteen structures that includes iron oxides, iron hydroxides and iron oxide hydroxides. All these structures consist of close packed anion arrays of O_2^- or OH^- , which are usually hexagonal or cubic close packed. The structure of the oxide is determined by the valence of the iron and its arrangement in octahedral and tetrahedral sites.¹ Trivalent iron is often located in octahedral and sometimes tetrahedral sites,¹ as discussed in Section 3.3.6, which introduces the crystal structures of the iron oxides wüstite, hematite, magnetite and maghemite.¹

Iron oxide hydroxides can readily transform to iron oxides as these compounds have similar anion frameworks; the loss of OH from the crystal structure is often accompanied by the rearrangement of iron cations. Goethite (α -FeOOH) can readily transform to hematite through losing H_2 molecules from its crystal structure, leaving the common anion array unchanged.¹ Alongside hematite and magnetite, goethite is one of the most stable iron oxides; goethite and hematite both have a hexagonal close packed anion lattice.

The high energy of crystallisation of iron oxides results in small crystals with high specific areas (often greater than $\sim 100 \text{ m}^2 \text{ g}^{-1}$) and many exposed functional groups; these are useful properties for catalytic applications.¹

5.3.3 Metal Carbides

The size and electronegativity of the metal will determine whether ionic carbides, such as calcium carbide, or interstitial carbides, such as tungsten carbide, are formed.¹ Transition metals containing dissolved carbon are referred to as transition metal carbides and often have unique chemical and physical properties.¹ According to the Engel-Brewer theory, the s-p electron count of the metal will determine the structure it adopts, with the lattice structure changing from bcc to hcp to fcc with increasing s-p electron count.¹ Bonding in interstitial compounds takes place between the s-p orbitals on the non-metal and the s-p-d band on the metal atom.¹ The carbide structure is determined by both geometric and electronic factors.² Carbon atoms will occupy the largest interstitial sites.¹ In orthorhombic/cubic structures and hexagonal structures, carbon will occupy the octahedral sites and trigonal prismatic sites respectively.¹

5.3.4 Iron Carbides

Chromium, manganese, iron, cobalt and nickel do not form interstitial carbides, as the metal lattices are distorted and carbon atoms will directly interact with each other.¹ These structures can be considered as a chain of carbon atoms running through the distorted metal lattice.¹ These compounds are regarded as a mixture between ionic and interstitial carbides, with the influence of carbon observed on the d-band occupation and Fermi level of the metal.¹ In the early transition metal carbides, which are ionic in nature, electrons are donated from the metal atom to the carbon atom and a shift towards higher binding energies in the carbidic state indicates charge transfer from the carbon to the metal.¹

Iron is widely known to dissociate carbon monoxide and dissolve carbon into its interstices, forming carbides.¹ Carbon atoms are located within a distorted hcp lattice of zero-valent iron atoms.³ Ferrite is reported to dissolve 0.02 wt% of carbon before it undergoes a transition

to form ferrite and cementite (θ -Fe₃C).¹ Many carbides are not stable in air therefore *in situ* measurements are required to further understand the properties of these carbides.³

5.3.5 The Structures of Iron Carbides

Carbon atoms can occupy octahedral and trigonal prismatic sites within the iron lattice. The number and location of the carbon atoms in the carbide will determine the structure, stability and properties of the iron carbide. The characteristics of different carbide phases are outlined in Table 5.1. Cementite (θ -Fe₃C) and Hägg carbide (χ -Fe₅C₂) are widely reported to be the most stable and common carbides, with Fe₇C₃ also widely observed in Fischer-Tropsch catalysis.^{1,4}

Metastable carbides include ϵ -Fe₂C and ϵ' -Fe_{2.2}C which have carbon atoms in octahedral interstices.¹ It is difficult to differentiate between these phases, with their small crystallite size further complicating this distinction.^{1,3}

The thermal stability of these carbides increases from ϵ' to χ to θ and the Fe-C bond strength is expected to increase accordingly.⁵ Ribeiro *et al.* studied the formation of carbides from pure Fe₂O₃ catalysts, pre-reduced with H₂, and found ϵ -carbide to form below 250°C, Hägg carbide to form between 250 and 350°C and cementite to form above 350°C while some oxide structure remains.⁶

In addition to the crystalline iron carbides outlined in Table 5.1, amorphous carbides are also observed.

5.3.6 Transformations of Iron Oxides

Iron oxides are observed to undergo structural changes as reactions occur on their surface. Analogies to Fischer-Tropsch catalysis, where carbon monoxide and hydrogen are used to produce hydrocarbons, provide valuable insights into transformations occurring on iron oxide surfaces in carbon-rich environments. Magnetite and wüstite are intermediates observed in the reduction of hematite (α -Fe₂O₃) to ferrite (α -Fe) in Fischer-Tropsch catalysis.^{1,7} Meanwhile in Fenton catalysis, where the decomposition of hydrogen peroxides is catalysed by iron surfaces, maghemite is observed as a weathering product of magnetite.⁸ The inverse spinel structure of magnetite is maintained, Fe(III) ions remain within the spinel framework and Fe(II) cations

Table 5.1: The characteristics of iron carbide phases.^{1,6}

	Formula	Crystal lattice	Interstitial occupation of carbon atoms	wt% car- bon	Temp. observed at (°C)
Hexagonal carbide (ϵ)	Fe_2C	hcp to monoclinic	octahedral	9.7	<250
Hexagonal carbide (ϵ')	$\text{Fe}_{2.2}\text{C}$	hcp	octahedral	8.9	<250
Eckstrom and Adcock carbide	Fe_7C_3	orthorhombic	trigonal prismatic	8.4	-
Hägg carbide (χ)	Fe_5C_2	monoclinic	trigonal prismatic	7.9	250-350
Cementite (θ)	Fe_3C	orthorhombic	trigonal prismatic	6.7	>350
	Fe_xC_y				-

migrate to the surface where they are oxidised before migrating from octahedral to tetrahedral sites.⁸ By assuming that vacancies only occupy octahedral holes, the oxide layer found in this work can be described by $[\text{Fe(III)}]_{T_d}[\text{Fe}_{1-3x}(\text{II})\text{Fe}_{1+2x}(\text{III})\text{V}_x]_{O_h}\text{O}_4$ where x is the number of vacancies V and the subscripts T_d and O_h refer to tetrahedral and octahedral sites respectively.⁸

5.3.7 Transformations of Iron Carbides

Studies on the formation of iron carbides and their transitions in Fischer-Tropsch synthesis (FTS), are reviewed here to gain insights that may be applicable to the system studied in this work. Crystallite size, morphology, surface texture and the presence of promoters or inhibitors have been outlined as factors affecting the formation of carbide phases as well as the initial surface.³ In FTS iron carbides are widely accepted to form from the diffusion of carbon atoms (from the dissociation of adsorbed carbon monoxide) into the metal lattice, as shown in Reaction 5.1, where $*$ represents an active site on the iron surface, C^* represents an adsorbed carbon species and $\text{C}\cdot$ represents a carbon radical species. The formation of hydrocarbons on iron surfaces is shown in Reaction 5.2. The structure of the carbide is determined by the ratio

of carbon to iron atoms and their location within the metal lattice. As discussed in Chapter 3, the iron surface is shown to be a dynamic surface with its chemical and physical environment determining its structure and properties; temperature and exposure to air are shown here to modify the surface chemistry. In air, iron carbides will readily oxidise to form predominantly magnetite;¹ therefore, the use of *in situ* techniques is required to characterise their structures, compositions and the transitions occurring during reactions.

ϵ -carbides are found to form at low temperatures, with Hägg carbide and cementite forming as the temperature increases. These transitions correspond to a change in the iron lattice from hcp to monoclinic to orthorhombic. The carbon atoms will occupy trigonal prismatic sites instead of octahedral sites to lower the deformation energy of the iron lattice and increase the entropy. The strain in the lattice can also be reduced through twinning.³ Although carbons in octahedral sites have a lower internal strain energy contribution, at higher temperatures trigonal prismatic structures are observed due to lower strain, carbon diffusion limits and a lower vibrational entropy, ultimately resulting in a higher relative thermodynamic stability and kinetic preference.³

In addition to metallic iron, iron carbides are proposed - with some debate - to display catalytic activity in the hydrogenation of carbon monoxide to produce hydrocarbons in FTS.³ Iron carbides are typically formed from an oxide precursor, with the pre-treatment of the catalyst found to determine the final catalyst structure and performance.³ The carbides θ -Fe₃C, χ -Fe₅C₂ and Fe₇C₃ are commonly observed in FTS conditions, although their detection may be a consequence of their relative stability. The activation energy for FTS is similar to the activation energy for carbon diffusion in iron (43.9–69.0 kJ mol⁻¹). The rate of diffusion is higher than the rate of the FTS reaction resulting in an induction period when both the concentration of carbon species at the surface and the FTS activity are low.¹ With nickel and cobalt catalysts, the activation energy for carbon diffusion is lower (138–146 and 145 kJ mol⁻¹ respectively) but the carbon diffusion rate is 10⁵ lower than for iron, therefore the carbon diffusion rate is negligible and all carbon is converted into FTS products.^{1,9} Carbides have been reported to form from the interaction between metallic iron (ferrite) and adventitious carbon, following the reduction of iron oxide to zero-valent iron.¹⁰ Upon carburisation of the iron surface, the surface

area is found to increase due to the shearing and separation of carbide crystallites from the underlying oxide.³ The iron carbide crystallites that are found to be active in FTS reactions are very small in size.³

The formation of iron carbides can promote the formation of unexpected metallic phases; austenite (γ -Fe) has been observed at temperatures as low as 200°C in FTS.⁶ A change in the surface enthalpies and energetics of phase transformations due to the nanometer-sized particles may be a possible explanation for the unexpected observation of this phase in this temperature range.⁷ The γ -Fe phase may form due to the lattice expansion caused by the dissolution of carbon atoms.⁷ Austenite is more stable to carburization than ferrite, with austenite able to accommodate 2 wt% of carbon (compared to 0.02 wt% for ferrite) before disproportionating into a mixture of iron carbides and austenite.⁷ Upon cooling, the γ -Fe phase is proposed to undergo an eutectoid reaction forming α -Fe and θ -Fe₃C (pearlite reaction), which accounts for the fact that austenite is not observed at low temperatures *ex situ*.⁷

Alternatively, upon cooling to room temperature, a carbonaceous layer is formed on the surface from the precipitation of carbon from these structures that had a higher carbon content under reaction conditions.¹

In FTS a distinction is made between bulk and surface carbides, however these carbides are difficult to define.¹ The diffusion rate of carbon could be used to distinguish between the bulk and surface carbides, as carbon will rapidly diffuse into the bulk, however bulk carbides, unlike surface carbides, are difficult to hydrogenate meaning the migration of carbon from the bulk to the surface is slow.¹ Surface carbides are required for FTS, although their surface chemistry remains unclear.¹ Bulk carbides are also observed yet their potential role in determining the nature of sites and the potential catalytic activity is also unclear.^{1,7} Both the definition of surface and bulk carbides as well as the information depth of the characterisation technique will account for the discrepancy between results from different studies on iron carbides. Ribero *et al.* illustrated the complexity of these systems, through the observation of a surface iron carbide surface on nanoparticles with a magnetite core.⁶

5.3.8 Deactivation of Iron Surfaces

Four causes for FTS catalyst deactivation are outlined in the literature, including: i) the conversion of the active catalytic phase into a less active catalytic phase, ii) the deposition of inactive carbonaceous material, iii) sintering of the catalyst and iv) catalyst poisoning due to sulfur contamination.^{1,4} The pre-treatment of the catalyst is a principle factor in the amount of carbon fouling observed.¹ The formation of an inactive phase and the deposition of inactive material, shown in Equation 5.3, are discussed in detail to elucidate similarities, if any, to the system studied in this work.

In FTS, the loss of the active phases is often associated with the formation of amorphous θ -Fe₃C, although the active phase may also be lost through oxidation.^{6,7} θ -Fe₃C is also widely observed to form very small crystallites.⁷ The formation of cementite is frequently linked to the build up of carbonaceous species; surface carbon is even found in the synthesis of cementite.⁴ A likely explanation for these observations is the formation of carbon-poor cementite from other carbon-rich phases, resulting in precipitation of carbon from the iron carbide lattice when cementite forms. Using a catalyst pre-treatment (catalyst pre-treated in 1% CO/H₂ at 350°C), de Smit *et al.* found θ -Fe₃C to form directly from α -Fe without the formation of excessive levels of surface carbon.³ θ -Fe₃C is reported to break up into small clusters as a result of carbon deposition. In addition to the increase in catalytic activity observed upon the formation of bulk carbides, the formation of bulk carbides is reported by de Smit *et al.* to significantly reduce the deactivation of the catalyst.¹ These findings suggest that the formation of a bulk carbide plays some role in mitigating against the formation of cementite. Catalyst deactivation in these systems is attributed instead to the formation of carbonaceous material on the surface.¹

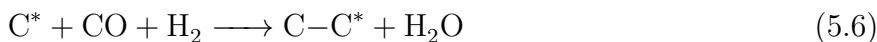
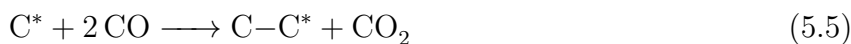


5.3.9 Deposition of Carbonaceous Material

The formation of carbonaceous material on the surface can reduce the catalytic activity of the substrate through acting as a physical barrier blocking catalytic sites on the surface and/or by acting as a barrier to reactant diffusion.¹ Types of carbonaceous material identified on iron surfaces includes: atomic carbon, amorphous carbon, oxygenated carbon, polymeric condensed hydrocarbons, amorphous graphitic carbon, vermicular (filamentous) carbon, crystalline graphitic carbon as well as iron carbides.⁵ The conversion of adsorbed reactive carbon species to inactive carbon species and the corresponding conversion of FTS-active iron carbide phases to FTS-inactive iron carbide phases will result in surface fouling.⁵ Atomic carbon can be converted to polymeric and graphitic carbon on the surface.⁵ Meanwhile, the formation of inactive carbon-poor phases (θ -Fe₃C) from active carbon-rich phases (ϵ -carbide), through the reduction of carbides or thermal processes, will result in the precipitation of carbon atoms as discussed in Section 5.3.8.^{1,4,5} Carbon atoms precipitated from carbide phases are speculated to provide nucleation points for: polymerisation to β -carbon; crystallisation to graphitic δ -carbon and Boudouard reactions, which are outlined in Reactions 5.4-5.6 and also in Reaction 5.3. However, the characterisation of this carbonaceous layer in FTS is complicated by the presence of hydrocarbon products on the surface.⁴

The formation and growth of carbonaceous deposits, typically graphite, is outlined by the Boudouard reactions (Reactions 5.4–5.6), where C* represents a carbon species adsorbed at an iron active site. According to these reactions, high partial pressures of H₂O and CO₂ should reduce the formation of Boudouard type carbonaceous deposits.¹ Pena *et al.* reported the most deleterious effects to result from polymeric carbon; these polymers are believed to form from the polymerisation of the alkyl groups formed on the surface.⁴ Amorphous carbon is reported to form at low temperatures, whilst the formation of graphitic carbon is favourable at higher temperatures.¹ Surfaces with high surface areas were less susceptible to the formation of graphitic carbon, although even on these surfaces graphite is observed at temperatures above 275°C.¹ Surface carbon, with the exception of graphite, can be removed through hydrogenation.¹





5.3.10 Reactions on Iron Surfaces

The autoxidation of hydrocarbon species is a radical reaction that is proposed to be initiated and catalysed by iron surfaces. In Chapter 4, the transfer of electrons to solution was proposed to initiate free radical oxidation whilst iron(II) and iron(III) were proposed to catalyse the breakdown of peroxides that formed as a result of insertion of molecular oxygen into the hydrocarbons. Here, other reactions that occur on iron surfaces producing hydrocarbons and oxidised hydrocarbons are discussed to gain any further insights into the reactions—and their mechanisms—that can take place on iron surfaces.

