THE APPLICATION OF XPS TO THE STUDY
OF THE PASSIVE LAYERS FORMED ON
METALS IN AQUEOUS CONDITIONS.

A thesis presented to the University of Surrey for
the Degree of Doctor of Philosophy in the Faculty
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by

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SUMMARY

The repassivation of a commercial grade 18% Cr 8% Ni austenitic stainless steel in neutral deoxygenated water at 313, 353, 393, 433 and 473°K was studied by XPS, obtaining composition profiles by argon ion etching. Evaluation of the technique revealed the negligible effect of the sample transfer through air from the spectrometer to the corrosion cell, but photoelectron attenuation and reduction in peak definition resulted from organic carbon pick-up from water and spectrometer vacuum.

Where necessary multiplet analysis by curve synthesis was carried out to determine the spectral peak heights of overlapping peaks. Quantitative analysis was based upon spectral peak normalization using experimentally determined sensitivity factors.

For the experiments in the temperature range 393 to 473°K, a PTFE corrosion cell with a built-in heater was constructed which was used in a nitrogen filled pressure vessel.

XPS analysis revealed three types of passive layer:

1. An outer water-rich contaminant layer
2. A passive film consisting of \( \text{Cr}^{3+} \), \( \text{Fe}^{2+} \), \( \text{Fe}^{3+} \), \( \text{O}^{2-} \) and \( \text{OH}^{-} \)
3. An interfacial zone consisting of internally oxidised regions of the steel.

The outer contaminant layer was most prominent in the 313 to 353°K temperature range. It consisted of water possibly hydrogen-bonded to acreted organic molecules.

At 313 and 353°K, the unreacted nickel of the alloy showed an attenuation of the \( 2p^{3/2} \) signal with exposure, which presented a unique opportunity to calculate film thickness. This was only possible at these
lower temperatures where no interfacial zones were observed. The film thickness was estimated at approximately 2.0 nm. At the higher temperatures it was possible to consider the etch-time to be proportional to the film thickness. The films formed at 393 and 433°K were found to be of a comparable thickness to those formed at 313 and 353°K.

The passive films formed at 313 and 353°K revealed chromium-rich and iron-rich areas. Slight chromium enrichment was found at 353°K. The more comprehensive analysis at 393 and 433°K found evidence of a distinct iron-rich, possibly spinel region in the outer layer, and an inner chromium-rich region, possibly of a corundum structure. There was no strong evidence of selective oxidation or dissolution in these outer layers. The films in this range of temperature were concluded to conform to the Mott-Cabrera, field-induced growth theory for the low temperature oxidation of metals. The outer layer was thought to correspond to the initial barrier film. The inner layer was thought to be the result of a solid-state reduction/oxidation reaction between chromium metal and magnetite, and the original metal/film interface, resulting in Cr2O3 and iron. Such a reaction could be responsible for the chromium enrichment of films formed at 313 and 353°K. This reaction would precede the internal oxidation of the steel at these higher temperatures where anion diffusion would be sufficient to penetrate these passive films. On passing through breaks in the chromium-rich inner-layer the oxygen and hydroxyl anions were then able to react with the underlying steel, along grain boundaries and surface imperfections, resulting in an interfacial zone. The thermodynamically more favourable direct oxidation of the chromium metal would tend to arrest the former reaction.

At 473°K, the higher cation diffusion resulted in considerable film growth, corresponding to approximately 7 and 18 nm after 1 and 3 h respectively. The iron-rich and chromium-rich zones were again in evidence
at this temperature. No selective dissolution or oxidation of the outer layers was observed. However, a considerable concentration of nickel ions as well as traces of copper ions were found to be enriched in the outer layers of the passive films. The nickel was thought to be incorporated in the film as NiFe$_2$O$_4$, an extremely stable spinel. The concentration profile of nickel ions was assumed to be a function of the rate of film growth. The overall film growth appeared to correspond to a logarithmic growth rate.

Whereas the thickness of the interfacial zones formed at 393 and 433°K were comparable to the passive film thickness, at 473°K the greater rate of cation diffusion compared to anion diffusion resulted in interfacial zones to a depth of a fraction of the passive film thickness.

Throughout this work the suitability of XPS to a study of this kind was evaluated, and various aspects of the analysis have been closely examined including the procedure for multiplet analysis and the experimental determinations of peak sensitivity factors for quantitative analysis.
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1.1 INTRODUCTION

The chemical and physical properties of the initial passive film formed on stainless steel when exposed to an aqueous environment, determines the resistance of the steel to stress-corrosion cracking and to corrosion product release or dissolution. It is intended here to survey some of the major contributions that have been made to the study of these film properties and to outline some of the inherent difficulties involved in such a study. It will be shown how many such difficulties have been largely overcome by the recent developments taking place in the field of surface chemical analysis.

1.2 PASSIVITY: GENERAL THEORY

Two theories have emerged describing the passive or deactivated state: the 'oxide film theory' and 'the adsorption theory'. The 'oxide film theory' attributable originally to Faraday\(^1\) suggests that a diffusion barrier of corrosion products such as metallic oxide, forms next to the metal surface, thus protecting the metal by reducing the rate of further attack. Evidence of the presence of an oxide film in many cases is now abundant: the oxide stripping technique of U. R. Evans\(^2\) was later adapted by Vernon et al\(^3\) and has led to extensive chemical and structural studies. The adsorption theory postulated by Langmuir\(^4\) considers that passivity may be achieved by the formation of a layer of chemisorbed oxygen between the metal and solution, displacing adsorbed water and therefore increasing the activation energy for dissolution of the metal lattice. Mueller\(^5\)
presents a link between these two theories in suggesting that passivation may be a two stage process. The first stage is the coverage of the nude metal surface by a monolayer of oxygen which decreases the anodic dissolution, followed by a second stage whereby a monolayer of a stable compound, e.g. oxide is produced from the chemisorbed layer. Further film growth may then follow. Iron, the principal component of stainless steel, itself shows the phenomenon of passivity in sulphuric acid and even in deaerated water its corrosion rate is reduced to an imperceptible level at ordinary temperatures. The problem of identification of surface phases on iron is merely one of structural analysis, e.g. by electron diffraction and not compositional analysis as is necessary with alloys. The situation with this metal is therefore better understood.

1.3 COMPOSITIONAL AND STRUCTURAL ANALYSIS OF THE PASSIVE FILM FORMED ON IRON IN DEOXYGENATED WATER

It is thermodynamically possible for either Fe(OH)$_2$ or Fe$_3$O$_4$ to form by the interaction of iron and deoxygenated water. The following reactions are possible:

(a) $\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + \text{H}_2 + \Delta G^0 = -2190 \text{ cals}$

(b) $3\text{Fe(OH)}_2 \rightarrow \text{Fe}_3\text{O}_4 + \text{H}_2\text{O} + \text{H}_2 + \Delta G^0 = -9070 \text{ cals}$

(c) $3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2 + \Delta G^0 = -15640 \text{ cals}$

These chemical reactions may, in fact, occur electrochemically, e.g. reaction (c) could be expressed:

$$3\text{Fe} + 4\text{O}^{2-} - 8\text{e} \rightarrow \text{Fe}^{2+} + 2\text{Fe}^{3+} + 4\text{O}^{2-} \quad \text{(ANODE)}$$

$$8\text{H}^+ + 8\text{e} \rightarrow 4\text{H}_2 \quad \text{(CATHODE)}$$

$$3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$$

The necessary anions are derived from ionization of the water.
Linnenbom\(^6\) found that on exposing iron to deoxygenated neutral water at 298°K, no signs of magnetite were apparent, and solubility data and pH changes suggested the likely presence of Fe(OH)\(_2\). These results agreed with the earlier work of Schikorr,\(^7\) who found evidence that reaction (b) occurred very slowly in suspension. At 333°K and 573°K Linnenbom\(^6\) observed the formation of magnetite by the more thermodynamically favoured reactions (b) and (c) which he considered were too slow to operate at 298°K. At 573°K, others\(^8\)-\(^10\) have considered the reaction to form Fe\(_3\)O\(_4\) to be almost instantaneous. This was found not to be the case by Castle and Thompson\(^11\) who discovered that the reaction rate was only fast when enhanced by metal catalysts, even at high temperatures.

Perhaps the worker who has contributed most to the understanding of the passivation of iron is Cohen.\(^12\) His pioneering model of the iron/deoxygenated water reaction was that of a rapidly formed initial film of magnetite by reaction (c) being perhaps 1 or 2 unit cells thick (i.e. 0.8-1.6 nm). Across this film Fe\(^{2+}\) cations would drift under the influence of the anion potential field at the oxide/water interface and be released to the solution, whilst electrons pass to complete the cathodic reaction at the oxide/water interface to release hydrogen, leaving an excess of hydroxyl ions from water.