In Fischer-Tropsch catalysis, the dissociative adsorption of carbon monoxide is key in the formation of hydrocarbons, as shown in Equation 5.2. The Blyholder model is used to interpret the bonding of carbon monoxide on iron surfaces. In this model, the non-bonding σ levels on the CO molecule interact with empty d levels on the metal surface, increasing the adsorption rate of CO.⁶ The metal can also donate electrons from its populated d level into the empty $2\pi^*$ (anti-bonding) levels on the CO. The scission of the adsorbed CO molecules is attributed to the interaction between populated d levels of the metal and $2\pi^*$ (anti-bonding) empty levels of the CO molecule.⁶ Alkali promoters can influence this bonding and will be discussed in Section 6.4. Montemore *et al.* reported that molecular oxygen will adsorb dissociatively on metals in groups 4-8, until the surface coverage is high; once this level of surface coverage is reached, molecular oxygen can physisorb or chemisorb at low temperatures.¹¹

Following the dissociative adsorption of CO and H₂, hydrocarbon chain growth in FTS occurs through the formation of CH₂ entities, which will combine and insert into the growing chain. These CH₂ entities may adsorb close to where they react, or may be mobile across the catalyst surface. Chain termination occurs through abstraction or addition of hydrogen atoms

to or from the growing chain.¹

Enol formation offers an alternative mechanism for the formation of hydrocarbons.¹ Emmett and co-workers collated extensive evidence for these reaction mechanisms.¹²⁻¹⁶ In this case, carbon monoxide chemisorbs on to the iron surface and does not dissociate.¹ The chemisorbed CO groups will react with surface hydrogen atoms forming enolic entities.¹ These groups are proposed to combine through a surface polymerisation condensation reaction with loss of water, or individual enolic entities are expected to form water and CH₂ groups, which can result in hydrocarbon growth as outlined above.¹

Alternatively, carbon monoxide molecules can be inserted into metal-hydrogen bonds; this mechanism has been widely used in coordination and organometallic chemistry since it was proposed in 1958.¹⁷ In this mechanism, a carbon monoxide molecule is inserted into the metal-hydrogen bond, forming a surface aldehyde. This aldehyde is hydrogenated in the rate limiting step to CH₃ by hydrogen atoms chemisorbed on the surface. Chain growth occurs through the insertion of a carbon monoxide molecule into the metal-carbon bond and the subsequent hydrogenation of this enolic group. Chain termination will occur through the hydrogenation of the growing chain, resulting in a free olefin chain and an adsorbed hydrogen atom.¹

5.3.11 Elements Influencing Changes at the Iron Surface

Both structural and basic promoters are used to enhance catalysis in FTS. Structural promoters are used to enhance the mechanical properties of the catalyst, whilst chemical promoters alter the electron distribution at the surface. The presence of alkali metals as basic promoters increases the activity of the catalyst and its selectivity for high molecular weight and olefinic products.⁶ Promoters will not be discussed here, however, it is worth noting, that a mechanistic understanding of the role of basic promoters in FTS catalysis may provide valuable insights into the effect of diesel contaminants on engine deposits. Basic promoters are found to have an influence on the rate of formation of free carbon, with the more basic elements observed to have a higher promotional effect.¹ The rate of carburization of the catalyst increases according to: unpromoted < lithium < sodium < nitrogen, rubidium and caesium.⁶

5.3.12 Interpretation of Surface Changes Using XAFS

Other studies on iron surfaces are reviewed in this section with a focus on the analysis and interpretation of these data. Unlike X-ray diffraction measurements which will only probe regions of the sample with long range order, XAFS can be used to investigate poorly defined, non-crystalline phases. XAFS also provides a mechanism for looking at surface structures, which may not exhibit the same long range order that is observed in the bulk.⁶ As discussed in Section 2.4.6, the XAFS spectra is widely divided into two regions, X-ray absorption near edge spectroscopy (XANES) and the extended X-ray absorption fine structure (EXAFS). These regions can be used, with varying degrees of analysis, to elucidate information about the chemical systems investigated.

Fingerprinting, whereby the measured spectra is compared to the reference spectra, is the simplest form of analysis for the XANES region as the white line and spectra have unique shapes for different oxidation states. Ribeiro *et al.* observed a decrease in intensity of the white line as Fe_2O_3 was reduced to Fe_3O_4 .⁶ The white line was observed to decrease in intensity upon the formation of carbides as the Fe-C bond is more covalent in character than the Fe-O bond.¹⁸

The iron absorption edge corresponds to the 1s to 4p electronic transition.¹⁹ The edge position of 7112.0 eV corresponds to metallic iron. Upon reduction, the edge position is observed to shift towards lower energies, although these shifts can be as small as 0.5 eV.⁷ A decrease in the edge feature at 7112.0 eV and a concurrent increase in a feature around 7125 eV demonstrate partial oxidation.⁷ The position of the pre-edge, typically around 10 eV below the absorption edge, can be used to determine the oxidation state of iron in mixed valence samples. The pre-edge adsorption feature originates from the 1s to 3d electron transition.¹⁹ The position and characteristics of the pre-edge is sensitive to the binding geometry, symmetry and the extent of distortion of the polyhedron around iron.⁸ A pre-edge at 7113.5 eV and an edge position of 7123.5 eV is characteristic of hematite ($\alpha\text{-Fe}_2\text{O}_3$).⁷ A 0.5 eV shift in the position of the edge and enhanced intensity at 7130 eV are characteristic for the presence of a carbide phase.^{20–23} Ribeiro *et al.* used changes in the intensity at the pre-edge to justify the reduction of Fe(III) in Fe_2O_3 in octahedral sites to Fe(II) in Fe_3O_4 .⁶

The identity and amount of species in a mixture can be determined by linear combination

fitting, whereby a combination of reference spectra in varying ratios are used to fit the XANES spectra determining the relative composition of the measured sample. Ribeiro *et al.* fitted the spectra over a range of 7100–7162 eV.⁶

The XANES region can also be simulated, however this is complicated and will not be discussed in detail here. Pinakidou *et al.* used a Voigt function to simulate the XANES spectra; they found Fe(II) with octahedral coordination at 7112.5–7112.6 $\pm$ 0.2 eV, Fe(III) with octahedral coordination at 7113.5–7113.8 $\pm$ 0.2 eV and Fe(III) tetrahedral coordination at 7114.8–7115.1 $\pm$ 0.2 eV.⁸

The EXAFS region of the spectra provides additional information on the local atomic structure of the material. The EXAFS region is presented in terms of energy, wavenumber and as a Fourier transform of the wavenumber. A k-weighting of 1 (k^1) is used to emphasise the contribution from lighter scatterers, such as oxygen and carbon, compared to heavier scatterers such as iron.⁷ Similarly, a k^3 -weighed Fourier transform of these data, will show a larger relative contribution from the iron-iron scatterer distance.⁷ Changing the k-weighting will alter the relative contributions of different phases; the LCF estimates produced by fitting the XANES spectra can be used as a comparison.⁷

Whilst the Fourier transform of the wavenumber plot is not a radial distribution function, it can be used to interpret the arrangement of atoms around the absorber. Ribeiro *et al.* reported two major peaks which were located between 1 and 2 Å and between 2 and 3 Å; these peaks were reported to correspond to the first Fe–O and Fe–Fe coordination shells at distances of 1.9–2.1 Å and 2.9–3.5 Å respectively, associated with hematite.⁶ In their study Ribeiro *et al.* reported the reduction from hematite to magnetite to a mixture of iron carbides and iron oxide at elevated temperatures, observed through the decrease in intensity of both peaks and the formation of less intense broad peaks between 1 and 3 Å.⁶ In their study, they looked at the effect of basic promoters on this transition.⁶

De Smit *et al.* used the positions of the peaks attributed to the first iron-iron coordination shell to gain insights into the carbides species present.⁷ The intensity of the contribution from the carbon scatterer cannot be correlated to the amount of carbon in the lattice as the highest symmetry is observed for the ϵ -Fe₂C carbide phase and the measurement represents contributions

from all iron scatters in all phases.⁷ A shift in the position of the first iron-iron coordination shell from 2.2 Å to 2.3 Å is associated with the transformation of θ -Fe₃C to ϵ -Fe₂C; the α -iron bcc lattice, which has its first iron-iron coordination shell at 2.1 Å, is believed to expand to accommodate the higher amounts of dissolved carbon.⁷ In their work they observed a species with a high intensity of scattering at both very short distances and 3.2 Å, which was identified by WAXS to be an ϵ -carbide, however that hypothesis does not fit these data, suggesting instead a ‘carbon lean’ θ -Fe₃C phase.⁷ The observation of a ‘carbon lean’ θ -Fe₃C phase further demonstrates the complexity of investigating carbide phases.⁷

Pinakidou *et al.* used their measurements of the EXAFS spectra to interpret the coordination of iron and oxygen atoms in magnetite. In the first shell, iron was observed in both tetrahedral and octahedral co-ordinations, located at 1.87–1.89 and 1.97–2.01 Å respectively.⁸ In outer shells, the FeO₆ polyhedra share corners with adjacent FeO₆ and FeO₄ polyhedra.⁸ They fitted EXAFS to the first 5 nearest neighbours.⁸ By assuming that vacancies are located in octahedral sites following the transformation from magnetite to maghemite, Pinakidou *et al.* used the EXAFS results to determine the number, x , of vacancies, V , in the oxidised layer - $[\text{Fe(III)}]_{Td}[\text{Fe}_{1-3x}(\text{II})\text{Fe}_{1+2x}(\text{III})V_x]_{Oh}\text{O}_4$.

EXAFS can be used to gain quantitative information regarding the phases present in a material. The ATOMS software is used to generate spatial coordinates from structural information files.²⁴ Scattering paths are then calculated from these spatial coordinates using the FEFF package.²⁵ The parameters used by Ribeiro *et al.* for their structural fitting of the EXAFS equation will be discussed here.⁶ Scattering paths up to 3.5 Å were considered for fitting the first coordination shells, which were fitted in the k - and r - ranges of 2.5–10 Å⁻¹ and 1.0–3.0 Å respectively.⁶ They used two α global lattice expansion coefficients; one for both Fe-C and Fe-Fe in the carbides and the other for both Fe-O and Fe-Fe in magnetite.⁶ ΔE_0 and an overall energy shift were applied to each path. The Debye-Waller factors, σ_1^2 and σ_2^2 , were used for carbides (both the Hägg and ϵ) and magnetite respectively. The amplitude coefficients account for the fraction of each phase, and changes in the amplitude can be attributed to changes in particle size as surface atoms have lower degrees of coordination.⁶ Their experiments aimed to determine the effect of basic promoters on the surface transitions, and therefore these

spectra were fitted simultaneously to achieve physically meaningful results.⁶ Global parameters were used for the isotropic lattice expansion (α) and the Debye-Waller factors (σ_1^2 and σ_2^2) for the carbide and oxide fractions.⁶ Local parameters were used for the energy shift E_0 and the amplitude function multipliers of each component.⁶ From their analysis, Ribeiro *et al.* proposed that the sample was composed of Hägg carbide and magnetite; the inclusion of ϵ -carbide into the fit was ruled out, as its presence had a negligible difference on the fit and the observed differences were attributed to changes in temperature.⁶ LCF of the XANES data provided further support for this fit.⁶ Ribeiro *et al.*, noted that deviations from the bulk value for the lattice expansion coefficient may be caused by the small domain sizes which result in a contraction of bond distances and therefore the carbide lattice.⁶

Due to the instability of carbides, with the exception of θ -Fe₃C and mixed Fe_xC phases, experimental reference spectra are not widely available for carbide phases. It is possible to model the XANES region, but this is complex and not widely done. The absence of iron carbide reference spectra mean that interpretation of the XANES data, for samples expected to contain iron carbide, using fingerprinting and/or LCF is not possible. As an alternative, it is possible to calculate theoretical scattering paths and amplitudes from the crystallographic information files, from within the Artemis program.²⁶ De Smit *et al.* used the positions of the peaks in the Fourier transform of the EXAFS region to determine the phase present but did not attempt to fit the measured data.⁷

5.3.13 Interpretation of Surface Changes Using a Combination of WAXS and XAFS

WAXS is used to gain information on the long range order of crystalline phases within a sample. WAXS analyses are complementary to XAFS measurements, which provides a comprehensive understanding of the local environment of iron atoms.⁷ The phases identified by WAXS can be used to aid interpretation of X-ray absorption fine structure measurements, although as XAFS will also measure amorphous phases these findings may not necessarily correlate. The combination of WAXS and XAFS will provide an insight into both the crystalline and amorphous

regions of a sample.

De Smit *et al.* used WAXS in combination with XAFS to elucidate changes occurring at the iron surface in FTS. Here, they collected WAXS data at $1.781 \text{ \AA} / 6.980 \text{ keV}$, which is below the iron adsorption edge.⁷ Iron carbides were identified by WAXS. In this work De Smit *et al.* used a Psuedo-Voigt line shape to fit reflections that were assigned as iron carbides; for the carbide phases these peaks were broad due to the small size of these crystallites.⁷ Differences in experimental broadening was noted for measurements taken on synchrotron and laboratory set ups.⁷ Using the assumption that the most reduced iron species are present in the sample as carbides, they exploited the similarity between the XANES regions of ferrite and iron carbides using the XANES spectra for ferrite (bcc α -Fe) to estimate the contribution from iron carbides (Fe_xC). These comparisons provided an indication of relative amount of carbides compared to magnetite, but were not used to determine phase compositions.⁷

5.4 Results and Discussion

In Chapter 4 the effect of hexadecane at 200°C on iron substrates was investigated. Using XPS, iron surfaces containing near-surface Fe(0) and Fe(II) species were observed to undergo a transformation to iron (III) oxide hydroxide. No change in the oxidation state of iron was observed for hematite. This Chapter aims to further understand the transitions occurring at the hexadecane-iron interface. As discussed above, the structure and chemistry of iron surfaces are known to be highly complex dynamic surfaces, which are strongly influenced by their chemical and physical environment. *In situ* studies were conducted at synchrotron facilities to characterise the structural and chemical changes at the interface as a function of both time and temperature using wide angle X-ray scattering (WAXS) and X-ray absorption spectroscopy (XAS), specifically X-ray absorption fine structure. To gain further insights into the system's structure and composition *ex situ* analyses were conducted using transmission electron microscopy (TEM), specifically electron diffraction, and Raman spectroscopy respectively.

5.4.1 Structural Characterisation of Iron Substrates

Grazing incidence wide angle X-ray scattering (GI-WAXS) was used to characterise the structure of the iron surface. Figure 5.1a and c show the 2D WAXS measurements for the rough as-received iron substrate and the polished substrate. The solid rings in Figure 5.1a demonstrate that the as-received iron substrate is poly-crystalline with no preferred orientation. To deconvolute the effects of surface roughness and surface chemistry on deposition on engine surfaces, polished surfaces were used in Chapter 4. Figure 5.1c suggests that the texture at the surface is increased upon polishing. The 1D patterns, obtained from integrating the intensity along the rings, are shown in Figure 5.1b and d for the rough and polished samples respectively. The reflections at 17.4° , 24.7° , 30.3° , and 35.3° are attributed to reflections of the (110), (200), (211) and (220) planes respectively for ferrite (ICDD 00–006–0696). In Figure 5.1d the additional reflections with small intensities that appear upon polishing are attributed to silicon and silicon oxide. The silicon carbide paper used to polish these samples is believed to be the source of silicon contamination, demonstrating that a more robust cleaning procedure is required to remove debris left from the surface preparation.

To ensure high quality GI-WAXS measurements, the sample should be positioned to cut half the beam. Due to the nature of substrate preparation, the edges of the iron substrates frequently had rounded edges and/or lips complicating the alignment of the sample. Furthermore, imperfect polishing can lead to scratches and bevels on the surface that may complicate further measurements. For these reasons, investigations into the effect of hexadecane on iron surfaces is conducted on iron films (150 nm), which were grown on silicon substrates, as discussed in Section 2.2.5.3. These substrates were flat with orthogonal edges.