Schematically:

![Diagram](image)

**Fig. 1:** Development of steady-state corrosion of iron water
The magnetite thickens and becomes visible on increasing temperature or by addition of certain chemicals, i.e. when the oxidation of ferrous ions reaches the correct proportions required to form magnetite at a greater rate than that of the Schikorr reaction (b).

In oxygenated water the main products of the reaction are hydrated oxides. The initial film is magnetite, which Cohen found to oxidise to $\gamma$-Fe$_2$O$_3$ by reaction with adsorbed oxygen anions. In stagnant solutions oxygen depletion will reduce the rate of diffusion of Fe$^{2+}$ ions through the layer and $\gamma$-Fe$_2$O$_3$ growth will be reduced. In such a case ferrous ions in solution will tend to be oxidised to FeO(OH), by dissolved oxygen, which may precipitate onto the surface of the film, acting as an oxygen diffusion barrier.

Cohen notes that identification of the $\gamma$-Fe$_2$O$_3$ phase is sometimes complicated by the inclusion of two other diffraction lines and a d-spacing greater than 0.6 nm. He concluded that the phase did not appear to be spinel-type, and was found to be less soluble in acid than the magnetite phase.

The kinetics of the initial passive film formed was, much later, studied by Kruger and Ambrose. They monitored anodic current transients on an oscilloscope, and, correlating this data with in situ ellipsimetric measurements, the passivation of an in situ abraded mild steel specimen was observed to occur within the millisecond range. This paper is important because of the indication which it gives of the very high speed of passivation. It does not, however, provide support for any particular film structure.
1.4 STRUCTURAL STUDIES OF PASSIVE FILMS FORMED ON IRON IN SULPHURIC ACID

Most studies on the aqueous passivation of iron, have been carried out in sulphuric acid under potential controlled conditions - usually in the range 0.2-0.3 volts above the passivation potential. Vetter(14) observed a Fe$_3$O$_4$ phase adjacent to the metal and an outer layer of $\gamma$-Fe$_2$O$_3$. Foley et al(15) observed an epitaxial $\gamma$-Fe$_2$O$_3$ phase next to the metal with some Fe$_3$O$_4$. Nagayama and Cohen(16) determined an inner layer of Fe$_3$O$_4$ and an outer layer of $\gamma$-Fe$_2$O$_3$. They proposed that the lower conductivity of $\gamma$-Fe$_2$O$_3$ would suggest a high field susceptibility of that phase to layer growth, i.e. a Mott-Cabrera(17) type growth mechanism. Foley et al(15) also showed that whereas a $\gamma$-Fe$_2$O$_3$ structure was produced in the passive range, a Fe$_3$O$_4$ structure formed in the active and transpassive regions.

The general model proposed is that of a duplex structure: an inner conductive layer of magnetite in contact with the metal, and an outer insulating $\gamma$-Fe$_2$O$_3$ layer which may have an excess of vacancies, causing the higher d-spacing noted by Cohen.(12) This film is remarkably similar to that proposed for oxygenated water and it seems that the SO$_4^{2-}$ plays no particular role in film stability.

1.5 PRACTICAL LIMITATIONS TO THE STUDY OF THE PASSIVE FILMS FORMED ON STAINLESS STEEL

Most of the knowledge we have on the passivity of stainless steels has been gained from electrochemical(18-20) and ellipsometric studies.(15,20-23) There is a deficiency of compositional and structural data, to enable one to identify the roles of the constituent elements in the films. The main reason for this lack of information lies in the
fact that the films are in the ultra-thin film range: ellipsometric investigations on films developed on Fe-Cr alloys and stainless steels vary from 1.0-6.0 nm\(^{(15,20-23)}\) according to composition of the material, and environment as well as other external factors like temperature and electrochemical potential.

These inherently thin films eluded direct chemical analysis for many years. In his very comprehensive study, Rhodin\(^{(21,22)}\) sought to overcome this problem by applying the procedure of Vernon et al\(^{(3)}\) to strip the thin films from a variety of stainless steels exposed to different environments, using an iodine/methanol etchant. Rhodin\(^{(21,22)}\) used micro-colorimetry and X-ray fluorescence to obtain the bulk chemical composition of the films. He also used electron diffraction to characterise the film structure and ellipsometry to measure the pre-stripped film thickness. No distinct diffraction pattern was obtained suggesting a micro-crystalline or amorphous structure. The chemical analysis indicated the presence of a mixture of oxides of the transition elements Fe, Cr, Ni and Mo. It was considered likely that chromium conferred an overall chemical stability to the film. Water was present in all films in no fixed proportions, and in some cases a hydrated silica was also present. Rhodin\(^{(21,22)}\) concluded that the films have a gel-like structure having a high ionic and gaseous capacity, and that film formation was achieved through selective dissolution and deposition of reaction products from solution. There were two main limitations to this work, firstly that bulk chemical data from an undefined structure tells little of the role played by each of these additions, and accordingly at this early stage in the development of film analysis, the original chemical composition of the surface could not be accurately determined. Internal oxidation of the steel may have influenced the growth of the passive film. Another unknown factor was the effect of the etchant upon the composition
of the film, or the possible pick-up of etch products by the film from solution.

Nakayama\(^{24,25}\) demonstrated the important need to characterise the original surface composition of the steel prior to corrosion. Nakayama applied transmission electron diffraction and characteristic X-ray microanalysis to stripped films formed on 18% Cr 8% Ni and 18% Cr stainless steel exposed to water at 573°K. The films contained some resolvable crystals in an amorphous matrix. The work showed that spinel structures were more likely to occur in deaerated water, whilst in the presence of aerated water, corundum-type oxides occurred. However, the work also showed the strong dependence of film composition on the original surface cleaning method used prior to corrosion. Three types of polishing were evaluated for their possible effect on the final corrosion product: mechanical, chemical and electrochemical. Nickel was only found in the films of specimens that were chemically or electrochemically polished, whereas the structure of the products on 18% Cr stainless steel was not effected by surface preparation. The nickel was found to stabilize the structure, such that holding the stripped film at 1273°K for three hours did not oxidise the spinel to corundum oxide.

Lumsden and Staehle\(^{26}\) in 1972 published the first Auger Electron Spectroscopy (AES) study on the passive film composition of stainless steel in which several of the experimental limitations mentioned above were overcome. It is well known that molybdenum in stainless steel reduces their susceptibility to pitting and crevice corrosion. Lumsden and Staehle\(^{26}\) analysed the film formed on such a steel, namely type 316. The film was grown potentiostatically in a pH 7 \(1\text{ M} \text{NaCl} \cdot 0.1 \text{ M Na}_2\text{SO}_4\) solution. The metal surface was cleaned cathodically in solution. Using the techniques of Goswami and Staehle\(^{23}\) ellipsometric determination of the oxide film was estimated at 4.0 nm. Mild ion-milling enabled a
chemical profile to be built up, thus avoiding film stripping. Chromium was found to be enriched with respect to alloy proportions, whilst iron and nickel were slightly depleted. Silicon and molybdenum were found to be absent. The results contradicted Rhodin's\(^\text{(21,22)}\) stripped film analysis. Although the two groups of workers used different solutions, the large discrepancy is not explained in terms of the aggressiveness of the corrodant or by the selective boiling off of molybdenum or silicon at the low pressure used in AES (1.333 x 10\(^{-7}\) N/M\(^2\)). In addition the lack of molybdenum in the oxide was not in accord with the suggestion of Hoar\(^\text{(27)}\) that molybdenum may form an 'acidic' oxide between the metal and the more 'basic' iron oxide or that the molybdenum may be responsible for a glassy film structure. Such a structure was thought more stable due to the lower ion mobility generally found in glasses compared with crystals which have defects and grain boundaries.

This early paper of Lumsden and Staehle\(^\text{(26)}\) in the field of surface chemical analysis indicated the potential value of a technique able to reveal slight concentration gradients and requiring no oxide stripping. However, stoichiometric evaluation of the film could not be achieved for, unlike X-ray photoelectron\(^\text{(20)}\) spectroscopy and soft X-ray\(^\text{(28)}\) analysis, little distinction can be made between signals from oxidised and non-oxidised species in Auger Electron Spectroscopy.

Owing to the problem of gaining direct chemical analysis of the passive film earlier workers deduced the composition from electron diffraction analysis of the structure. Consequently various workers have made electron diffraction studies on iron/chromium alloys\(^\text{(18)}\) with a view to understanding the role of chromium in enhancing corrosion resistance by varying the structure of the film. This work will now be reviewed.
1.6 COMPOSITIONAL AND STRUCTURAL STUDIES ON THE PASSIVATION OF STAINLESS STEELS AND IRON CHROMIUM ALLOYS

McBee and Kruger\(^{(18)}\) found that 5% Cr alloys produced a $\gamma$-$\text{Fe}_2\text{O}_3$ layer, as formed on iron under the same conditions. As the chromium content of the alloys was increased, the films, though protective, were not the same as those formed on iron. The lattice parameter of the spinel structure increased with films on alloys of higher chromium content, suggesting an iron chromium spinel structure, as opposed to solid solutions such as $\text{Fe}_x\text{Fe}^{(2-x)}\text{Cr}_x\text{O}_4$ studied by Yeamian et al\(^{(19)}\) which showed lower lattice parameters. The spinel was found to be epitaxial up to 12% Cr alloys, whereupon epitaxy and discernable lattice structure started to diminish. All films were found to be ca. 1.5 nm thick by ellipsometry, and corresponded to the same thickness of film formed on iron under the same conditions.

It would appear that within the critical range of chromium content, electron diffraction analysis cannot offer structural identification of the films so as to enable some implicit chemical information about the films to be made.

Holliday and Frankenthal\(^{(28)}\) applied the same experimental conditions as McBee and Kruger,\(^{(18)}\) and used soft X-ray analysis to determine bulk changes in composition of the attached passive films of a series of Fe-Cr alloys, thus avoiding film stripping altogether. They found that as the Cr content of the alloys increased, so did the chromium content of the film. Above the critical 12% Cr content, the chromium content in the film accelerated, accompanying loss of epitaxy and electron diffraction pattern for the film structure. At the present time the hydrated (gelatinous) structure suggested by Rhodin\(^{(21,22)}\) has not been investigated, nor the possible role of chromium in such a structure further been elucidated.
1.7 INCORPORATION OF BOUND WATER INTO THE PASSIVE FILMS OF IRON AND STAINLESS STEEL

1.7.1 Passivity of Iron

Bloom and Goldenburg\(^\text{(29)}\) correlated a mass of data concerning hydrated iron oxides and assembled a new model of the passive film formed on iron. Two principal findings of their survey will be outlined here. Firstly, that \(\gamma\text{-Fe}_2\text{O}_3\) could not be generated in the absence of water, nor dehydrated without conversion to \(\alpha\text{-Fe}_2\text{O}_3\). Secondly, that oxidation of magnetite resulted in a structure analogous to \(\text{LiFe}_5\text{O}_8\), suggesting that protons may be occupying the positions of Li and the actual crystal would be \(\text{HFe}_5\text{O}_8\). They suggested that the films are probably not merely spinels containing vacancies, but are modifications of the \(\text{Fe}_3\text{O}_4\) structure in which protons are substituted for some of the ferrous iron and that \(\gamma\text{-Fe}_2\text{O}_3\) is the end product of such a substitution when \(\text{Fe}^{2+}\) is depleted.

Radio-tracer work by Yolken, Kruger and Calvert\(^\text{(30)}\) indicated that some form of H is present in the passive film on Fe, and is associated with the outer layer. The amount of H that is needed to stabilize \(\gamma\text{-Fe}_2\text{O}_3\) was found to be the same as that calculated by Bloom and Goldenburg.\(^\text{(29)}\) Sato\(^\text{(31)}\) compared ellipsometric measurements with film measurements estimated by cathodic reduction, and determined an outer hydrated layer of \(\gamma\text{-Fe}_2\text{O}_3\) and an inner anhydrous \(\gamma\text{-Fe}_2\text{O}_3\) layer. The amount of bound water in the outer layer was seen to diminish with the lowering of pH and with solutions containing other anions. Anion contamination of the film was not ruled out. Similar work was carried out by Kudo et al.\(^\text{(32)}\) who confirmed the presence of bound water.
1.7.2 Passivity of Stainless Steel

Okamoto\(^{(20)}\) in a series of investigations studied the structure, composition and thickness of the passivating film of a type 304 stainless steel in sulphuric acid by electrochemistry, infra-red spectroscopy, radio-tracer techniques, ellipsometry and X-ray photoelectron spectroscopy. After 60 and 120 minutes passivation time distinct high and low potential films were formed with a dividing potential around 0.4 V (see Fig. 2). Numerous changes occurred in the composition of these films in this range, e.g. SO\(_4^{\text{-}}\) anions were detected by infra-red spectroscopy in the high potential film, but not in the low potential one. Radio-tracer work using tritiated water showed that the bound water content of the low potential film was substantially greater than that of the high potential one. The substitution of anions for bound water is suggested in the structure below. It would appear that Okamoto's work explains the reduction in bound water found by Sato\(^{(31)}\) when anions are present. The lower potential films were found by ellipsometry to be the thinnest, with the films formed after 120 minutes being even thinner than those formed at 60 minutes.

![Diagram of high and low potential films](image)

**Fig. 2:** Showing the postulated development of the high and low potential films.
Using X-ray photoelectron spectroscopy (described in Chapter 2), which is a more sensitive and flexible technique than soft X-ray analysis, Okamoto was able to chemically analyse the attached films to a depth of less than 1.5 nm. It was found that the content of chromium and nickel relative to iron was markedly increased at the dividing potential of 0.4 V, and that chromium was generally enriched in the lower potential films. The chromium enrichment was seen to increase with time of passivation.

Comparison of the polarization curves for stainless steel and its constituent elements indicated that the enrichment of chromium in the potential range was likely to be caused by the selective dissolution of iron, which has a higher passivation potential than chromium, i.e. around the dividing potential 0.4 V. The water was thought to be bound to the chromium as it was enriched in the thinner chromium rich films.

Okamoto\(^{(20)}\) in this work had been able to uncover what could be the main role of chromium in the passivity of stainless steel, i.e. that the chromium oxide formed an amorphous gel with the bound water. This gel was believed to age with passivation time, i.e. to increase its content of oxygen anions, through a process of deprotonation of initial hydroxo-bridges (\(-\text{HO-M-OH}\-) to oxo-bridges (\(-\text{O-M-O}\-) (see Fig. 3). Okamoto agreed with Sato,\(^{(31)}\) who suggested that the bound water will tend to hydrate metal ions dissolving at breakages in the film and reform, forming first hydroxo-bridges followed by more stable oxo-bridges below a protective film. Okamoto also believes that breakdown of passivity may be due to the lowering of the bound water content, therefore, self-repairing of the film would be decreased on lowering the chromium content in the film. The way in which chloride anions can attack, and lower corrosion resistance, is suggested in the figure below.
Fig. 3: Metal ions dissolved through the undeveloped part in the film (a) are captured to form the film (a') due to the bridging of OH bond surrounding the part. Chloride ions replacing water molecules (b) inhibit the bridging reaction (b'), resulting in the breakdown of the film.

Chloride ions are shown to replace the bound water in the lattice, and, when dissolution occurs at an anodic break in the film, instead of hydration occurring and eventually bonding, the chloride complex which is formed is then leached out of the film instead.

From Okamoto's work we may assume that thinner, more corrosion resistant films are produced when the chromium content is enriched due to a concurrent increase in the degree of bound water. It appears from Holliday and Frankenthal's\(^\text{[28]}\) work that films become especially enriched with chromium in alloys having greater than 12% Cr, and that it is the effect of chromium and bound water enrichment that produces the
amorphous, glassy or micro-crystalline (the structure is uncertain) structure.

1.8 INTERMEDIATE HYDRATED PHASES IN THE FORMATION OF MAGNETITE

The bonding arrangement of the passive films formed on stainless steel suggested in Fig. 2 is analogous to the mechanism of growth of the green rusts formed on iron, and may suggest that the mechanism of film formation on iron is not quite as straightforward as suggested in the original papers of Cohen.

The two main green rusts are classified as green rust I and II respectively, and are known to form in the presence of $\text{Cl}^-$, $\text{SO}_4^{2-}$ and dissolved oxygen. They may be formed directly from $\text{Fe}(	ext{OH})_2$ or via a green complex. A reaction path diagram, Fig. 4, after Misawa et al.\(^{(33,34)}\) shows the complexity of the routes available for the formation of magnetite by the overall reaction (c), Section 1.3. The green rusts are crystalline, unlike green complexes.