5.4.2 Comparison of WAXS Measurements of Iron Substrates and Iron Films

Figure 5.2 presents diffraction patterns for the iron substrate and 150 nm iron thin films. Similarly to the iron substrate, the iron film has a ferritic structure. The increase in peak width of the reflections on the iron film compared to the the iron substrate demonstrates that the size

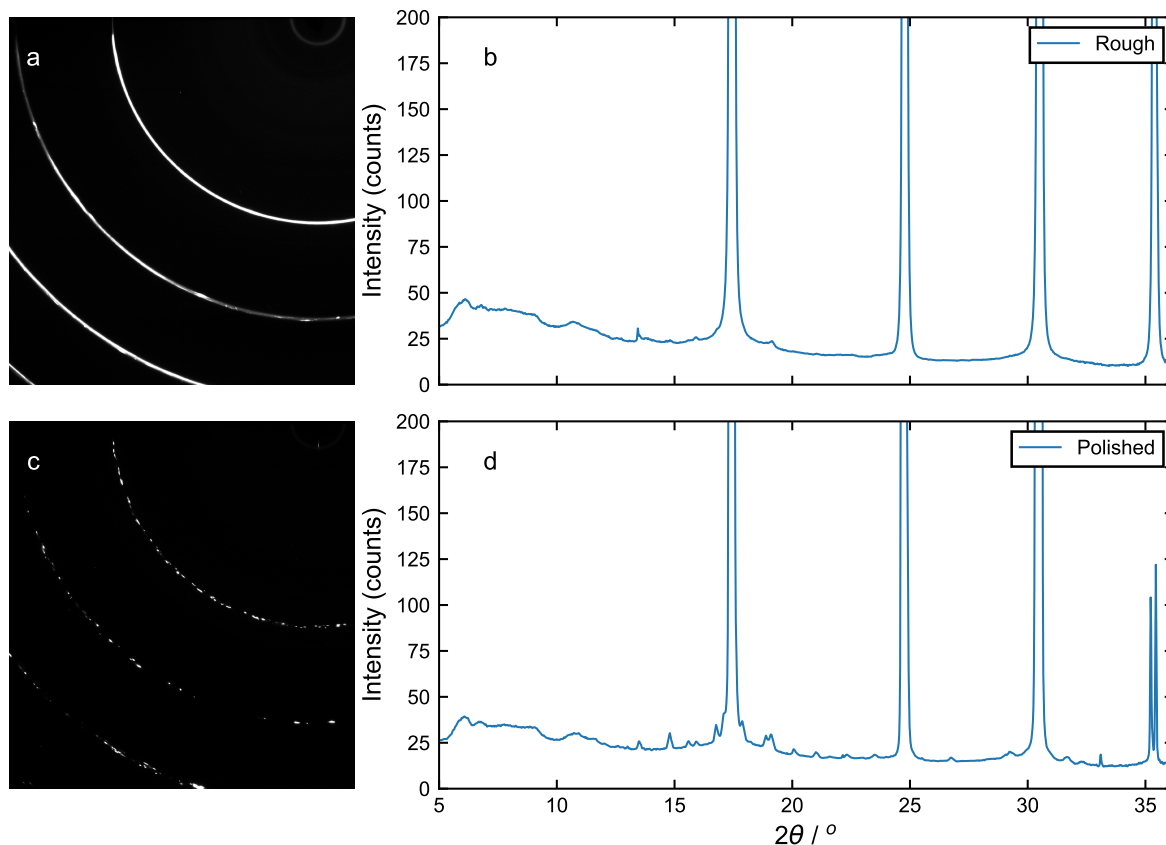


Figure 5.1: 2D and 1D WAXS measurements respectively at an incident angle of 1° for a-b) an as-received and c-d) a polished iron substrate.

of ferrite crystallites in the film are significantly smaller. Upon oxidation of the iron film in air, the reflections associated with ferrite are significantly reduced, suggesting that iron is oxidised over the depth measured.

5.4.3 Determining the Critical Angle for Iron Substrates and Iron Films

The critical angle is defined as the X-ray incident angle below which total external reflection of the X-ray beam occurs. By obtaining diffraction patterns below the critical angle for the substrate and above or below the critical angle of the film, the bulk structure or the near surface structure will be probed respectively.²⁷ For a known material it is possible to calculate the critical angle, however, as the film surface chemistry is undefined, the critical angle was determined experimentally. Through comparing the relative ratios of intensities from both a

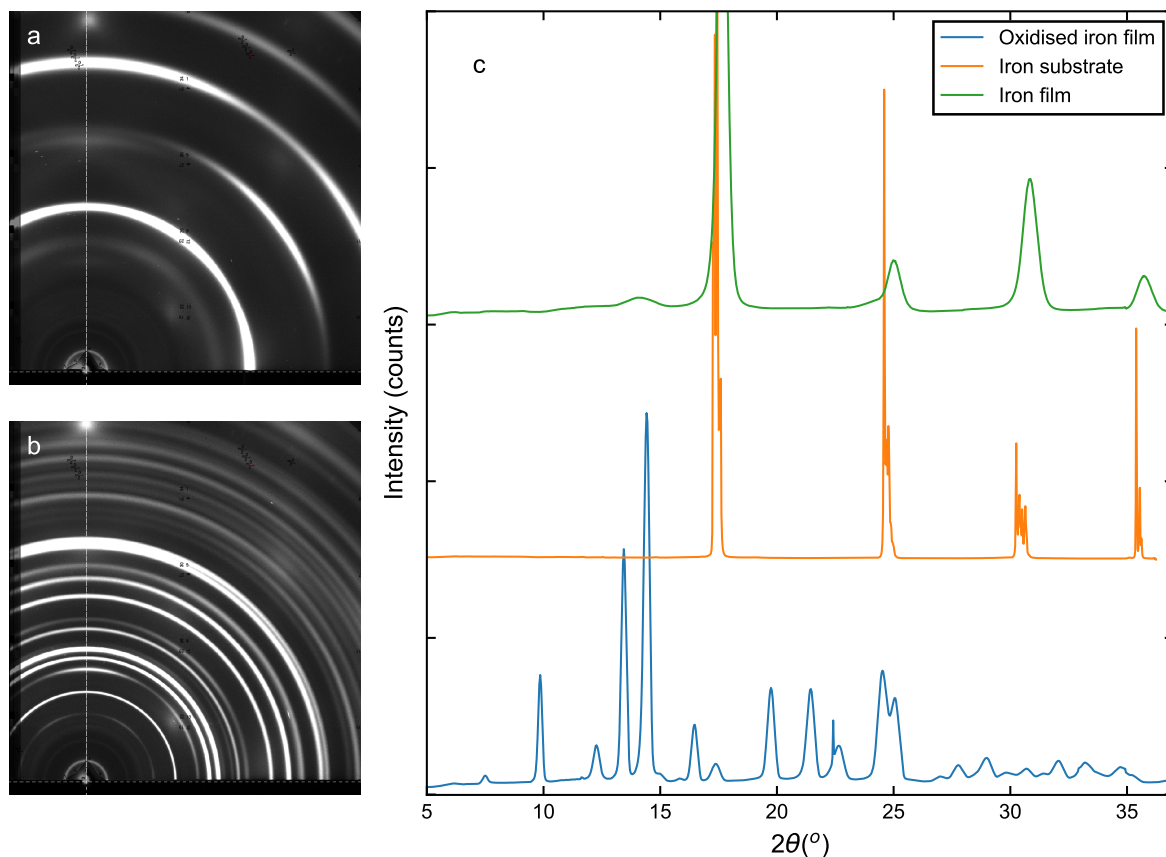


Figure 5.2: 2D WAXS measurements of a) iron film and b) oxidised iron film. c) 1D WAXS measurements of a polished iron substrate, an iron film and an oxidised iron film at an incident angles of (0.5° , 0.2° , 0.2° respectively)

reflection associated with the bulk and the surface, it is possible to determine the critical angle for probing the surface.

The treatment of iron thin films with hexadecane at 200°C for 1 hour will be referred to henceforth as ‘treated’ substrates. Figure 5.3 illustrates how the critical angle is determined. Figure 5.3a shows an example of a diffraction pattern for a treated iron substrate; the blue and red dashed lines highlight peak positions of a reflection associated with the substrate and a new phase formed following the treatment respectively. Figure 5.3b and c demonstrate how the intensities of these peaks change as a function of incident angle (0.1° to 1.0°). These intensities were normalised and have been plotted in Figure 5.3d. The critical angle for the substrate was determined as 0.8° , whilst the critical angle for the surface species was determined as 0.2° . The incident angle chosen for subsequent measurements was 0.2° to maximise the contribution of

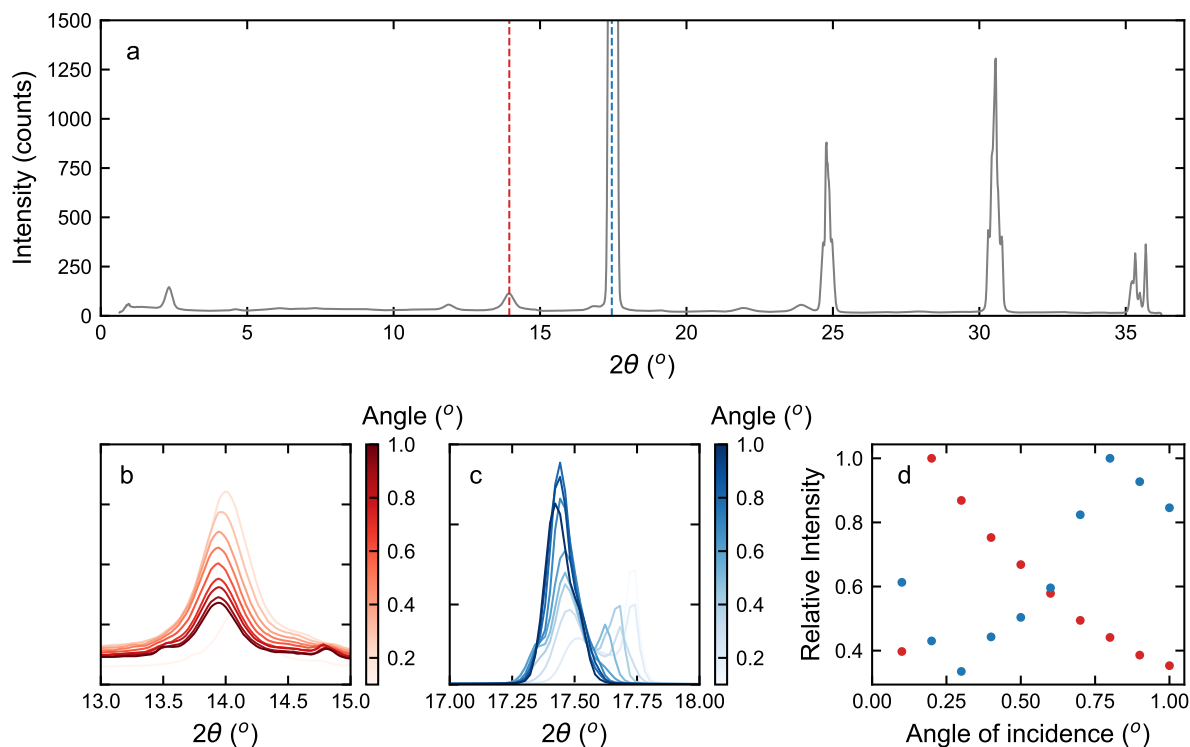


Figure 5.3: a) WAXS measurement of an iron substrate that has been treated with hexadecane obtained at an incident angle of 0.5° . The red and blue lines highlight peaks associated with the unknown species and the substrate respectively. b, c) demonstrate how these reflections intensities vary as a function of incident angle from 0.1° to 1.0° . d) Plot of relative intensities of these reflections.

the surface layer compared to the bulk.

As mentioned above, due to practical difficulties with aligning iron substrates, iron films were used for subsequent experiments. Figure 5.4a demonstrates the diffraction pattern for the treated iron film measured at a variety of incident angles. As above, the intensities of the reflections at 14.2° and 17.8° were compared to determine the critical angle. These normalised intensities are shown in Figure 5.4b. The critical angle is determined at 0.18° for both the surface species and the substrate, suggesting that the film is homogeneous across its depth. A possible explanation for the difference in critical angle between the iron substrate and the iron film may be a consequence of the smaller crystallite sizes observed in iron films. Smaller crystallite sizes will enable enhanced diffusion through the film upon treatment with hexadecane, perhaps resulting in changes across the depth of the iron film. Previously, Wang *et al.* produced a nanocrystalline iron microstructure and reported increases of 4–5 orders of magnitude in

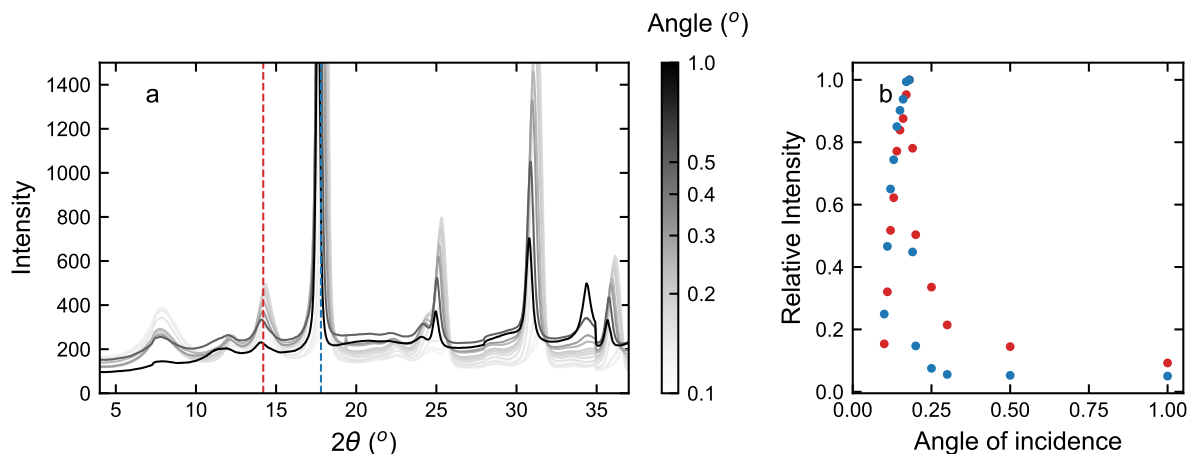


Figure 5.4: a) WAXS plots for an iron film treated with hexadecane at incident angles varying from 0.1° to 1.0° . The red and blue lines highlight peaks associated with the unknown species and the substrate respectively. b) Plot of the relative intensities of the reflections at the positions marked by these lines.

the diffusion rate of chromium compared to diffusion through the grain boundaries of ferrite.²⁸ A critical angle of 0.3° was chosen for subsequent measurements on iron films as the relative intensity ratios of the surface species to the bulk was highest at this incident angle.

5.4.4 Identification of Iron Carbide Phases on Iron Substrates

Through comparison to reference databases, the new phase on treated iron substrates is identified as cementite FeC_3 (COD 1008725). Reflections corresponding to (111), (200), (212) and (222) are annotated in Figure 5.5. The identification of cementite, an iron carbide, demonstrates that the findings in Chapter 4—that an oxidation to Fe(III) occurs at the iron surface—are insufficient to full explain the behaviour at this iron-hexadecane interface.

The broader reflections suggest that the crystallite size of cementite is smaller than that of ferrite.