The general formulae for the green rust II and green complex II are given below:

- **Green complex II:** $\text{Fe}_1^{2+} \text{Fe}_1^{3+} \text{Ox(OH)}_y (5-2x-y)^+ \text{Fe}^{3+} \text{SO}_4 \cdot x\text{H}_2\text{O}$

- **Green rust II:** $2 \text{Fe}_1^{3+} (\text{OH})_3 4 \text{Fe}_1^{2+} (\text{OH})_2 \text{Fe}^{3+} \text{SO}_4 \cdot x\text{H}_2\text{O}$

These structures have a mixture of 'hydroxo' and 'oxo' bridges similar to coordination polymers. Misawa et al.\(^{(33,34)}\) who have studied the chemistry of iron solutions at 298$^\circ$K under deoxygenated conditions, suggest that magnetite may form in solution via a green rust or a complex phase, and that such reactions were affected by pH and aeration. In neutral, high purity water, the necessary anions to form the green rusts
I and II are not present. However, under such conditions one reaction path to magnetite remains open according to their work - the route via the dark red complex phase.

Fig. 4: Schematic diagram of formation processes of intermediates, oxide and oxyhydroxides of iron in aqueous solutions at room temperature. In general, pH decreases with the progress of oxidation. However, lines drawn parallel to the ordinate do not mean the necessity of pH change unless OH⁻ addition is stated.

For such a reaction route initiated in a neutral solution, a depression in pH to pH 3 is needed at the metal/solution interface. As reported above, Linnenbom⁶ deduced from pH and solubility changes that Fe(OH)$_2$ formed on the surface of iron in deoxygenated water at 298°K.
The initial formation of this compound at one active sight would produce a local decrease in pH. The extra supply of $|H^+|$ would be needed to enhance the cathodic reaction and thus facilitate anodic dissolution of reaction (c) mentioned above. In Fig. 4 it will be seen that a depression in pH to ~3.0 is accompanied by the $|H^+||Fe^{2+}|:|Fe^{3+}|$ ratio of 0.67. Solution refreshment or ionic diffusion would be sufficient to raise the pH environment of the $Fe^{2+}$ and $Fe^{3+}$ species to form the 'dark red complex'. This complex must then be neutralised to form the stable magnetite end-product.

The reaction may be expressed as follows:

$$\begin{align*}
    \left[Fe^{2+}_{1}Fe^{3+}_{2}O_{x}(OH)_{2(3-x)}\right]_{m} + 2MOH^- + mFe_{3}O_{4} + (4-x)mH_2O \\
    \text{DARK RED COMPLEX}
\end{align*}$$

The necessary pH variations needed for this reaction would be present in the immediate layers of solution over the surface of the metal. Indeed such concentrations of $|OH^-|$ over cathodically polarized sites would encourage magnetite precipitation. However, it should be noted that a large pH variation is not required to convert the green rusts into magnetite.

However, these reaction routes to magnetite formation on iron, are kinetically dependent upon the solution diffusion, and are not consistent with the very high passivation rates found by Kruger and Ambrose. (13) However, recent work by McGill and McEnauley (35) has led to the observation of a third type of green rust that is independent of $|SO_4^{2-}|$, $|Cl^-|$ and dissolved oxygen concentration. In addition, this new green rust has shown epitaxial or topotactic magnetite formation, i.e. a solid-state growth mechanism. The discovery of this green rust opens up the
possibility that a passive film of this species of green rust may form exptaxially on iron in deoxygenated water, very rapidly, ageing to the more stable magnetite structure - consistent with Cohen's\(^{(12)}\) early work. This could be followed by \(\text{Fe}^{2+}\) diffusion through the primary layer to produce an outer layer of solution precipitated magnetite via the dark red complex route suggested by Misawa et al.\(^{(33,34)}\) This second reaction route producing the outer layer is consistent with Sato's\(^{(31)}\) observation that the outer \(\gamma\text{Fe}_2\text{O}_3\) (\(\gamma\text{Fe}_2\text{O}_3\) structure is based on that of \(\text{Fe}_3\text{O}_4\)) layer thickens with increase of pH. In addition one might expect from the ageing of the inner layer, to find a higher proton concentration in the outer layer, and a higher degree of bound water in the outer precipitated layer.

1.9 CONCLUDING REMARKS

High passivation rates have been found for stainless steels,\(^{(36)}\) corresponding to the same order of magnitude as for mild steel. Hence, the initial passive film may well undergo a rapid solid-state topotactic or epitaxial growth mechanism analogous to the formation of magnetite on iron via the green rust phase. The ageing of this initial film seems, from Okamoto's\(^{(20)}\) work, slowest for the films of higher chromium content, and that the retention of bound water may well be important to repassivation at anodic breaks in the film. The stabilization of the bound water in the film structure appears to be dependent, therefore, on the chromium content and, from Holliday and Frankenthal's\(^{(28)}\) work, it would appear that such stabilizing can only be affected by a critical chromium concentration in the film. It would appear that it is not the increased enrichment of chromium in the films beyond the 12% Cr alloys that causes loss of epitaxy and well-defined crystallinity, found by McBee and Kruger,\(^{(18)}\) but the conjoint effect of chromium retaining the bound water in the film, more effectively.
The development of a crystalline film, therefore, seems inhibited by the retention of bound water. Such a film would be presumably less likely to form an efficient diffusion path for ferrous ions. It is interesting to speculate that such ageing may be accelerated in water by raising the temperature, thus facilitating a more ordered inner structure to the film, with easier diffusion and final release of ferrous ions from the film. Such iron-release would be best examined by varying temperature and refreshment rate. From McDonald et al.\(^{(37)}\) it would appear that in neutral solution, the solubility of iron will be greatest in the range 373 - 473\(^{\circ}\)K; Castle\(^{(38)}\) and Wankling et al.\(^{(39)}\) have reported the important need to study the iron-release process in this temperature range. It would be interesting therefore to see if the release of iron to solution is a maximum in stainless steel as well as for iron in this temperature range, and to correlate this finding with the chromium and bound water contents of the passive film.

The early X-ray photoelectron spectroscopy study of Okamoto,\(^{(20)}\) though crude in terms of the full potential of such a technique, has shown that this technique can give very definite knowledge of the composition of very thin films. When used with an ion-gun to remove successive layers of the film, the technique should yield variations in composition through the film. In addition to characterising the cleaned metal surface, say prepared by ion milling, to study compositional changes in passive films under different conditions of corrosion, the technique should be able to yield such structural information as film thickness and uniformity, i.e. whether layered or island growth has occurred. It is therefore proposed to explore as far as possible in a study of this nature the full use of XPS to gain chemical and structural insight into these important passive films.
In the next section in this thesis an introduction to the basic theory underlying the technique of XPS will be given, followed by an outline of some of the problems that a study of this nature would encounter.
2.0 ESCA THEORY

2.1 INTRODUCTION

ESCA (Electron Spectrometer for Chemical Analysis)

The technique owes its development to Swedish physicist Kai Siegbahn\(^{(40)}\) and his colleagues. Siegbahn first improved a beta-ray spectrometer for measuring core electrons, and then, in order to obtain wider application to chemistry, devised an electron spectrometer using an X-ray source. The basis of the technique is the examination of the energy spectrum of photoelectrons emitted from a source under the influence of the X-ray beam. The spectral peaks have positions characteristic of specific quantum states in sub-orbitals, and thus by the Pauli Exclusion principle we have a means of establishing the surface atomic species. Also in many cases discrete spectral shifts due to reduction or oxidation can be detected. The sampled depth is commonly up to 2 nm for inorganic or up to 10 nm for organic compounds and varies according to the order of magnitude of the photoelectron energy.

In addition to photoelectron ejection, electron deexcitation is likely to occur, which, as will be seen later, can result in an Auger electron transition. ESCA therefore offers two main spectral series for the core level: X-ray Photoelectron Spectra (XPS) and Auger Electron Spectra (AES). Many commercial instruments also provide a low energy photon source such as ultra-violet (UV), which produces ultra-violet photoelectron spectra (UPS) of the valence band as well as Auger Spectra of the same region. UPS was first developed by Turner et al\(^{(41)}\) for gases and was originally called Photoelectron Spectroscopy (PES) - an acronym which will be dropped in this text to avoid possible confusion.
2.2 THEORETICAL BACKGROUND

2.2.1 The electron processes and their uses

Electron ejection and electron deexcitation are two fundamental processes likely to occur in electron spectroscopy. A brief outline will now be given.

The main electron processes may be summarised as follows:

**Electron Ejection**

(1) Photoionization

\[ A + h\nu_1 \rightarrow A^{++} + e^- \]

(2) Electron Bombardment

\[ A + e_1^- \rightarrow A^{++} + e_1^- + e_2^- \]

**Electron Deexcitation**

(3) X-ray emission

\[ A^{++} \rightarrow A^+ + h\nu_2 \]

(4) Auger emission

\[ A^{++} \rightarrow A^{++} + e_3^- \]

2.2.2 Photoionization

Photoionization requires that the incident energy be greater than the electron binding energy. Consequently UV radiation ca. 20 eV will eject the outer lying electrons whereas X-radiation ca. 1500 eV will eject the tighter bound core electrons as well. Fig. 1 shows the process of photo-ejection of the K electron and the L2 and L3 shells.
2.2.3 Electron bombardment

Electron bombardment results in losses in kinetic energy of the bombarding electron. The simple model of electron scattering in XPS proposed by Baer[42] et al suggests that when scattered electrons are distributed over a larger energy range, they will contribute little to the primary peak (see Fig. 2a).