5.4.5 Structural Measurements of Iron Thin Films

In situ measurements of the changes occurring at the surfaces of iron films were obtained in this project, however, due to the challenges associated with interpreting these data, see Section 5.4.6, the kinetics of these transitions is outside the scope of this work. Diffraction patterns of the iron

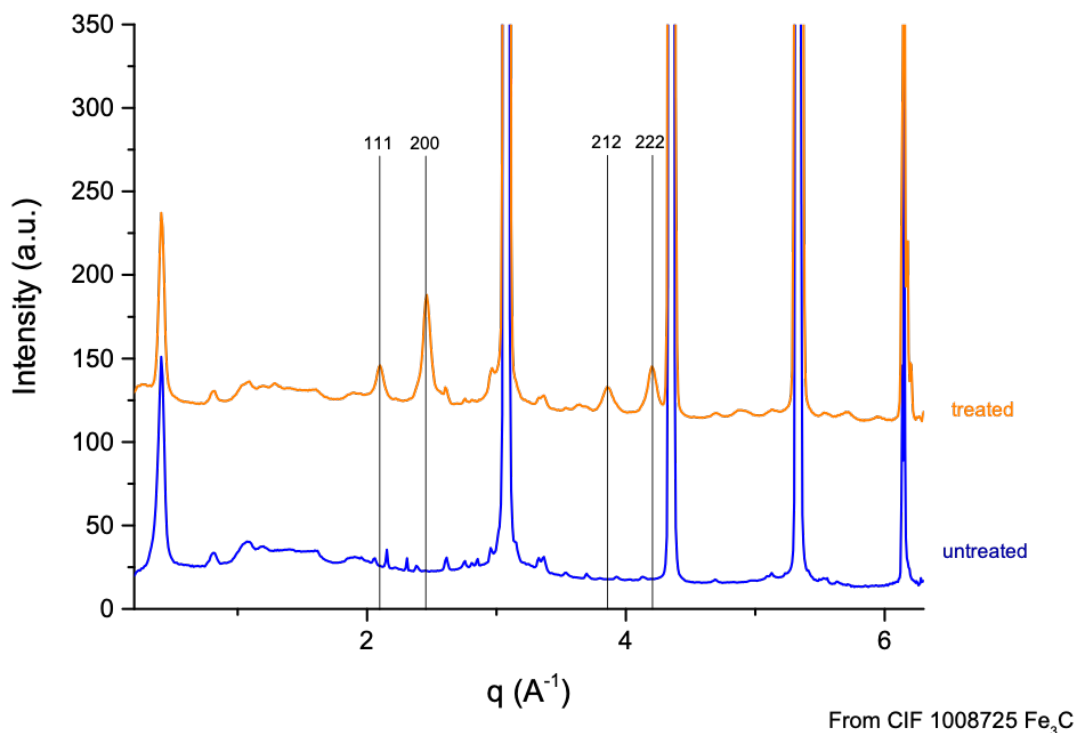


Figure 5.5: 1D WAXS measurements of a treated and an untreated polished iron substrate at an incident angle of 0.2° . Reflections associated with cementite (COD 1008725) are annotated with their corresponding planes.

and oxide films before and after exposure to hexadecane in *in situ* experiments are presented in Figure 5.6. These patterns demonstrate that, under these conditions, a transition occurs on both the iron and the oxidised film. Upon treatment of the iron film with hexadecane, broad low intensity reflections are observed at $2\theta = 7.8^\circ$, 12.1° , 22.3° and 24.2° . The broad shape of these low intensity reflections suggests the formation of a small amount of very small crystallites. The oxidised film however remains largely unchanged upon exposure to hexadecane, with the exception of the doublet at 24.1° and 24.7° . These results support findings by XPS that the metal than the oxidised surface. The reflections observed on the iron film may be present but obscured on the oxidised film, as reflections from the oxide phase have similar values.

5.4.6 Challenges Associated With Performing *In Situ* Measurements

In order to determine the phases present in these films, it is necessary to consider the effect of the experimental set-up on the measurements. Figure 5.7a-c demonstrates the 2D diffraction patterns

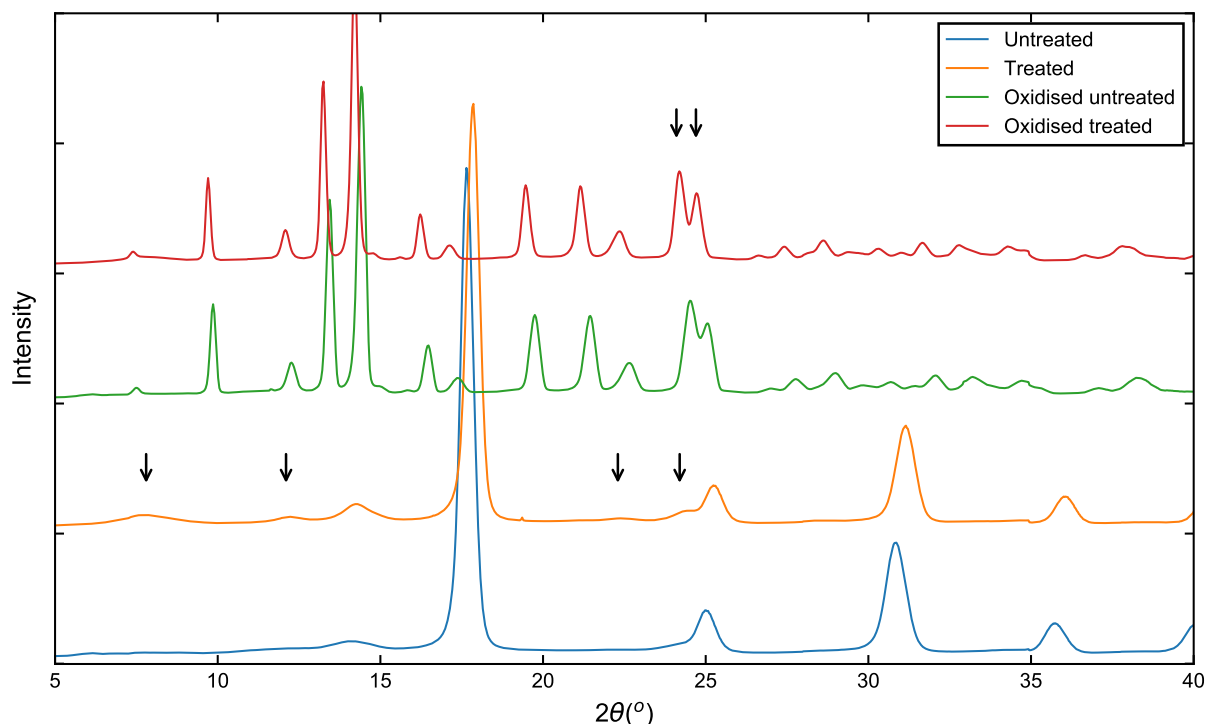


Figure 5.6: WAXS measurements of the iron substrate and the oxidised substrate before and after treatment with hexadecane at an incident angle of 0.2° .

for the untreated iron film at incident angles of 0.1° , 0.3° , and 1.0° respectively. Figure 5.7d illustrates the effect of incidence angle on the width of reflections. At low incident angles the beam has a larger footprint on the sample and therefore reflections from across the beam footprint will be measured and the detected signal will be broader.²⁹ In addition, the absence of post sample collimation on the beam line will lead to broader peaks. As the probing depth increases with the incident angle, the surface sensitivity of the measurement decreases; this decreased surface sensitivity is illustrated in Figure 5.7a-c, by the appearance of reflections from the underlying silicon substrate at higher angles, as highlighted by pink circles. At an incident angle of 0.1° , the measurement is surface sensitive, with limited contributions from the underlying crystalline silicon substrate. Therefore, a compromise must be made between surface sensitivity and attaining useful data in terms of peak resolution.

The incomplete diffraction rings in Figure 5.7a at an incident angle of 0.1° suggest that iron crystallites at the surface are oriented. With increasing depth, the surface appears less textured; unlike the broadening, these trends are believed to be real effects. A possible explanation for

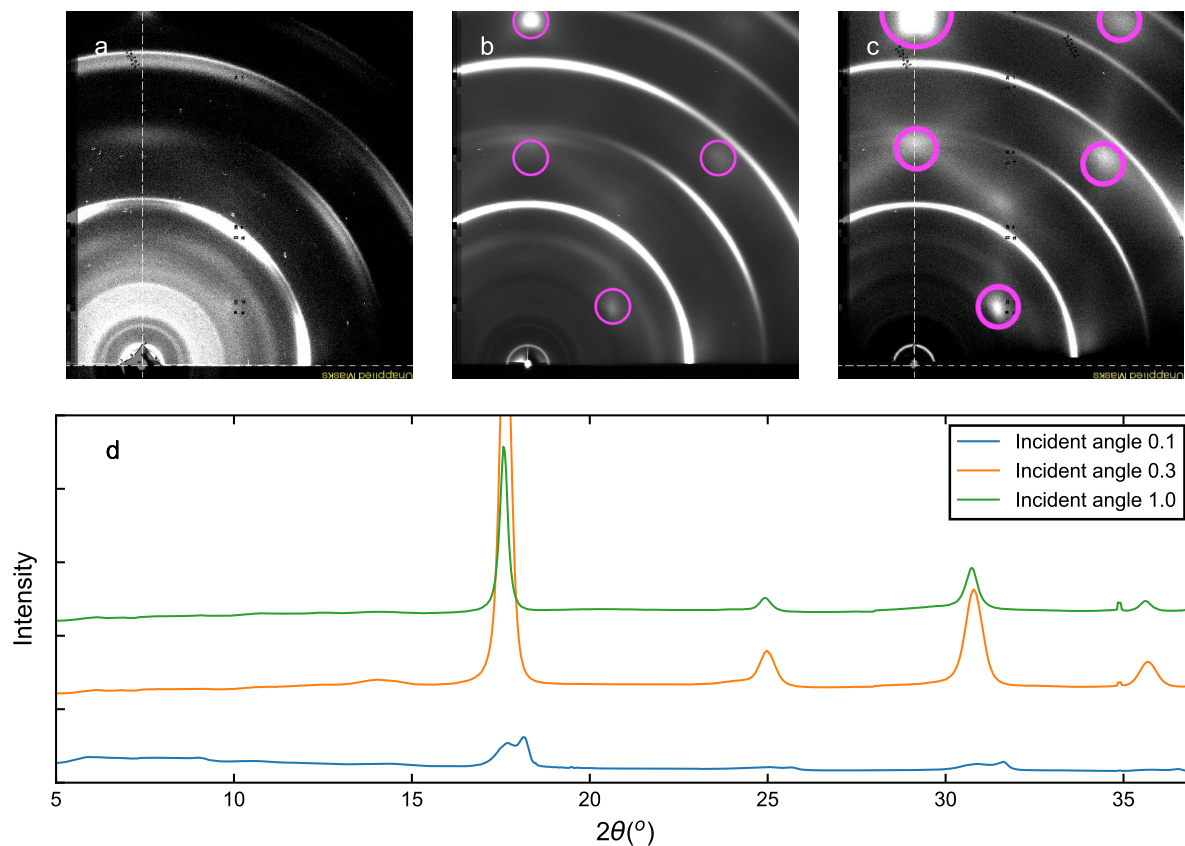


Figure 5.7: 2D WAXS measurements of the untreated iron film at incident angles of a) 0.1° , b) 0.2° , c) 1.0° . d) 1D diffraction pattern of the untreated iron film at these incidence angles.

the appearance of a doublet at approximately 18° at incident angles of 0.1° is a combination of a well-defined oriented phase at the surface and broadening due to the experimental set up.

It is possible to exclude the contribution of the underlying crystalline silicon substrate. To illustrate the procedure, the 2D diffraction patterns are presented in Figure 5.8a and b with the regions excluded from the integration highlighted in green in Figure 5.8b. The position of these silicon reflections are highlighted by turquoise lines in Figure 5.8b and c. The 1D diffraction pattern in Figure 5.8c illustrates the contribution of the underlying silicon substrate; at 28.9° and 34.1° removing the silicon signal has the effect of decreasing the background. Decreasing the background through removing the silicon reflection at 11.2° , reveals the maxima of the broad peak, which was identified in Figure 5.6, is now at 12.2° instead of 12.1° .

An additional challenge in interpreting these data are shifts in 2θ position. Typically small shifts in peak positions are attributed to stress and strain. Due to the precise beam alignment

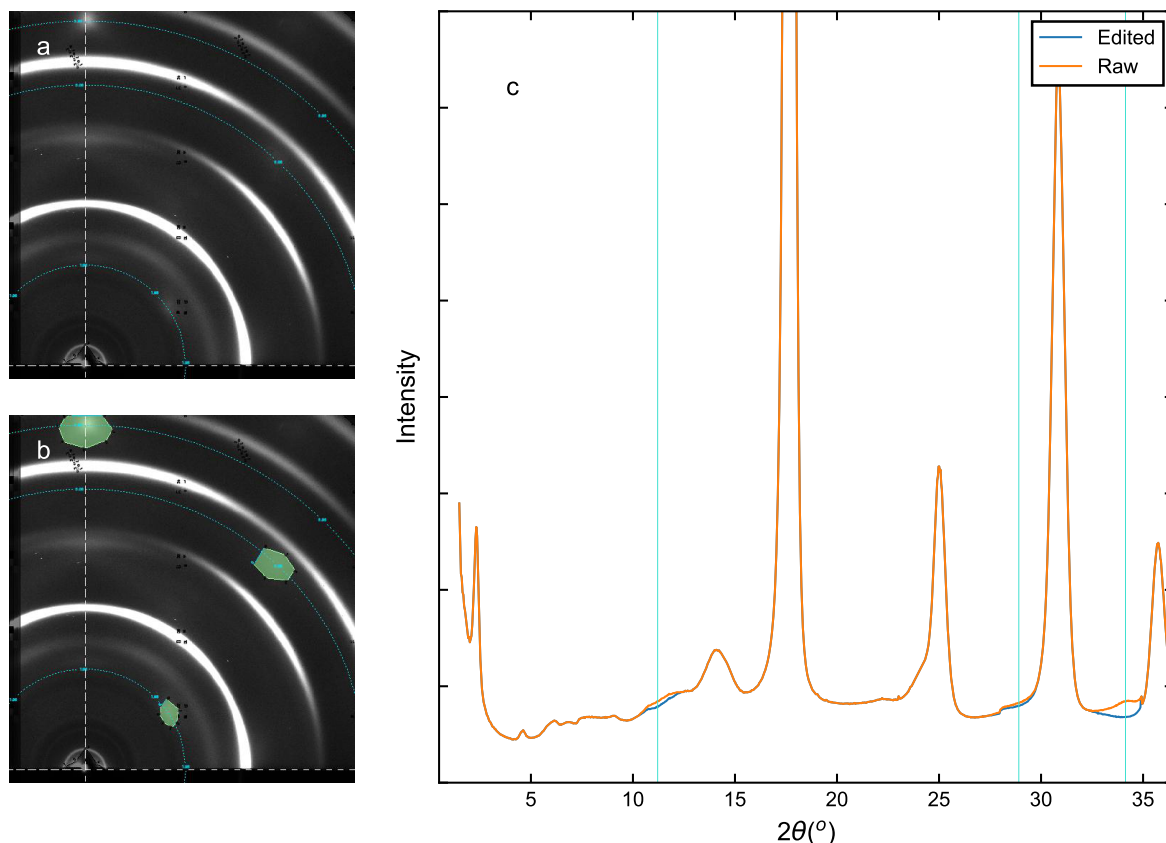


Figure 5.8: 2D WAXS measurements of the untreated iron film at an incident angle of 0.3° a) as measured; b) with masks removing the contribution of the underlying silicon substrate. c) 1D WAXS plots comparing the patterns of the iron film before (raw) and after (edited) removal.

required for grazing incidence experiments, small changes in sample height and angle will have significant effects on the peak position. Polyether ether ketone (PEEK) was chosen as the material to make the reaction chamber due to its chemical and temperature resistance, however, for the high accuracy required from the WAXS measurements, its thermal properties are not sufficiently stable. Due to the large thermal expansion coefficients for plastics and the operation of the cell above the glass transition temperature for PEEK, rather predictably the cell expanded and the alignment of the beam was lost over the course of the *in situ* experiments. Therefore, it is difficult to distinguish between structural transitions at the surface and experimental artefacts in *in situ* measurements. This difficulty is illustrated in Figure 5.9, where all iron CIFs are presented that have been matched with the data measured over the course of an *in situ* measurement (shifts of 0.7° are observed). The ferrite structure of the iron thin films is

assumed not to change over the course of the experiment, therefore, shifts in position attributed to geometric factors must be accounted for in able to convincingly assign phases, especially when these phases demonstrate similarities.

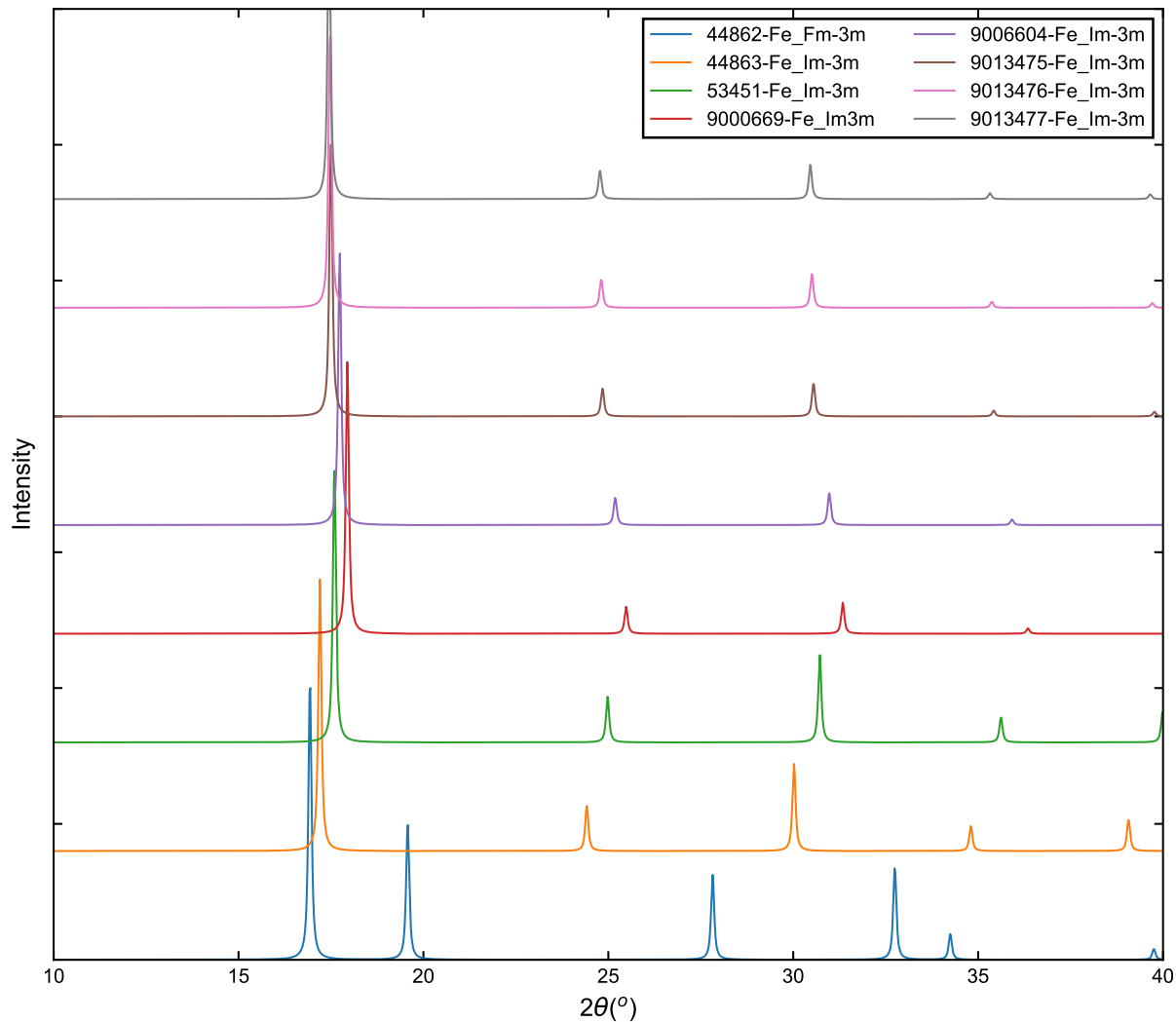


Figure 5.9: Examples of crystallographic information files (CIFs) from the Crystallography Open Database (COD) that were fitted to the the iron film over the course of *in situ* experiments.

To facilitate qualitative analysis of these data, a reflection associated with the substrate at approximately $2\theta = 17^\circ$, which is not observed to change over the experiment, is aligned to the relevant reflection in the published CIF for ferrite (00–006–069) from the International Centre for Diffraction Data (ICDD) database, i.e. the (110), (200), (211) and (220) planes at $2\theta = 17.8^\circ, 25.0^\circ, 30.7^\circ$ and 35.7° respectively. For measurements at elevated temperatures, in the absence of a relevant CIF measured under the same conditions, consideration must be

given to the effect of the thermal expansion of the lattice. Therefore, changes in peak position as a result of structural changes at the surface, for example, a lattice expansion due to the dissolution of carbon, will be difficult to distinguish from differences in temperature.

5.4.7 The Effect of Hexadecane on the Structure of Iron and Iron Oxide Films

Figure 5.10 shows the diffraction pattern for the untreated and treated film, which have been aligned to the (110) plane reflection for ferrite (ICDD 00–006–069). As mentioned above, four broad reflections associated with ferrite are due to reflections from the (110), (200), (211) and (220) planes respectively; the peak width demonstrates that the crystallite size on the iron thin films is smaller than on iron substrates. The low intensity broad peaks at $2\theta = 7.8^\circ$, 12.2° , 22.3° and 24.2° and increased intensity of the peak at $2\theta = 14.5^\circ$ indicate a small amount of this phase is formed at the surface and it has a very small crystallite size. Due to the broad nature of these reflections it is difficult to unambiguously determine the crystal phases present, especially due to the similarities between iron species and the overlap of peak positions combined with the uncertainty associated with the 2θ position. Nonetheless, these low intensity reflections were assigned to iron oxide hydroxide (ICDD 00–044–1415), in line with previous findings. The reflection at $2\theta = 11.8^\circ$ is attributed to a reflection from the (110) plane, whilst the reflection at $2\theta = 14.5^\circ$ may be associated with a reflection from the (130), (041) or (111) planes; the reflection at $2\theta = 22.3^\circ$ is attributed to the reflection at (112) and lastly, the shoulder at $2\theta = 24.2^\circ$ may be a result of a reflection from the (220) or (081) planes.

From earlier studies in Chapter 4, the oxidised surface is not expected to undergo any transitions following exposure to hexadecane at elevated temperatures. Characterisation of the untreated oxidised film identifies the surface to consist of both hematite and magnetite phases, as shown in Figure 5.11. Following treatment, the oxidised surface consists of hematite and magnetite phases; the only notable variations between these surfaces can be observed by the changes in peak shape for the reflection at $2\theta = 24.1^\circ$ and 24.7° . These variations are attributed to the contribution from the (3–14) and (300) planes for hematite and the (440) plane for

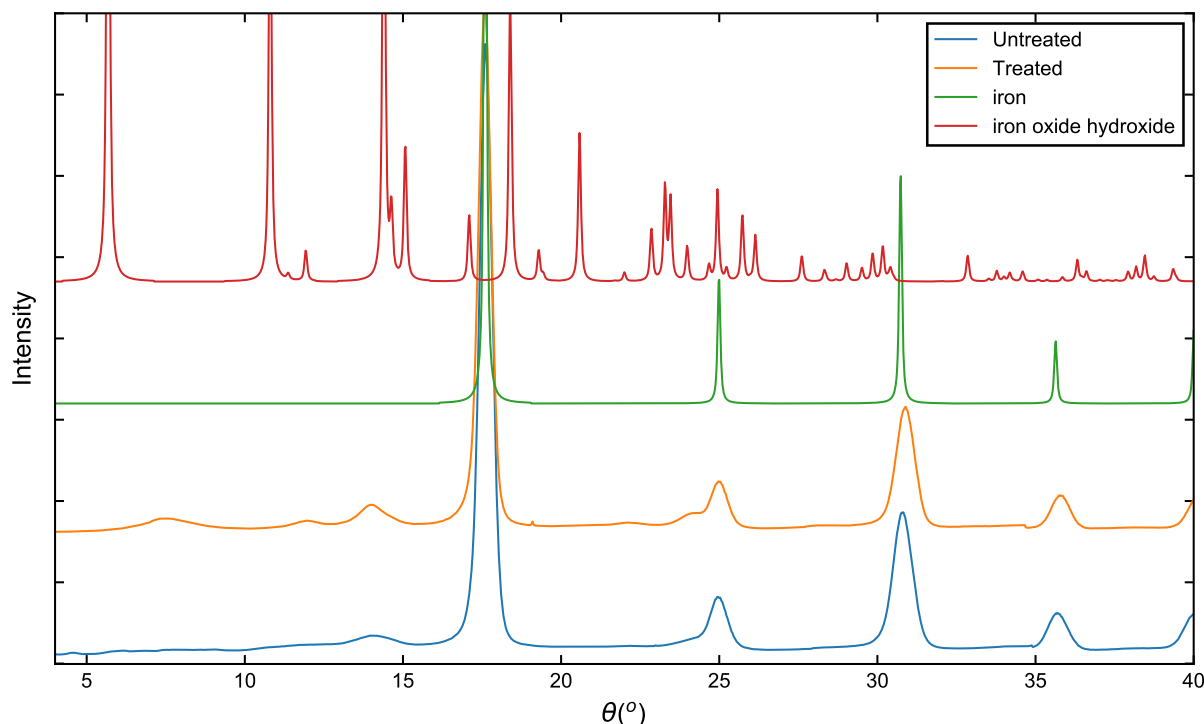


Figure 5.10: 1D diffraction patterns of the untreated and treated iron films, aligned to the 110 reflection in the ferrite CIF with the contribution from the underlying silicon substrate removed. Ferrite (ICDD 00–006–0696) and iron oxide hydroxide (ICDD 00–044–1415) phases were identified in the measured samples.

magnetite. Qualitatively, the increased resolution of the hematite doublet is enabled by the decreased contribution from the magnetite reflection. The partial oxidation of magnetite to hematite following hexadecane treatment further supports a surface oxidation, even on the oxidised surface where no changes are observed with XPS.

5.4.8 Species Identification by Raman Spectroscopy

Raman spectroscopy was used to identify iron oxide and iron hydroxide species present at the surface. De Faria *et al.* demonstrated the potential of Raman spectroscopy to differentiate between different phases, presenting reference spectra for hematite (α -Fe₂O₃), magnetite (Fe₃O₄), wüstite (FeO), maghemite (γ -Fe₂O₃), goethite (α -FeOOH), lepidocrocite (γ -FeOOH) and δ -FeOOH.³⁰ On the oxidised film, limited changes are observed on the oxidised film, whilst the iron film is observed to undergo an oxidation.

Figure 5.12a shows the changes occurring on an iron film, which is believed to have accessible

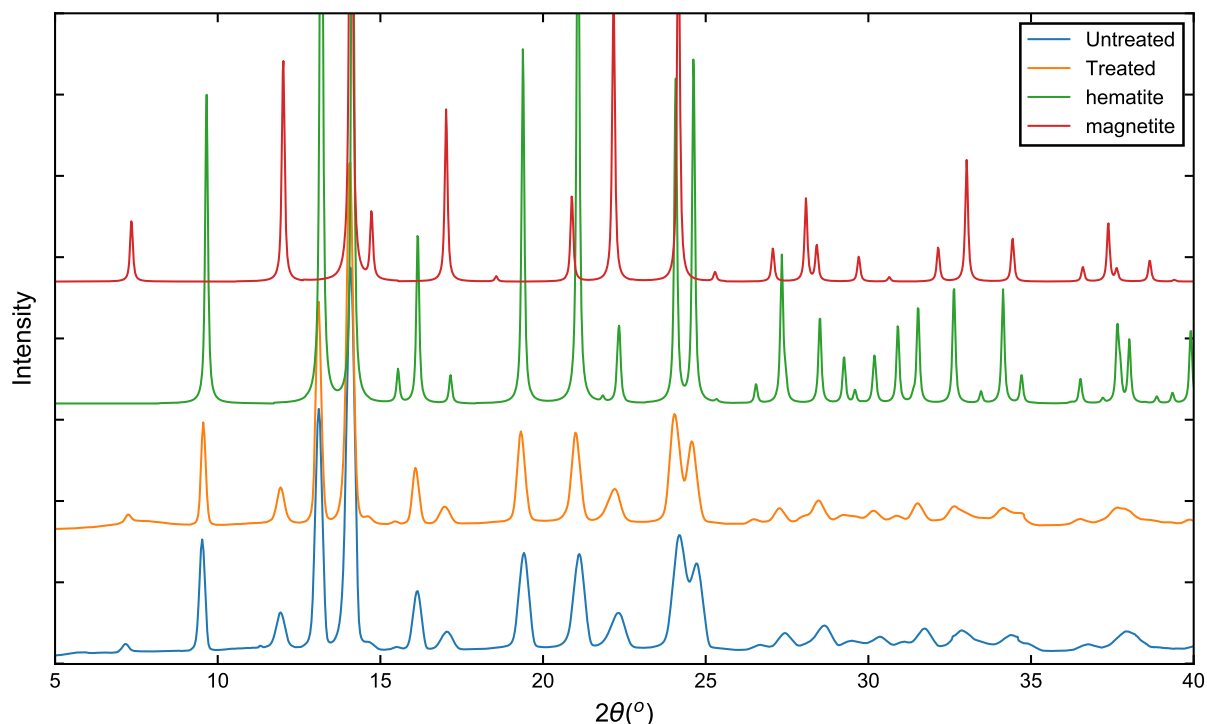


Figure 5.11: 1D diffraction patterns of the untreated and treated oxidised iron films, aligned to the 2–10 reflection in the hematite CIF, with the contribution from the underlying silicon substrate removed. Hematite (ICDD 00–033–0664) and magnetite (ICDD 00–019–0629) phases were identified in the measured samples.

Fe(0). The appearance of the peak at 547 cm^{-1} upon treatment with hexadecane could be attributed to either goethite ($\alpha\text{-FeOOH}$) or magnetite (Fe_3O_4). The peak at 670 cm^{-1} is observed to increase in intensity; this peak could be attributed to hematite, magnetite or wüstite. Whilst these spectra do not identify the phase on the surface, they provide further convincing evidence of a surface oxidation, as observed using both XPS and GI-WAXS.

Figure 5.12b demonstrates the differences between the untreated and the treated oxidised film. From comparison to reference spectra, the oxidised film is identified as predominantly hematite.³⁰ As hematite surfaces cannot be further oxidised, the spectra for the treated film is not expected to undergo any further changes. The peak at 520 cm^{-1} , observed to decrease in intensity with treatment, is attributed to the underlying silicon substrate; an explanation for its increase remains unclear, however assuming the iron film thickness remains constant, these results suggest a decrease in probing depth.