In Fig. 2b below, the distribution of scattered electrons is seen to be smaller, producing a larger distortion in the primary peak. For the deeper lying core electrons analysed by XPS, the distribution of scattered electrons is larger because of the greater variety of scattering mechanisms. Consequently, the larger energy losses tend to limit the importance of the smaller electron losses, though increasing the total number of scattered electrons. The summed component of many
Fig. 2: Distribution ($I_\tau$) of electrons emerging from a sample calculated as the sum of electrons which have been scattered $n$ times ($I_n$, $n = 0,1,2$). Unscattered electrons are assumed to have a Lorentzian distribution with FWHM = 2$\Gamma$. In (a) it is assumed that upon each scattering the electron loses energy between 0 and 25 $\Gamma$ and with a constant probability in this interval. In (b) the corresponding range is 0-10 $\Gamma$.

Collisions, represented by $I_\tau$ in the figures above, are called energy loss tails. This skewness in the main peak hinders the measurement of the main peak height and therefore background subtraction is usually carried out prior to measuring the peak height. In addition smaller distortions on the high kinetic energy side may occur, which represents energy losses from a higher kinetic energy peak.

A study by Swingle\textsuperscript{[43]} on graphite, a conductor, and polyethylene, an insulator, has shown that the graphite C$_{1s}$ peaks show a higher degree of scattering than for polyethylene, probably due to the interactions of photoelectrons with the conduction band electrons (see Fig. 3 below).

This example serves to indicate that energy loss tails can be a potential
source of important material information, enabling in this case a
distinction to be made between photoelectron peaks having the same
binding energy of $C_{1s}$. This is an area of XPS that has yet to be fully
developed.

Fig. 3: $C_{1s}$ photoelectron peak-shapes in graphite
and polyethylene\(^{(43)}\)

The relationship between the mean free path of electrons and
their kinetic energies follows approximately the relationship of the
curve below\(^{(44)}\). A more accurate interpretation would require a band

Fig. 4: Experimental determinations of $\lambda$ in XPS (X), UPS (O) and AES (A)\(^{(44)}\)
rather than a curve to be drawn. However, the various groupings of data for UPS (O), XPS (X) and AES (Δ) suggest that XPS is in the region of >1.0 nm.

More will be said later on the mean free paths.

2.2.4 Electron deexcitation processes

Two deexcitation processes will be dealt with here: Fluorescence and Auger Electron transitions.

As seen below in Fig. 5 a low lying electron vacancy can be filled by the deexcitation of an electron from a higher state and can result in either a discrete X-radiation emission corresponding to the energy level transition which is known as Fluorescence or, an electron is released from a higher or degenerate level to that of the deexciting electron, known as an Auger electron.

*Fig. 5: Electronic deexcitation processes for atom containing primary C₁s vacancy.*
Fluorescence is typified by the 3d → 1s transition resulting in Kβ X-ray emission, and by 2p → 1s transition resulting in Kα.

The KLM Auger electron emission is due to a 2p → 1s transition and a 3p emission. Similarly KLL Auger electron emission is due to a 2p → 1s transition and a 2p emission.

The Auger process is basically an internal process and therefore is independent of the strength of the X-ray energy. A reciprocal relationship has been found to exist\(^\text{40}\) between these two processes. Whereas fluorescence yields are lowest for low atomic number species and highest for the higher atomic number species, the reverse behaviour is found for the Auger electron yields. This is shown below in Fig. 6. In contrast to these techniques XPS can measure any element that has a core shell, i.e. all elements of Z > 2.

![Diagram](image)

**Fig. 6:** X-ray fluorescence yield and Auger electron yield in the K shell as a function of atomic number Z for the light elements in the Periodic System\(^\text{40}\).
2.2.5 **Measurement of binding energies**

A further energy diagram is shown below to simplify the explanation.

![Energy Diagram](image)

**Fig. 7:** Energy considerations in measurement of electron binding energies.

\[ h\nu = E_B + \phi_{SP} + T_{SP} + E_r \]

- \( h\nu \): energy of exciting photon
- \( E_B \): binding energy of photo-ejected spectrum
- \( \phi_s \): work function of sample
- \( \phi_{SP} \): work function of spectrometer
- \( T_S \): kinetic energy of photo-ejected electrons in the vicinity of the sample
\[ T_{sp} = \text{kinetic energy of photo ejected electrons in the vicinity of the spectrometer} \]

\[ E_r = \text{recoil} \]

The energy levels are shown for an insulator, for example an oxide film on stainless steel, and the spectrometer is assumed to be in the metallic state.

For ejection of a core electron as in XPS the incident photon energy will be distributed in four processes:

1. The binding energy relative to the Fermi level, which is ultimately measured by the spectrometer.
2. The work function \( \phi_s \) of the sample, which is the energy necessary to raise the electron from the Fermi level to the free electron state.
3. The recoil energy \( E_r \), resulting from the conservation of momentum in the photo ejection process, which is greatest at low atomic masses. Table 1, reproduced from Siegbahn\(^{(40)}\) shows that for AlK\(\alpha\), used in this work, the recoil energy is nearly zero.

| Table 1: Maximum Recoil Energies (ev) |
|-------------------------------|-----|-----|-----|
| Z  | AgK\(\alpha\) | CuK\(\alpha\) | AlK\(\alpha\) |
| H  | 1   | 16  | 5  | 0.9 |
| Li | 3   | 2   | 0.8 | 0.1 |
| Na | 11  | 0.7 | 0.2 | 0.04 |
| K  | 19  | 0.4 | 0.1 | 0.02 |
| Rb | 37  | 0.2 | 0.06 | 0.01 |
(4) Kinetic energy $T_s$ of electron in the free space after leaving the sample. The kinetic energy of the electron after passing through the work function potential gradients of $\phi_s$ and $\phi_{SP}$ will result in retardation or acceleration from $T_s$ and $T_{SP}$. Thus the binding energy can be obtained from:

$$E_b = h\nu - \phi_{SP} - T_{SP} - E_r$$

It is usually not necessary to know the work function of the spectrometer for comparative chemical information. The main uncertainty in $E_b$ comes from $h\nu$ measurement, as the binding energy of the core electron itself.

2.2.6 **Concluding remarks**

For the purpose of chemically analysing the passive films formed on metals, XPS appears to be of more practical use than either UPS or AES. UPS gives bonding information by describing the orbital variations in the valence band, a region where the energy states are typically represented as broad envelopes having less discrete definition than the core states, measured by XPS and AES. Since the passive layers on stainless steel are not thick compared with the sampled depth (60% of the photoelectron signal is obtained from the top 1 nm at kinetic energies of 1000 ev$^{(45)}$) the signal from the film must be separated from that of the underlying metal by deconvolution or curve resolving of the appropriate spectra. Additionally, it is likely that there will be concentration gradients within the sampled depth. For these reasons it seems that surface analysis is likely to be more easily achieved by means of XPS rather than with AES since, for the transition elements the 'chemical shifts' of the spectra are greater with the former technique.$^{(46,47)}$ The XPS shift is more easily measured because, whereas the XPS process depends on only
one core electron being ejected, the Auger process is dependent on three
electrons for the final ejection. The spatial resolution of AES is of
little advantage in the study of passive films. At present no data is
available to compare the local radiation dose of each system. However,
the Auger electron spectra are produced for free by the ESCA system along
with XPS spectra and, because the Auger electron spectra are not directly
dependent on the source of radiation, they may serve as useful spectral
standards in any analysis where different radiation sources are used.\(^\text{[46]}\)
The chemical shifts of Auger spectra follow different rules from X-ray
photoelectron spectra and indeed the transition series show no appreciable
shifts, hence, this property of Auger lines can be of value in determining
chemical shift when charging occurs.\(^\text{[46,47]}\)

2.3 INTERPRETATION OF XPS SPECTRA

2.3.1 Photoelectron peak position and profile

Below are shown the Binding Energy values for metal and metal oxide
\(2p3/2\) peaks, taking the \(C_{1s}\) peak position at 283.7 ev.\(^\text{[47,48]}\) The change
of peak position between the metallic and oxidised states is called the
'chemical shift'. In the cases mentioned below the shift is positive.

<table>
<thead>
<tr>
<th>Metal</th>
<th>BE (ev)</th>
<th>(2p3/2)</th>
<th>Oxide</th>
<th>BE (ev)</th>
<th>(2p3/2)</th>
<th>(\Delta E) (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>572.5</td>
<td></td>
<td>(Cr_2O_3)</td>
<td>575.0</td>
<td></td>
<td>+ 2.3</td>
</tr>
<tr>
<td>Mn</td>
<td>640.3</td>
<td></td>
<td>(MnO_2)</td>
<td>642.5</td>
<td></td>
<td>+ 2.5</td>
</tr>
<tr>
<td>Fe</td>
<td>706.0</td>
<td></td>
<td>(Fe_2O_3)</td>
<td>710.2</td>
<td></td>
<td>+ 4.2</td>
</tr>
<tr>
<td>Ni</td>
<td>851.6</td>
<td></td>
<td>(NiO)</td>
<td>854.1</td>
<td></td>
<td>+ 2.5</td>
</tr>
<tr>
<td>Cu</td>
<td>930.9</td>
<td></td>
<td>(CuO)</td>
<td>931.7</td>
<td></td>
<td>+ 0.8</td>
</tr>
<tr>
<td>Zn</td>
<td>1021.1</td>
<td></td>
<td>(ZnO)</td>
<td>1021.3</td>
<td></td>
<td>+ 0.2</td>
</tr>
</tbody>
</table>
Negative shifts are found with increase in the oxidation state of an anion. Of relevance to this work is the example of $O_{1s}$ peak shift:

\begin{align*}
O^2^- & \quad 529.7 \\
OH^- & \quad 531.5 \text{(49)}
\end{align*}

2.3.2 A model for interpreting oxidation state shifts

The 'simple ionic model' postulated by Siegbahn et al\textsuperscript{(40)} considers the valence shell as a spherical envelope having a charge $q$ removed to an infinite distance. Hence, the potential energy of the inner (core) electrons will be given by:

$$E = \frac{q}{r} \quad \text{where} \quad r = \text{radius of valence shell}$$

If $r = 0.1$ nm, the result $E = 14$ ev is found, which is too high for unit charge removal. Here, the erroneous assumption is that the valence electrons are removed an infinite distance when in reality they would be expected to move to the counter-ion.

Assuming an internuclear distance $R$, then:

$$\Delta E = \left[ \frac{1}{r} - \frac{1}{R} \right]q$$

for core electrons where the opposite sign is used for the two atoms.

When $A^{+}_{q} \cdot B^{-}_{q}$ ions are arranged in a crystal lattice there is exerted upon the core electrons a coulombic force from the other ions. A Madelung constant, $\alpha$, is thus added:

$$\Delta E = \left[ \frac{1}{r} - \frac{\alpha}{R} \right]q$$

Common values for the Madelung constant are 1.7 for 5 a.u. nearest neighbour distances. Siegbahn\textsuperscript{(40)} eventually arrived at 5 ev per unit
charge. This high value is due to the omission of valence orbital overlap or penetration which would tend to change 'r'. The model therefore more applicable to ionic crystals rather than organic compounds. It is because this work is primarily concerned with oxides such as Cr₃O₇, Fe₃O₄, etc. which are ionic compounds, that this simple model has been adopted throughout this work.

The 'simple ionic model' of the 'chemical shift' suggests that as electrons are removed from the valence state so the nuclear field has a greater effect on the remaining electrons as the repulsive shielding becomes smaller. Consequently the mean radius of the orbital is reduced, corresponding to higher binding energy values. Thus when the oxidation state increases for a metal so will the binding energies of the electrons in the core and valence states - the reverse holding for anions, which produce a negative shift on increasing the oxidation state.

Comparison of metallic fluorides and sulphides indicates a lowering of chemical shift of the cations of the sulphides even though they may be of comparable oxidation state. This is due to the increased covalency found among the sulphides. When electron sharing occurs, the simple ionic model of the 'chemical shift' is not obeyed, because shrinkage of the electron orbitals of the core electrons in the cations has only partially been completed, and so the sharing of electrons brings about a reduced degree of chemical shift.

It is therefore important when interpreting the content of the chemical shift, in terms of the oxidation state, to note that covalency or partial covalency may be involved.

2.3.3 Charging effects

The photoelectron ejections produce vacancies which in turn produce
a positive field which attracts electrons from the surroundings to fill the vacancies. The spectrometer being metallic thus feeds the surface states of the sample with electrons. If the surface condition or the entire specimen is insulating then electron conduction will be negligible. A potential field is thus built up from the conducting interface of the surface layer.

![Diagram](image)

**Fig. 8:** Photoelectron emission from a charged surface

The diagram above shows a positive field due to the positive charge $\Delta E^+$ in the top layer accelerating electrons coming from the conducting layer, but on passage of the electrons through the charged layer, outwards towards the Faraday Cage, the charge tends to decelerate the photoelectrons by an equal amount. However, a photoelectron emitted from the charged layer will only experience a deceleration due to the charge field. Consequently the difference in net kinetic energy of the two photoelectrons will result in two peaks separated by the difference in the surface charging.

Grimvall\(^{(50)}\) has shown that the potential gradient depends on phase
geometry. The nearer the phase/conductor interface the less will core electrons be shifted. Thus peak broadening would be expected to accompany the shift due to the interaction of attenuating effects and potential gradients. Though of course attenuating effects may be reduced by lowering the angle of take-off. However, in so doing, one also increases the total contribution of the outer layers to the total photoelectron signal, from whence the highest degree of charging is produced.

In addition, Allen et al\(^{(51)}\) have found a correlation between the cation size in the lattice with the degree of charging: the larger the cation size the larger the charging shift. Though not entirely consistent with some Cr-O systems investigated, peak broadening was seen to be reduced with an increase in the degree of crystal hydration. Hydration is known to occur more readily in the crystallization of smaller cation crystals.

Olefjord and Fischmeister\(^{(52)}\) have attempted to use the differences in charging susceptibility of the oxides Fe\(_3\)O\(_4\), Cr\(_2\)O\(_3\) and FeCr\(_2\)O\(_4\) in order to discriminate between the Cr\(^{3+}\) \(2p^{3/2}\) signal originated from the corundum oxide or the spinel. Synthetic oxides showed distinct variations in the binding energy values for chromium signal. However, this cannot with confidence be applied to aqueous formed ultra-thin films, due to the high level of bound water present, which as Allen points out tends to increase conductivity. And, more to the point, selecting liganding of Cr\(^{3+}\) would lead to a reduction in the chromium \(2p^{3/2}\) charging shifts, greater than for the species of iron present which show less hydration susceptibility. This method of phase identification is not, therefore, suitable for the ultra-thin films studied here.

An internal standard is thus needed to calibrate the absolute
binding energy values where necessary. The value of binding energy for the $C_{1s}$ peak is used at 283.7 eV; this signal results from vacuum oil contamination. However, gold may be used, applying the decoration technique, in the belief that the noble and highly conductive metal will exhibit equilibrium with the surface states of the surrounding oxide. However, not only is this assumption doubtful in itself, but it has also been found that water may be adsorbed on gold,\textsuperscript{(53)} producing as much as 1 eV shift.

### 2.3.4 Multiplet splitting

Multicomponent lines lead to some complications in spectral analysis, but may also lead to a deeper level of understanding of the bending involved in various crystal structures of the same elemental species.

Multiplet splittings arise in a core level when an exchange interaction occurs as a result of the photoelectron ejection which can leave the unpaired electron in a parallel or antiparallel state of spin to the d-band unpaired electrons. It is a prominent feature of the transition elements, which have d-band vacancies. In the Cr(III) compounds for example,\textsuperscript{(51)} the uncoupled d electrons interact with the parallel spin of the remaining 3s electrons, left uncoupled after photoelectron ejection of the other one. Consequently, there appears in the 3s level a splitting, which is shown in the appropriate spectra in Fig. 9. The result is more complicated in the p-shell due to a greater variety of arrangements possible from the 3p electron ejection, depending on the number of electrons present. The exchange interaction will only weakly affect the 2p level, and the resolving power of XPS is not great enough to show up the individual perturbations in the 2p level. The splitting is not a function of surface charging, only of the electronic system of
the sample. Covalency, however, can reduce the difference between the two levels. Carver\textsuperscript{54} has shown from a study of compounds of forty transition elements, that the exchange interaction is dependent upon the number of unpaired electrons and the involvement of d-band electrons in bonding. In the figure below it is seen that the splitting is larger for the more ionic compounds such as the halides, and smaller for the more covalent sulphides. In particular the liganded chromium d-band of \( K_2 \text{Cr(CN)}_6 \) shows no such splitting. Finally, Fadley\textsuperscript{55} has pointed out that multiplet splittings can also affect splittings in shake-up satellites (see next section).

\[ \text{Fig. 9:} \]

Multiplet splitting in the 3s level in a series of chromium(III) compounds
2.3.5 **Satellites**

Of direct importance to the investigation of passive film on 18/8 stainless steel is the energy loss process which results in a shake-up satellite, in NiO. This satellite was discovered by Novakov\(^{(56)}\) in copper and nickel oxides. The satellites (see Fig. 10) are associated with discrete energy losses from the \(2p^{3/2}\) photoelectrons, due to perturbations caused by the promotion of valence electrons to the crystal conduction band. The importance of this discovery is that even if chemical shifting is difficult to pin-point, in sub-escape depth sample volumes, due to contributions from the metallic \(2p^{3/2}\) peak, the satellite is well resolved.