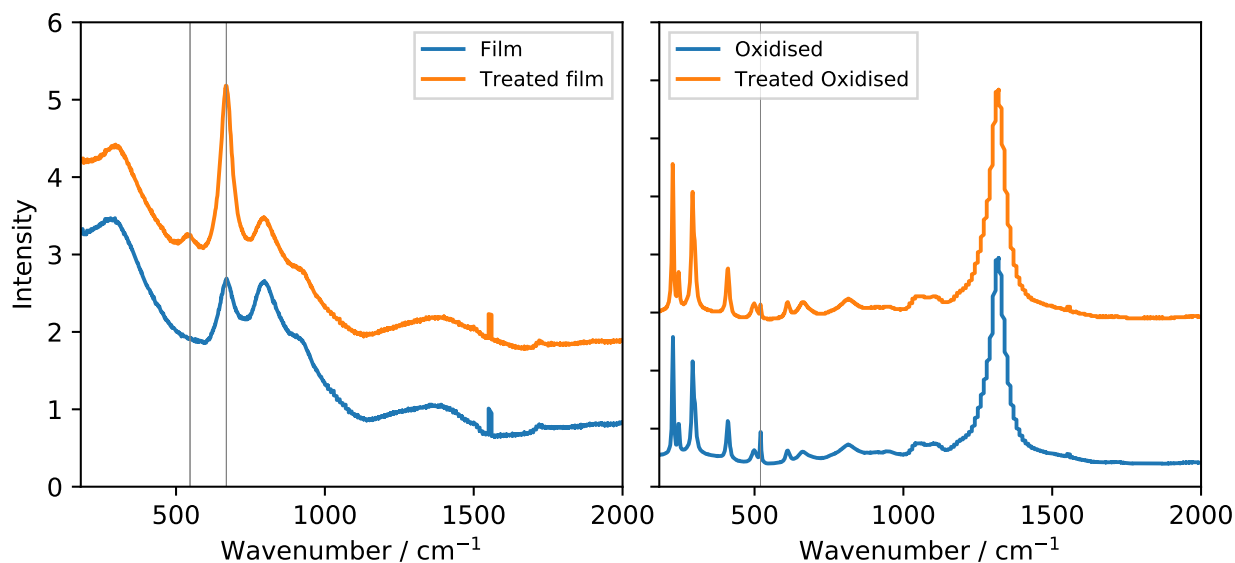


Figure 5.12: Raman spectra of both a untreated and treated a) iron thin film and b) oxidised iron thin film. The grey lines are used to highlight the key changes between these spectra. These measurements were taken by Dr. Hossein Yadegari at a wavelength of 533 nm.

5.4.9 Structural Characterisation by Transmission Electron Microscopy

Iron thin films were grown on TEM grids to enable the structural characterisation of the film before and after treatment with hexadecane at 200°C by electron diffraction. The 1D data, extracted from the 2D transmission electron diffraction patterns, are presented in Figure 5.13 with a variety of iron reference patterns for comparison (detailed in the caption). The untreated iron thin film appears to be made up of ferrite, as annotated by the black lines. Upon treatment with hexadecane, the peaks associated with metallic iron are largely lost and the new trace resembles a combination of Fe_7C_3 (blue guide lines) and magnetite (green guide lines).

Fe_7C_3 , or Eckstrom and Adcock carbide, is frequently observed in FTS and considered to be stable in air at room temperature. Compared to other stable carbides, Fe_7C_3 has a relatively high proportion of carbon (8 wt.%) with the carbon atoms also located in the trigonal prismatic interstices. Based on the literature of similar systems outlined previously, the formation of an iron carbide in this temperature range is unsurprising, yet there are limited studies on the formation of iron carbides in hydrocarbon stream systems.³¹ For iron carbides to form in this system, iron surfaces must break down hexadecane molecules, enabling carbon atoms to diffuse into the iron lattice forming an iron carbide.

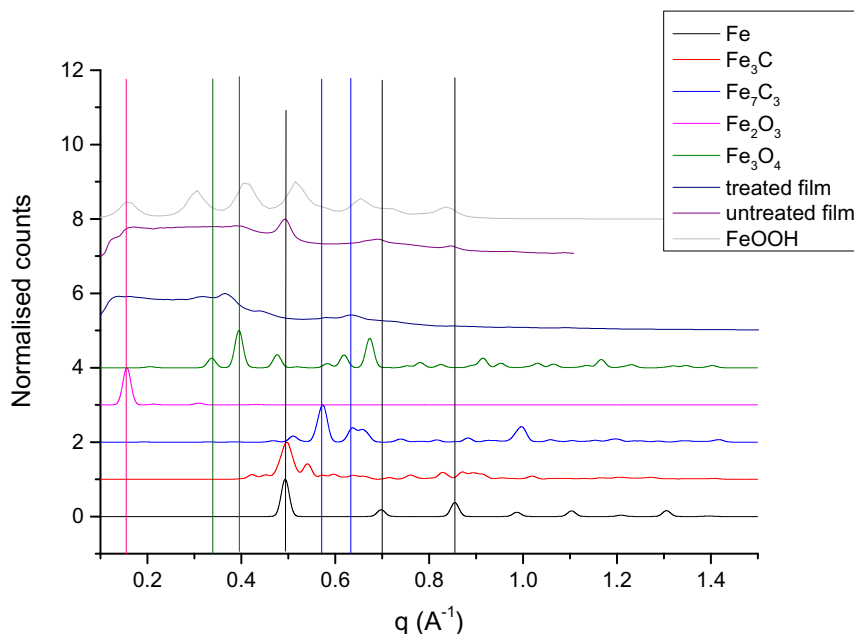


Figure 5.13: Comparison of 1D electron diffraction of treated and untreated iron films with references ferrite (ICSD 159352), hematite (ICSD 671713), cementite (ICSD 673006), magnetite (COD 1513304) and Fe_7C_3 (ICSD 187139). TEM measurements were conducted by Dr. Catriona McGilvery and analysis of these data was completed by Dr. Michal Klosowski.

5.4.10 Investigating the Chemical Environment of Iron Thin Films

Three iron thin films thicknesses - 10 nm , 50 nm and 100 nm - were used to investigate the chemical environment of iron atoms at the interface by X-ray absorption fine structure (XAFS) - constituted of X-ray absorption near edge (XANES) and extended X-ray absorption fine structure (EXAFS). All three film thicknesses produce sufficient signal during *in situ* experiments to enable comprehensive analysis and therefore the use of three film thicknesses provides an insight into the depth of the changes occurring at the surface. The EXAFS spectra for these film thicknesses are shown in Figure 5.14a.

The chemical environments of iron in the 10 nm film and the 100 nm iron film is shown to be significantly different (Figure 5.14). Fingerprinting is the most basic form of analysis that is used for interpreting EXAFS spectra; the features of unknown spectra are compared to spectra measured from known standards. The iron references used for comparison are shown in Figure 5.14b. These references were measured by Prof Carlo Segre at the Advanced Photon Source MR-CAT beam line. The similarity between the 100 nm film and the measured standard

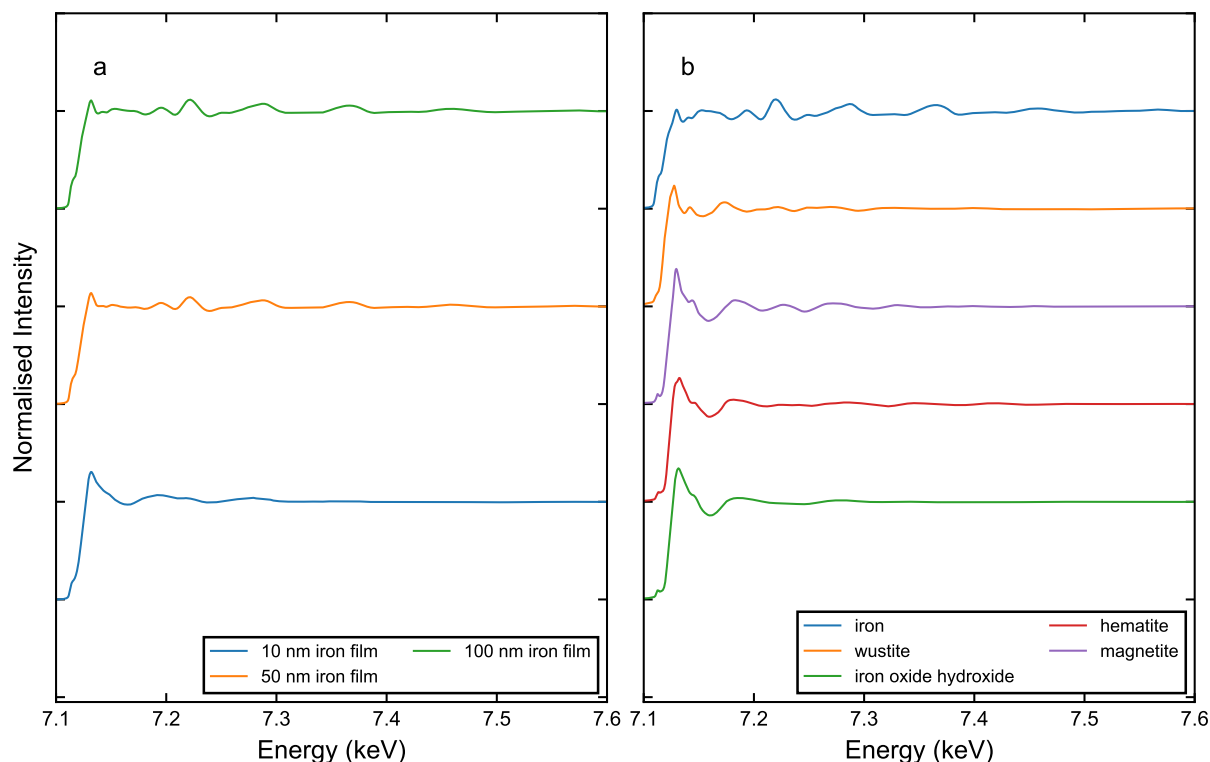


Figure 5.14: a) EXAFS spectra for untreated 10 nm, 50 nm and 100 nm iron thin films measured at the iron edge at Diamond Light Source. b) EXAFS spectra, measured at the iron edge, comparing the 10 nm film with reference samples iron, hematite, magnetite, iron oxide hydroxide, wüstite. Reference samples were measured on MR-CAT at APS by Prof. Carlo Segre.

for iron, shown in Figure 5.14, suggests that this film is predominantly iron, therefore, only a very thin native oxide is expected on this surface. The spectra for the 50 nm film resembles iron with some small variations in the oscillations after the edge. These similarities demonstrate that the 50 nm is largely metallic iron, yet, unsurprisingly, the surface oxide makes a larger contribution at this film thickness.

Through comparing the untreated 10 nm iron film (Figure 5.14a) to the reference samples (Figure 5.14b) the shape of the pre-edge on the 10 nm iron film is found to be comparable to metallic iron, whilst the shape of the XANES region displays similarities to iron oxide hydroxide. From these observations, it is possible to infer that the 10 nm iron film is a combination of iron and iron oxide hydroxide. If limited similarities are observed between the measured spectra and the reference spectra, the corresponding reference may not have been measured and/or the sample may contain a mixture of chemical environments.

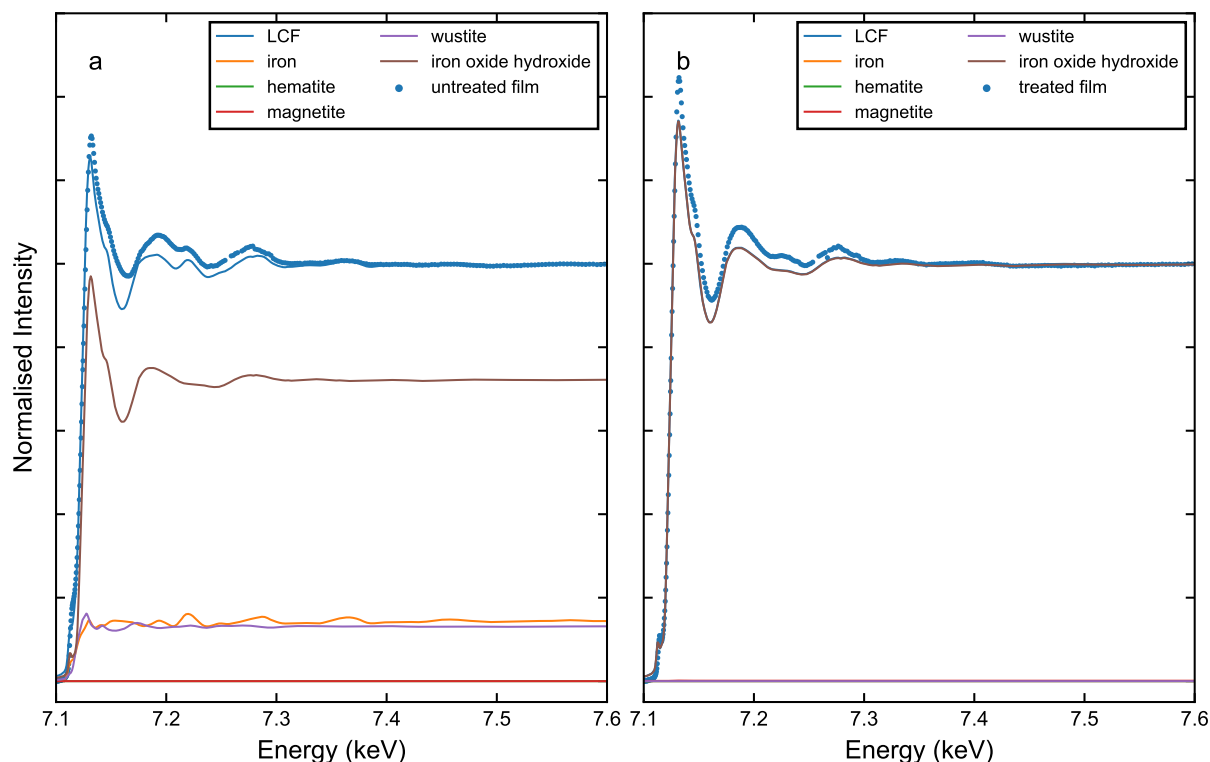


Figure 5.15: Linear Combination Fitting of the a) untreated and b) treated 10 nm iron film showing the weighted reference spectra.

Assuming the required references are available, linear combination fitting (LCF) enables the ratio of iron species within the material to be determined; LCF relies on the principle that the overall absorption of a material is due to the sum of the absorption of the species within the material. For the LCF of XANES data, the fit is expected to follow the shape of the features however variations are expected due to differences in measurement conditions and data processing. The quality of the fit is determined by the R factor; Kelly *et al.* reported that a reasonable LCF for XANES data has an R-factor of less than 0.05.³² The results of linear combination fitting of these films are presented in Table 5.2 with their corresponding R-factors. According to this guideline, reasonable fits have been attained for all films with the reference standards shown in Figure 5.14b.

Using these standards, LCF identified iron and iron oxide hydroxide species in each untreated film, with the 10 nm film also found to contain wüstite, whilst hematite was found in the thicker films. The LCF for the untreated 10 nm film is presented in Figure 5.15a. Upon exposure to

Table 5.2: Linear combination fitting for untreated iron thin films

	10 nm		50 nm		100 nm	
	Untreated	Treated	Untreated	Treated	Untreated	Treated
iron	0.144	-	0.577	0.529	0.650	0.613
wüstite	0.131	-	-	-	-	-
magnetite	-	0.001	-	-	-	-
hematite	-	-	0.087	0.124	0.187	0.235
iron oxide hydroxide	0.725	0.999	0.336	0.347	0.163	0.151
R factor	0.012	0.011	0.007	0.005	0.008	0.006

hexadecane at 200°C, each film was observed to undergo a transition; EXAFS spectra of these films before and after treatment are shown in Figure 5.16. The largest transition is observed for the 10 nm film, suggesting that these changes are localised within 50 nm of the surface. The increase in intensity of the white line following treatment with hexadecane suggests that the surface is oxidised.⁶ Using LCF fitting, the treated 10 nm film was found to consist essentially of iron oxide hydroxide (0.999, with 0.001 weight magnetite) as shown in Figure 5.15b and reported in Table 5.2. The oxidation of the surface and the formation of an iron oxide hydroxide has been found using XPS, Raman and WAXS. Similarly, as shown in Figure 5.16 and reported in Table 5.2, the 50 nm and the 100 nm iron films are found to undergo oxidation at the iron surface. For the 50 nm and 100 nm films, the weighting of hematite and iron oxide hydroxide increase and the amount of metallic iron decreases upon treatment, however no additional species are found.