![Image of shake-up satellites in nickel and copper oxides](image)

**Fig. 10:** Shake-up satellites in nickel and copper oxides

In this work Novakov and Prins\(^{(57)}\) have attempted to study the effect of excess oxygen on the intensity of the satellite peak. Only
copper seems to have some dependence on oxygen concentration. However, this work has yet to be confirmed. Castle and Epler\(^{(47)}\) have not found that this dependence holds for the copper oxides.

It is important to note that such energy loss processes as shake-up or shake-off satellites and multiplet splittings can seriously lead to underestimation of quantitative analysis based on peak integral intensities.

2.3.6 Crystal structure effects

It has been shown by the work of Allen et al\(^{(51)}\) on the Cr-O compounds that the Madelung potential can produce a significant contribution to the binding energy shift, providing other factors are not overriding such as multiplet splitting.

2.3.7 Surface contaminant effects on peak profile

Zechina\(^{(58)}\) has shown by infra-red spectroscopy that water reacts dissociatively with the very reactive Cr\(^{3+}\) sites on α-Cr\(_2\)O\(_3\) forming hydroxyl bonds. In addition, CO and O\(_2\), both common vacuum contaminants, are known to form chemical bonds. O\(_2\) is believed to form a double covalent bond which would certainly interfere with surface layer multiplet splitting.

Johnson\(^{(59)}\) has shown that a binding energy shift on transition elements may result from surface chemisorption of molecules of high electron density. The ligands tend to create a polarization of the surface states. CO, N\(_2\) and O\(_2\) have particularly high electron densities, which, it is believed, may tend to delocalize the electron density in the unfilled \(d\)-band levels in the metals. Thus we would expect, to a lesser extent, the same tendency in the \(d\)-bands of \(d^{10}\) ion cores.
2.3.8 The resolution of XPS spectral lines

The peak width, at half maximum height (FWHM) \( w \), is a product of the electrical properties of the sample material, the radiative lifetime and consequent Heisenberg uncertainty of measuring the kinetic energy of the photoelectron, and finally the instrumental broadening factors. Instrumental broadening will be dealt with in the next section.

The previous sections dealt with the material properties influencing peak shape, and ultimately FWHM values. Here peak width broadening may result from the process of photoelectron ejection. The uncertainty principle may be applied to the measurements of the kinetic energy of the ejected electrons because the radiative life-time for the filling of the vacancy formed by the ejected electron is usually faster than \( 10^{-16} \) s. The Heisenberg Uncertainty Principle states that the product of the uncertainty of an energy level and the time spent in its measurement is approximately Planck's constant, i.e.

\[
h = \Delta E \times \text{At}
\]

KINETIC ENERGY OF PHOTOELECTRON 
LIFETIME OF VACANCY

However, when such a process occurs in atoms of relatively large conduction band population, the life-time is shortest. The minimum time, however, must be \( 10^{-18} \) s for relativistic reasons, this being the time for a photon to traverse an atom (i.e. 0.3 mm).

Jorgensen et al\(^{(60)}\) have shown, using a Varian IHE-15 spectrometer with an analyser energy of 100 ev, that, whereas the FWHM values for the series \( Z = 37-55 \) varies from 1-12. ev, lutetium(III) broadened to 2.1 ev. This was explained by Shirley and Fadley\(^{(64)}\) as being attributable to the more rapid filling of the 4d vacancy by one of fourteen 4f electrons.
in the conduction band. They calculated that the Heisenberg Uncertainty Principle contribution to the 4d level is $0.1 \text{ ev for } 10^{-14} \text{ s}$, $1 \text{ ev for } 10^{-15} \text{ s}$ and $10 \text{ ev for } 10^{-16} \text{ s}$.

2.3.9 Concluding remarks

Rudimentary information on elemental species type and oxidation state is nearly always readily obtained from XPS analysis. However, it has been shown in this section that the final spectral product may be the product of several electron interactions. Whereas such processes may make spectral interpretation less straightforward they can, to the careful analyst, be useful in gaining deeper chemical and electronic structural information of the surface layers.

2.4 ESCA: INSTRUMENTATION AND SURFACE ANALYSIS

2.4.1 General features

The instrument used for all studies here is the ESCA II spectrometer (Vacuum Generators Ltd), with an attached PDP8E computer (Digital Equipment Corporation Ltd) for automatic scanning and data handling. The spectrometer is equipped with a separately pumped specimen preparation chamber connected to the analyser chamber by a linear transfer mechanism (see Fig. 10). The preparation chamber is capable of better than $1.33 \times 10^{-3} \text{ N m}^{-2}$ and is equipped with an argon ion gun, to be described in Section 3.1.2. The analyser chamber can be evacuated to a pressure of $1.33 \times 10^{-6} \text{ N m}^{-2}$.

X-radiation of AlK$_{1,2}$ with mean energy value of 1486.6 ev is derived from a water-cooled anode, with maximum power of 1000 watts (10 kV at 100 mA). Some K$_{3,4}$ is also produced at 1496.2 ev mean energy, but this has an intensity of only 5% of the major peak. An aluminium
window separates the X-ray source and the analyser chamber in order to screen out secondary electrons and some of the 'white' background X-rays.

The entire vacuum system is fitted with viton O-ring seals capable of bake-out up to 453°K, but this spectrometer is baked-out at about 443°K.

2.4.2 Electron energy analysis

Electron energy analysis is carried out in two stages in series. The first process utilises a Retarding Field Analysis to scan the entire energy range of the spectrum. This technique applies a potential between the specimen and a surrounding Faraday Cage which is negative with respect to the specimen holder. The energy range is scanned by varying the retarding field by altering a ramp voltage which is applied to the cage along with a pedestal voltage. Those electrons which are of the correct energy range to be further energy analysed in the next stage are not retarded, and are focussed through a window of the Faraday cage, into the slit aperture of an electrostatic hemisphere analyser. This stage is responsible for electron energy resolution.

The electrostatic hemisphere analyser is made of two gold plated copper hemispheres of mean diameter constituting a 150° sector. The Terrestrial Magnetic Field is balanced by Helmholz coils. Slits of about 2 mm width are used at the entry and exit sides of the hemispheres.

The relationship between the hemisphere potential \( V \) and the energy of electrons past \( E \) is given by:

\[
V = E \left( \frac{R_2}{R_1} - \frac{R_1}{R_2} \right) \quad R_1 = 9 \quad \text{radius} \\
R_2 = 11 \quad \text{radius}
\]

\[
\therefore V = \frac{E}{\text{H}} \quad \text{where H is hemisphere constant} \, = \, 2.48
\]
A voltage supply to the analyser may be pre-set to pass electrons of energy \(E\) equal to 5, 10, 20, 50 or 100 ev with a resolution of varying degree (see below). By applying the Retarding Field Analyser RFA the electrons passed have their energies varied to match \(E\). (62)

\[ E' = \text{voltage derived from the RFA} \]

Electrons of higher kinetic energy than \(E\) are, in fact, retarded, and those lower than \(E\) accelerated.

A variable power supply is used to select the energy region to be analysed (Pedestal Voltage), and a ramp generator which is capable of energy sweeps of 10, 30, 100, 300 and 1000 ev in 30-3000 secs enables the electrons to pass at specific values corresponding to \(E\). The collected electrons then enter the photomultiplier and a multi-channel analysis is then carried out in sequence with the sweep of the pedestal volts to provide via the computer, if desired, a visual display or X-Y plot (manual mode) of a histogram of a number of electron counts versus kinetic or binding energy (computer only).

2.4.3 Analyser resolution

This is given by

\[
\frac{dE}{E} = \frac{w}{2R}
\]

\(dE\) = FWHM for a signal
\(E\) = pass energy
\(w\) = total slit width
\(R\) = mean radius
As \( dE = E \) (const), then resolution will decrease with an increase in the Analyser Energy \( E \). But, as Transmission \( \propto E \), then sensitivity will, in practice, be lowest at highest resolution and vice versa.