The validity of this interpretation is discussed here: the R-factors determined for these fits are well within the limit considered reasonable; the fit appears to capture the main features of the measured data and these results support findings by other analysis techniques. From a review of the literature on other systems under similar conditions, iron carbides were hypothesised to form on iron surfaces. The iron carbide, Fe_7C_3 , was identified by electron diffraction, suggesting

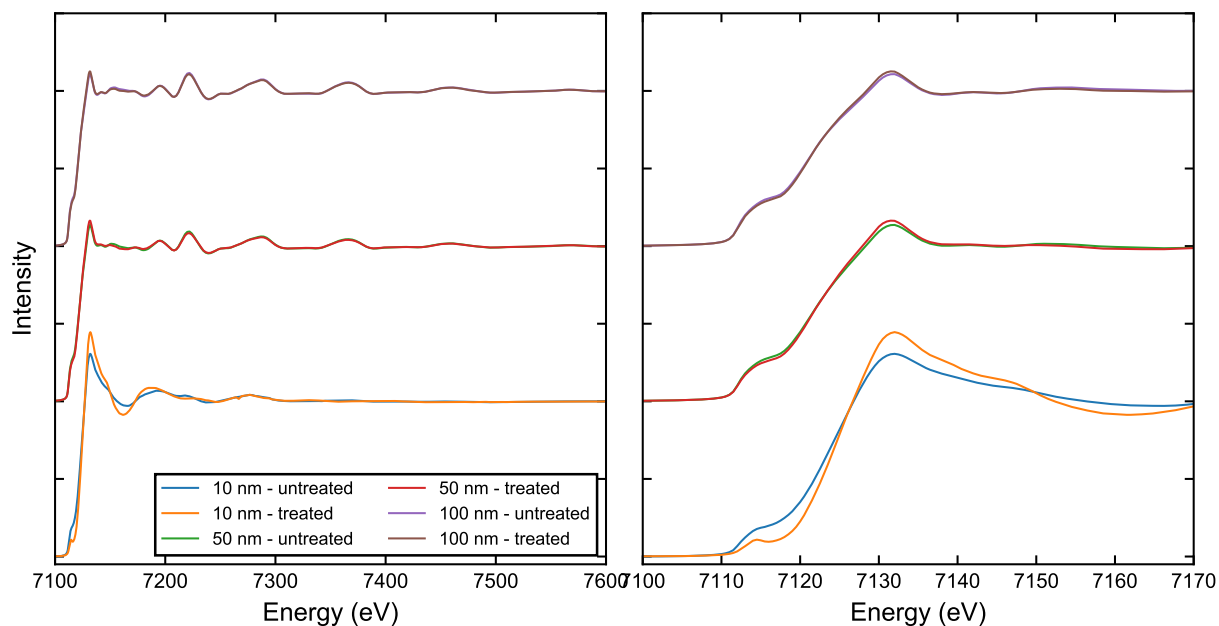


Figure 5.16: XAFS, measured at the iron edge, comparing the effect of exposure to hexadecane at elevated temperatures on 10 nm, 50 nm and 100 nm iron thin films.

the formation of a relatively carbon-rich carbide on upon treatment with hexadecane. Assuming the low intensity broad reflections in the diffraction pattern from WAXS measurements are correctly assigned as iron oxide hydroxide, the absence of iron carbides in these analyses could be attributed to the formation of carbides with low crystallinity or due to the lack of detection of iron carbides due to the very small size of iron carbide crystallites on iron films. In Raman spectroscopy, iron carbides cannot be identified as they are Raman inactive; Park *et al.* calculated the active lattice vibrational modes of a cementite single crystal, determining all four vibrational modes to be Raman inactive.³³

Whilst these analyses do not provide convincing evidence for the formation of iron carbides in this system, the formation of iron carbides cannot be ruled out. LCF of the XANES data, in the absence of iron carbide standards provided a reasonable fit by the accepted metric using iron, iron oxides and iron oxide hydroxide. Whilst these fits follow the trends of the measured data, the shape and the position of the pre-edge is not effectively captured by the fit, as shown in Figure 5.17a. Theoretical iron carbide standards are presented in Figure 5.17b.³ These standards show the pre-edge of iron carbide resembles a shoulder on the edge, rather than a resolved peak before the edge as observed for iron oxides. The pre-edge shoulder observed on the edge of the

iron thin film suggests that iron carbides may be present, however, the position of the edge, located at higher energies, is typical of a higher iron oxidation state, i.e. an iron oxide. The inability to capture the shape of the pre-edge using LCF suggests that additional reference compounds are required to robustly conduct linear combination analysis. To unambiguously determine the constituent species in the films, ideally linear combination fitting should be conducted with all the possible species that may be present in the film, albeit with the lack of iron carbide references available and their instability at room temperature, this is not trivial. EXAFS fitting, using crystallographic information files, provides another non-trivial method of determining the species present in this system.

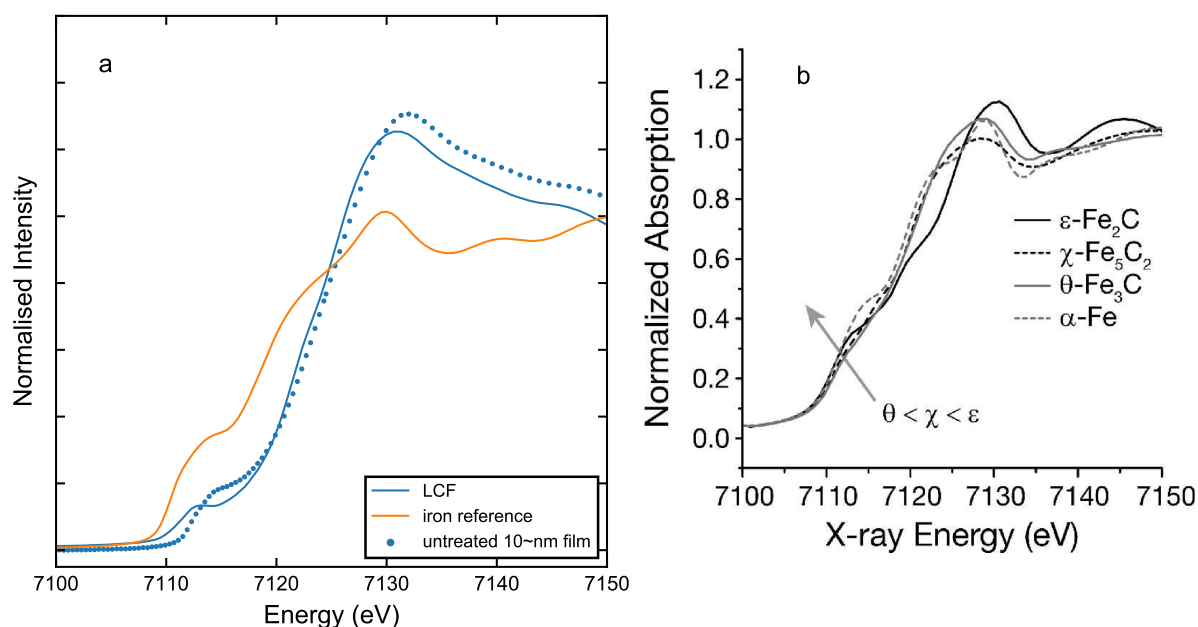


Figure 5.17: a) Comparison between the measured data for the untreated 10 nm film and the fit attained by linear Combination Fitting. b) Reference spectra from iron carbides modified from [3]. Iron is included in both plots for comparison.

5.4.11 Investigating the Transition of Iron Films

Figure 5.18 demonstrates the oxidation of the 10 nm iron film as a function of time during exposure to hexadecane at 200°C. Comprehensive analysis of the kinetics of this transition requires certainty on the nature of the transition. Assuming a correct fit by LCF, the predominantly iron oxide hydroxide film, which also contains wüstite and iron, is observed to convert to an

iron oxide hydroxide without going through any intermediates. The kinetics of this transition is outside the scope of this work.

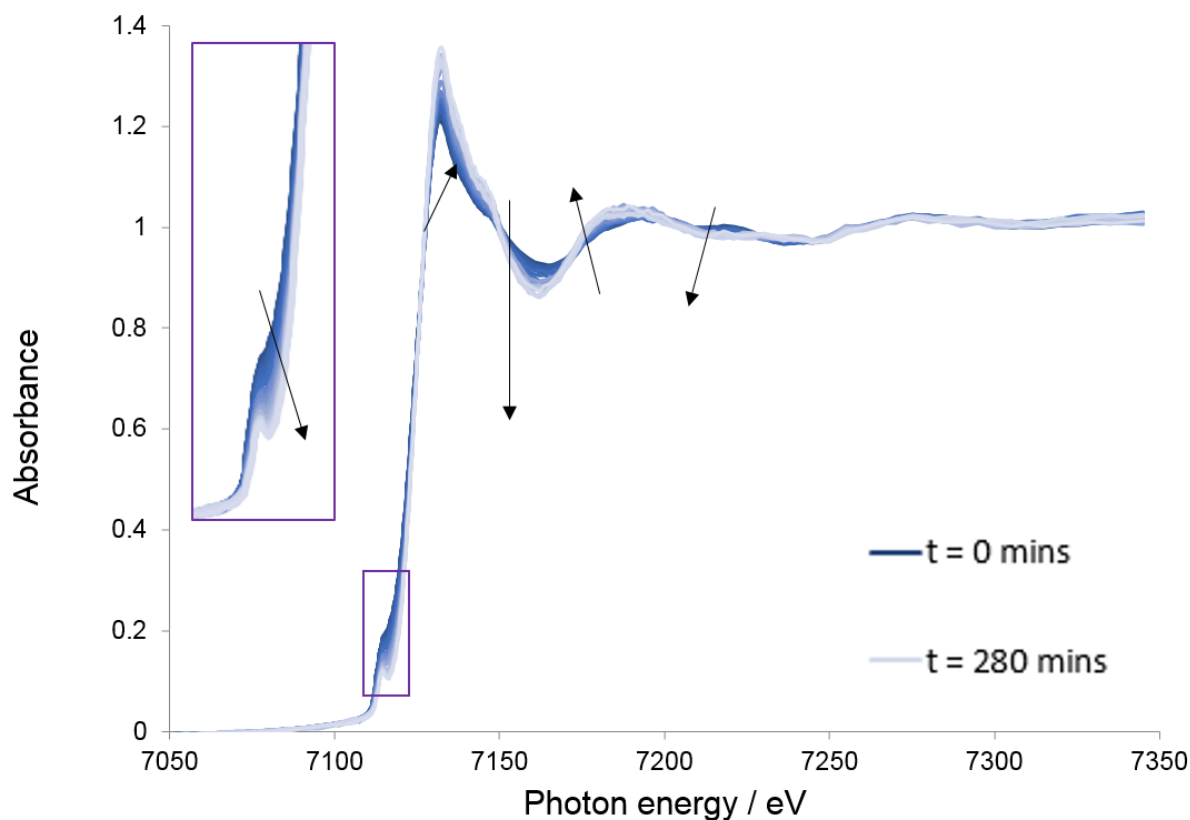


Figure 5.18: *In situ* XANES of the changes occurring on a 10 nm iron film upon reaction with hexadecane at 200°C

5.5 Conclusions

A reactive interface was observed between iron surfaces and hexadecane at elevated temperatures. In support of XPS findings (presented in Chapter 4) and Raman spectroscopy measurements (presented in this chapter), structural and chemical changes occurring at iron surfaces have been successfully measured *in situ*. Upon treatment with hexadecane at elevated temperatures, iron surfaces are observed to undergo an oxidation; the transition from iron and less oxidised iron oxides (magnetite and wüstite) to iron oxide hydroxide and more oxidised iron oxides (hematite) has been supported, in some way, by the four analysis techniques discussed here.

The formation of oxidised iron species was identified on the iron surface using Raman spectroscopy. Structural characterisation of the iron film using GI-WAXS identified the formation of small iron oxide hydroxide crystals, with characterisation of the chemical environment of 10 nm iron films supporting the oxidation of the film surface to iron oxide hydroxide. Both structural and chemical characterisation of the transitions occurring on these films demonstrates that the effect is localised on the surface (within the first 50 nm). Structurally, the appearance of a new low intensity iron phase is not accompanied by a significant reduction in the intensity of reflections from the underlying substrate in GI-WAXS, whilst chemically, significant changes are observed for the 10 nm iron film, whilst the transition on the 50 nm film is subtle, the transition observed on the 100 nm is almost negligible.

The oxidation of the iron surface upon exposure to hexadecane is observed to a lesser extent on oxidised films. Using XPS, magnetite films were found to oxidise to hematite, whilst hematite films remained unchanged following treatment. No changes were observed on the oxidised iron substrate by Raman Spectroscopy. Structural characterisation of oxidised iron films demonstrated that these films remain largely unchanged, with slight changes in the shape of overlapping magnetite and hematite peaks demonstrating that the oxidation of magnetite to hematite still occurs on these surfaces.

Artefacts from the sample and the experimental set up complicate the interpretation and assignment of the diffraction pattern measured by GI-WAXS. These artefacts include peak broadening as a result of both the use of thin films and the absence of collimators at the beam line, the contribution from the underlying crystalline silicon substrate and the shift in peak positions due to variations in sample height and angle over the course of the experiment. Section 5.4.6 discussed the assumptions and data manipulation that are required to interpret these patterns, however, due to the broad reflections and the similarity between the peak positions between different iron phases, there is still significant uncertainty associated with identifying iron phases.

Similarly, linear combination fitting of the XANES spectra identifies a good fit using iron oxide and iron hydroxide references. As these references were measured at different times on different beam lines, some degree of variation is expected between these samples; a high quality

fit is achieved here, by widely accepted standards. These findings support the oxidation of iron to iron oxide hydroxide observed by other techniques, however, independently, these findings are not overly convincing.

The variation in the shape of the pre-edge between the measured data and the fit suggest that a different species may be present. Through comparison to the reference values, the shoulder-like shape of the pre-edge appears more like iron or iron carbides, however its position is more consistent with iron oxides. The identification of a crystalline iron carbide, Fe_7C_3 , on a 10 nm iron film by electron diffraction and cementite, $\theta\text{-Fe}_3\text{C}$ on a polished iron substrate using GI-WAXS, further supports the formation of a carbide. Due to the instability of iron carbides, and hence the unavailability of reference spectra, linear combination fitting of the film with iron carbide reference spectra is not possible. Further insights into this system could be gained by using crystallographic information files to determine scattering paths which could be fit to the EXAFS region, however this is non-trivial. Iron carbides are not detected in Raman spectroscopy as iron carbides are Raman inactive. The absence of iron carbides on iron thin films measured by GI-WAXS could be attributed to the formation of an amorphous iron carbide or the difficulties in detecting and assigning phases to species which form small quantities of small crystallites. Therefore, further evidence is required for the formation of iron carbides to be confirmed and characterised.

From the *in situ* studies performed, there is significant potential to further understand this system, defining the transformation of iron phases as a function of both time and temperature. Whilst there is still some degree of uncertainty in these findings as outlined above, the evidence for a reactive interface between iron surfaces and hexadecane at engine relevant temperatures is indisputable. An overall oxidation of the iron present at the surface is observed, with iron oxide hydroxide proposed to form following exposure with hexadecane.

References

- (1) De Smit, E.; Weckhuysen, B. M. The renaissance of iron-based Fischer-Tropsch synthesis: On the multifaceted catalyst deactivation behaviour. *Chemical Society Reviews* **2008**, *37*, 2758.
- (2) Oyama, S. Preparation and catalytic properties of transition metal carbides and nitrides. *Catalysis Today* **1992**, *15*, 179–200.
- (3) De Smit, E.; Cinquini, F.; Beale, A. M.; Safonova, O. V.; Van Beek, W.; Sautet, P.; Weckhuysen, B. M. Stability and reactivity of ϵ - χ - θ iron carbide catalyst phases in Fischer-Tropsch synthesis: Controlling μ_c . *Journal of the American Chemical Society* **2010**, *132*, 14928–14941.
- (4) Peña, D.; Cognigni, A.; Neumayer, T.; van Beek, W.; Jones, D. S.; Quijada, M.; Rønning, M. Identification of carbon species on iron-based catalysts during Fischer-Tropsch synthesis. *Applied Catalysis A: General* **2018**, *554*, 10–23.
- (5) Eliason, S.; Bartholomew, C. Reaction and deactivation kinetics for Fischer-Tropsch synthesis on unpromoted and potassium-promoted iron catalysts. *Applied Catalysis A: General* **1999**, *186*, 229–243.
- (6) Ribeiro, M. C.; Jacobs, G.; Davis, B. H.; Cronauer, D. C.; Kropf, A. J.; Marshall, C. L. Fischer-Tropsch Synthesis: An *in-Situ* TPR-EXAFS/XANES investigation of the influence of group I alkali promoters on the local atomic and electronic structure of carburized iron/silica catalysts. *The Journal of Physical Chemistry C* **2010**, *114*, 7895–7903.
- (7) De Smit, E.; Beale, A. M.; Nikitenko, S.; Weckhuysen, B. M. Local and long range order in promoted iron-based Fischer-Tropsch catalysts: A combined *in Situ* X-ray absorption spectroscopy/wide angle X-ray scattering study. *Journal of Catalysis* **2009**, *262*, 244–256.
- (8) Pinakidou, F.; Katsikini, M.; Simeonidis, K.; Kaprara, E.; Paloura, E.; Mitrakas, M. On the passivation mechanism of Fe₃O₄ nanoparticles during Cr(VI) removal from water: A XAFS study. *Applied Surface Science* **2016**, *360*, 1080–1086.

- (9) Baker, R. T. K. *In Situ* electron microscopy studies of catalyst particle behavior. *Catalysis Reviews* **1979**, *19*, 161–209.
- (10) Van den Berg, F.; Crajé, M.; van der Kraan, A.; Geus, J. Reduction behaviour of Fe/ZrO₂ and Fe/K/ZrO₂ Fischer-Tropsch catalysts. *Applied Catalysis A: General* **2003**, *242*, 403–416.
- (11) Montemore, M. M.; van Spronsen, M. A.; Madix, R. J.; Friend, C. M. O₂ Activation by metal surfaces: Implications for bonding and reactivity on heterogeneous catalysts. *Chemical Reviews* **2018**, *118*, 2816–2862.
- (12) Blyholder, G.; Emmett, P. H. Fischer-Tropsch synthesis mechanism studies. The addition of radioactive retene to the synthesis gas. *The Journal of Physical Chemistry* **1959**, *63*, 962–965.
- (13) Kummer, J. T.; Podgurski, H. H.; Spencer, W. B.; Emmett, P. H. Mechanism studies of the Fischer-Tropsch synthesis. The addition of radioactive alcohol. *Journal of the American Chemical Society* **1951**, *73*, 564–569.
- (14) Kummer, J. T.; Emmett, P. H. Fischer-Tropsch synthesis mechanism studies. The addition of radioactive alcohols to the synthesis gas. *Journal of the American Chemical Society* **1953**, *75*, 5177–5183.
- (15) Hall, W. K.; Kokes, R. J.; Emmett, P. H. Mechanism studies of the Fischer-Tropsch synthesis. The addition of radioactive methanol, carbon dioxide and gaseous formaldehyde. *Journal of the American Chemical Society* **1957**, *79*, 2983–2989.
- (16) Hall, W. K.; Kokes, R. J.; Emmett, P. H. Mechanism studies of the Fischer-Tropsch synthesis: The incorporation of radioactive ethylene, propionaldehyde and propanol. *Journal of the American Chemical Society* **1960**, *82*, 1027–1037.
- (17) Wender, J.; Friedman, S.; Steiner, W. A.; Anderson, B. A. *Chemical Industry London* **1958**, 1964.

- (18) Ferro-García, M. A.; Rivera-Utrilla, J.; Bautista-Toledo, I.; Moreno-Castilla, C. Adsorption of humic substances on activated carbon from aqueous solutions and their effect on the removal of Cr(III) ions. *Langmuir* **1998**, *14*, 1880–1886.
- (19) Wilke, M.; Farges, F.; Petit, P. E.; Brown, G. E.; Martin, F. Oxidation state and coordination of Fe in minerals: An Fe K- XANES spectroscopic study. *American Mineralogist* **2001**, *86*, 714–730.
- (20) Takenaka, S. Formation of filamentous carbons over supported Fe catalysts through methane decomposition. *Journal of Catalysis* **2004**, *222*, 520–531.
- (21) Li, S.; O’Brien, R. J.; Meitzner, G. D.; Hamdeh, H.; Davis, B. H.; Iglesia, E. Structural analysis of unpromoted Fe-based FischerTropsch catalysts using X-ray absorption spectroscopy. *Applied Catalysis A: General* **2001**, *219*, 215–222.
- (22) Sarkar, A.; Jacobs, G.; Ji, Y.; Hamdeh, H. H.; Davis, B. H. FischerTropsch Synthesis: Characterization Rb Promoted Iron Catalyst. *Catalysis Letters* **2008**, *121*, 1–11.
- (23) Kopelev, N. S.; Chechersky, V.; Nath, A.; Wang, Z. L.; Kuzmann, E.; Zhang, B.; Via, G. H. Encapsulation of iron carbide in carbon nanocapsules. *Chemistry of Materials* **1995**, *7*, 1419–1421.
- (24) Ravel, B. ATOMS: crystallography for the X-ray absorption spectroscopist., 2001.
- (25) Rehr, J.; Kas, J.; Vila, F.; Prange, M.; Jorissen, K. Parameter-free calculations of x-ray spectra with FEFF9., 2010.
- (26) Ravel, B.; Newville, M. ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT., 2005.
- (27) Rivnay, J.; Mannsfeld, S. C. B.; Miller, C. E.; Salleo, A.; Toney, M. F. Quantitative determination of organic semiconductor microstructure from the molecular to device scale. *Chemical Reviews* **2012**, *112*, 5488–5519.
- (28) Wang, J.; Farrell, J. Investigating the role of atomic hydrogen on chloroethene reactions with iron using tafel analysis and electrochemical impedance spectroscopy. *Environ. Sci. Technol* **2003**, *37*, 3891–3896.

- (29) Breiby, D. W.; Bunk, O.; Andreassen, J. W.; Lemke, H. T.; Nielsen, M. M. Simulating X-ray diffraction of textured films. *Journal of Applied Crystallography* **2008**, *41*, 262–271.
- (30) De Faria, D. L. A.; Venâncio Silva, S.; de Oliveira, M. T. Raman microspectroscopy of some iron oxides and oxyhydroxides. *Journal of Raman Spectroscopy* **1997**, *28*, 873–878.
- (31) Farelas, F; Brown, B; Nesic, S In *NACE International Corrosion 2013 Conference and Expo*, 2013, pp 1–15.
- (32) Kelly, S. D.; Hesterberg, D.; Ravel, B.; Ulery, A. L.; Drees, R. L. In *Methods of Soil Analysis Part 5 - Mineralogical Methods*; Soil Science Society of America: 2008, pp 387–463.
- (33) Park, E.; Ostrovski, O.; Zhang, J.; Thomson, S.; Howe, R. Characterization of phases formed in the iron carbide process by X-ray diffraction, Mossbauer, X-ray photoelectron spectroscopy, and Raman spectroscopy analyses. *Metallurgical and Materials Transactions B* **2001**, *32*, 839–845.

Chapter 6

Conclusions and Further Work

This work aims to gain a mechanistic understanding of deposition within diesel injectors to inform the targeted development of fuel formulations and additive packs to prevent against deposition. Carbonaceous deposits, formed from thermal degradation products of the fuel, were the focus of this work. A model system of hexadecane and iron substrates/films were effectively used to simulate deposition and revealed key parameters in the deposition mechanism, which will be discussed below. Although further studies are required to fully understand the mechanism, the key findings of this thesis pave the way for new strategies to reduce and/or prevent deposition and thereby maintain optimum engine performance.

6.1 Key findings

The surface of Fe-13Cr substrates, heated to engine relevant temperatures, were characterised by dynamic SIMS and TEM measurements and found to be predominantly composed of iron with a chromium rich sub-layer. These results agreed well with TEM analyses of fouled injectors where an iron surface with a chromium sub-layer was also observed.

Increased hexadecane oxidation and deposition was observed on iron substrates compared to passive substrates such as silicon. As the speciation of the iron surface in the injector was unknown, three model iron surfaces, iron (II)(III) oxide (annealed), iron with a native oxide (polished) and iron (III) oxide (oxidised) surfaces, were produced, characterised and used to investigate the role of iron, and iron speciation, on oxidation and deposition. The surface

was found to affect the morphology and the amount of deposit forming on the surface, as well as the overall oxidation levels in the solution. The polished and annealed surfaces were observed to oxidise upon exposure to hexadecane at elevated temperatures and the resulting surface was identified as iron (III) oxide hydroxide. The iron (III) surface was found to be unchanged under the same conditions. Due to the enhanced level of oxidation on the polished and annealed samples, the surface is proposed to transfer electrons to the hexadecane, initiating its autoxidation. When the samples are cooled to room temperature, further hexadecane degradation and deposition are observed, suggesting that the iron (III) oxide hydroxide surface can further catalyse the breakdown of hexadecane. Through analogy to Fenton-like catalysis, the heterogeneous catalytic breakdown of peroxides by iron surfaces is proposed. At longer times, hexadecane degradation was found to be a result of the exposed surface area. The solubility of oxidised hexadecane in the hexadecane matrix is found to influence the level of deposition observed.

To follow these changes at the hexadecane-iron interface, two systems were developed to enable *in situ* measurements at high temperatures, with the additional capability for flow experiments. Structural and chemical changes were observed on iron thin films; thin films were used due to practical requirements but also enable better control over the surface chemistry of the film and provide an indication of the depth of the transition. Despite the difficulties associated with the interpretation of these data and ongoing interpretation, iron thin films were found to form iron (III) oxide hydroxide surfaces in support of previous findings by XPS. A combination of the beam line set up, the experimental configuration and a small crystallite size are accountable for the difficulties associated with interpreting the structural measurements. The combination of GI-WAXS, which detects crystalline species, with XAFS, which gives the full chemistry, provides a complete picture of the changes occurring at the interface. The subtle changes observed on the 50 nm film demonstrate that the changes occurring at the surface are within the first 50 nm. LCF analysis of the treated iron thin film with iron and a variety of iron oxides supported the transition of the surface to more oxidised iron species, whilst analysis of the 10 nm film supported the formation of an iron oxide hydroxide. Despite a relatively good R-value for the fit, it does not reproduce well the shape of the pre-edge; the shape resembles that

of iron carbide by qualitative comparison with the literature or metallic iron pre-edge, although its position is consistent with an iron oxide. These findings, combined with the detection of an iron carbide (Fe_7C_3) by TEM, suggests further analysis is required to convincingly determine the chemistry of this surface, although iron (III) oxide hydroxide is expected to be a key component.

6.2 Implications For Industry

The promoted degradation of hexadecane by iron surfaces similar to those found in engines is clearly of concern to the oil and gas industry as well as engine component manufacturers and additive companies. The characterisation of a fouled injector revealed an iron-based surface; the studies performed here on Fe-13Cr substrates demonstrated that iron oxide hydroxide surfaces will form under engine conditions regardless of the initial chemistry of the iron surface. The capacity for iron oxide hydroxides to promote the degradation of hexadecane at room temperature is troubling, especially for engine components that are left in contact with fuel that has experienced thermal stress. However, iron (III) oxide surfaces were shown to lead to less hexadecane oxidation and deposition than other iron oxide surfaces (although iron oxide hydroxide surfaces were not studied directly).

The iron-hexadecane model system used in this work was found to effectively reproduce deposition, with the morphology of deposits consistent with those observed in engine components. Using a combination of XPS, SIMS, and SEM the amount, chemistry and morphology of the deposits can be fully investigated. Transitions at the iron surface can be characterised *ex situ* by XPS, whilst the level of hexadecane oxidation was measured by ESI-MS and easily compared using the Kendrick mass defect. Despite these extensive analyses providing comprehensive insights into deposition, the experiment for simulating deposition is simple and these deposits can be compared qualitatively.

Furthermore, the development of the rig and cells for following changes at interfaces *in situ* can be used to investigate how different parameters influence the transition occurring at the metal surface. However, as the least hexadecane oxidation was observed with the iron (III) oxide surface, adopting this surface state in an engine, compared to less oxidised iron species,

may be preferable for the prevention of fuel degradation. In order to fully understand the effect of different parameters on deposition, the surface transitions should therefore be studied in combination with the fuel oxidation.

6.3 Specific Further Work

There are several experiments and/or analyses which help gain further insights into the work presented in this thesis. In Chapter 4, it was proposed that the homogeneous catalytic breakdown of peroxides by dissolved iron may further explain the intricacies of hexadecane oxidation and deposition. Elemental analysis on the solutions, for example through using inductively coupled plasma (ICP), would determine the presence and concentration of iron, identifying if iron dissolution occurs in this system and how the surface chemistry may affect the level of dissolution.

In Chapter 5, linear combination fitting of the XANES region provides evidence for the formation of iron oxide hydroxide. The presence of carbides however, cannot be determined in this fit due to the lack of available iron carbide standards. It is possible to compare and/or fit the EXAFS region using calculated scattering paths generated from crystallographic information files of potential phases. The similarity between carbon and oxygen, both in terms of their size and their bond lengths to iron, make distinguishing between iron oxide and iron carbide structures challenging. In addition, due to the use of crystallographic files, the determination of amorphous carbides by this method is non-trivial. Once the final structure and chemistry is determined for these surfaces, information on the kinetics of these transitions can be obtained as a function of time and temperature.

For completeness, it would be interesting to treat Fe-13Cr steel with hexadecane and compare these findings to the dynamic SIMS and TEM cross-section measurements in Chapter 3.

6.4 Further work in a wider context

As the primary goal of this work is to understand the deposition mechanism in order to prevent deposits, the natural extension of this work would be to investigate the potential of model

additives to disrupt the processes outlined in this work. As mentioned above, an approach of looking at both the surface transitions, deposition and solution oxidation is recommended to fully understand the system.

Furthermore, the effect of sodium contaminants, which typically form soapy injector deposits, on the chemical and structural transitions occurring at the iron surface would be interesting to investigate, as sodium, as well as other alkali metals, are used as promoters in Fischer-Tropsch synthesis. Alkali metals are reported to influence the surface in FTS, suggesting that sodium contamination in engines may have additional effects. In preliminary studies with sodium naphthanate and DDSA, the transitions occurring at the iron surface at 200°C with hexadecane are found to be altered.

Whilst a chromium-rich layer is predominantly found sub-surface, spikes in engine temperatures may expose a chromium-containing surface to the fuel. The potential of chromium to promote oxidation and deposition was not investigated in this work, however it may provide further insights into this system. It is recommended to study a pure chromium surface in order to identify the role of any chromium-based surface inclusions.

The work presented here has focused solely on hexadecane as a model diesel compound, however the combination of decalin, 1-methyl naphthalene and hexadecane were suggested by BP as a mixture to represent the chemical and physical properties of diesel range molecules. Therefore, the effect of the chemical structure of the model fuel on deposition, oxidation and the kinetics of the transition at the surface should be investigated. Preliminary studies have shown similarities between the transitions occurring on iron films with both decalin and 1-methyl naphthalene.

The capability for slow flow measurements were developed in this work, however diesel injector surfaces experience cycles of fuel which are then injected into the combustion chamber. The potential of the iron surface to promote the degradation of hexadecane, where ‘fresh’ fuel interacts with an iron oxide hydroxide surface, would be interesting.