Throughout this work \( E = 50 \) ev for narrow scan spectra. The resolution is then calculated as follows:

\[
\frac{dE}{2R} = \frac{E \cdot w}{2R} = 0.5 \text{ ev}
\]

\( w = 0.2 \text{ cm} \)
\( R = 10' \)
\( E = 50 \text{ ev} \)

In all cases the peaks were of greater kinetic energy than 50 ev and so all peaks were produced by retarded photoelectrons. Consequently, divergencies relating to the kinetic energy of the photoelectrons is expected to result. However, as yet no data is available to determine the loss in resolution due to optical lens aberration.

2.4.4 Radiation source: The effect on spectral resolution

The principle source of peak broadening, however, will be due to the natural line width of the \( \text{K}_{\alpha_{1,2}} \text{Al X-radiation} \), which is determined by the sum of the energy levels from which an electron transmission has occurred producing the X-radiation. For aluminium, used as the anode material in this work, the \( \text{K}_{\alpha_1} \) X-ray line corresponds to an electron transition from the \( L_{\text{III}} \) to the K shell. Fig. 12 below shows the increase in natural width for the K and \( L_{\text{III}} \) levels with \( Z \), atomic number. \(^{(40)}\)
Fig. 12: Inherent widths of K and $L_{\text{III}}$ levels versus atomic number $Z$. The diagram has been drawn up with the aid of data for level widths which have been published by Siegbahn.\(^{(40)}\)

The natural line width for $\text{AlK}\alpha_{1}$ is 0.5 ev. The second most intense line is that of $\text{AlK}\alpha_{2}$, produced from the $L_{\text{II}}$ to K shell electron transition. The $\text{K}\alpha_{1}$ and $\text{K}\alpha_{2}$ lines are separated by 0.5 ev, as seen in Fig. 13 below.

Fig. 13: Energy separation in the X-ray Kα doublet versus atomic number $Z$.\(^{(40)}\)
The $\mathsf{K}_{\alpha 2}$ line is about half the intensity as that of the $\mathsf{K}_{\alpha 1}$ line. The convoluted $\mathsf{K}_{\alpha 1,2}$ line is shown below in Fig. 14 taken from Siegbahn,\textsuperscript{(40)} and shows that the mean line width approximates to 1.0 ev, each component having a half width of 0.7 ev.

![THE X-RAY DOUBLET $K\alpha_1, \alpha_2$ IN ALUMINIUM](image)

**Fig. 14:** The X-ray $K\alpha_1 - K\alpha_2$ doublet in aluminium. Corrections have been made for the spectrometer broadenings.\textsuperscript{(40)}

The data therefore indicates that the X-ray line width of 1.0 ev is very nearly the limit found for the conventionally used anode materials, and that this broadening represents a serious limitation to the spectral analysis and must be borne in mind when curve resolving is carried out. This will be dealt with in Section 3.2.4.
2.4.5 Surface sensitivity and angular dependence of X-ray photoelectron spectra

Fadley and Bergstrom\(^{(63)}\) first demonstrated the enhancement of surface sensitivity by XPS by careful choice of collection angle. They found that in certain cases relative surface intensities could be enhanced by an order of magnitude.

Geometric considerations show that when the inelastic mean free path for the emitted electrons is short, the sample depth can be decreased considerably by collecting electrons at small angles from the surface plane. Fig. 15 indicates how increased path length for escape at a given perpendicular depth below the surface occurs as the exit angle \(\theta\) is decreased. Defining attenuation length as \(\lambda\) it is seen that the average depth of emission for an arbitrary exit angle \(\theta\) will be \(\lambda \sin \theta\).

Frazer et al\(^{(64)}\) and Fadley et al\(^{(63)}\) have made quantitative studies applying this technique to several systems and hence utilise a theoretical model first presented by Henke\(^{(65)}\) which will be outlined here.
Fig. 16: Definition of angles of X-ray excitation and electron emission, relative to the surface plane of the sample.\(^{(65)}\)

Electrons are collected at 90° from unpolarized X-ray beam through slits S x h (mms) as shown in Fig. 16. Only electrons in solid angle \(\Omega\) are considered to be detected from the projection of S-h on to the sample. This is particularly true of Retarding Field Analysers which have a collimating effect.

At a depth \(x\) in the solid, the differential intensity with respect to \(x\) can be expressed as follows:

\[
\frac{dI(E,\theta)}{dx} = \frac{F}{\Delta \theta} \times \left( \frac{\partial\sigma(E)}{\partial\Omega} \right) \times \left( \frac{n(x) \cdot s \cdot h \cdot dx}{\sin \theta} \right) \times \exp\left( - \frac{x}{\lambda(E) \sin \theta} \right)
\]
The assumptions in this model are as follows:

(1) Atomically smooth surface and flat.

(2) X-ray beam sufficiently broad and uniform that the area examined by the analyser is always excited by the same flux of X-rays at all angles of incidence.

(3) Energy loss by electrons can be described by a characteristic mean-free path.

(4) Only elastically scattered electrons contribute to observed photoelectron peaks.

(5) Sample is amorphous or polycrystalline with small grain size so that effects of diffraction of emitted electrons can be neglected.

(6) Neglect $\theta$ and $x$ dependence of the atomic cross-sections.

Assume $\lambda \gg \lambda E$ (commonly 100:1), then observed intensity $I(E,\theta)$ can be calculated for a number of interesting situations which are summarized below. Angular dependence of Intensity $I(E,\theta)$ varies with the sample type. Table 3 below summarizes the main cases.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Angular Dependence of Intensity $I(E,\theta)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) A clean solid of uniform composition</td>
<td>$I(E,\theta)$ independent of $\theta$</td>
</tr>
<tr>
<td>(2) A uniform substrate under a layer of</td>
<td>$I(E,\theta)\alpha \exp\left(-\frac{d}{\lambda'(E) \sin \theta}\right)$</td>
</tr>
<tr>
<td>different adsorbed material having $\lambda'(E)$</td>
<td></td>
</tr>
<tr>
<td>and thickness $d$.</td>
<td></td>
</tr>
<tr>
<td>(3) A monolayer of adsorbate</td>
<td>$I(E,\theta)\alpha (\sin \theta)^{-1}$</td>
</tr>
</tbody>
</table>
Fraser et al\(^{(64)}\) produced results for each of these three types for caesium coverage of molybdenum. These are set out in Fig. 17 below.

![Graph showing angular dependence of photoemission signal strength for different cases.](image)

**Fig. 17:** Angular dependence of photoemission signal strength (·) for:
(a) the Mo(3d\(_{5/2}\)) line from clean polycrystalline molybdenum,
(b) the same line from the molybdenum surface covered by a layer of caesium deposited to saturation, and
(c) the Cs(3d\(_{5/2}\)) photoline from the adsorbed layer of caesium. The continuous lines represent the best fit of the angular functions.\(^{(64)}\)

1. **Clean uniform substrate**

\[ I(E, \theta) \text{ independent of } \theta: \]

Assume \( n(x) = n_0 \)

\[
I(E, \theta) = \frac{J_0}{\Omega} \frac{\partial \sigma(E)}{\partial E} \frac{\Omega \cdot s \cdot h \cdot n}{\sin \theta} \int_0^\infty \exp \left[ - \frac{1}{\lambda \cos \theta} + \frac{1}{\lambda (E) \sin \theta} \right] \, dx
\]
\[
J_0 \sigma(E) \cdot r \cdot s \cdot n_o \cdot \frac{\lambda(E) \sin \theta}{2 \Omega} \cdot \frac{\lambda(E) \sin \theta}{\lambda(E) \sin \theta + \lambda(E) \sin \theta}
\]

since \( z \gg \lambda(E) \), then \( z/\lambda(E) \gg \tan \theta \), except where \( \theta \rightarrow 90^\circ \), and

\[
I(E, \theta) = \frac{J_0 \sigma(E)}{2 \Omega} \cdot r \cdot s \cdot n_o \cdot \lambda(E) = K(E)
\]

which is analogous to \( N = \text{onF}s \) when \( e^{-d/\lambda} = 1 \) (eqn. 2, Section 2.4.8).

2. A uniform substrate under a layer of depth, \( d \)

\[
I(E, \theta) = \exp(-d/\lambda'(E) \sin \theta)
\]

\[
I(E, \theta) = K(E) \exp(-d/\lambda'(E) \sin \theta)
\]

Escape probability for an electron of \( \lambda'(E) \) at energy \( E \), through \( d/\sin \theta \) of overlayer.

3. A monolayer of adsorbate

\[
I(E, \theta) = (\sin \theta)^{-1}
\]

Assume no self-absorption of photoelectrons in the adsorbate layer.

\[
I(E, \theta) = \frac{J_0 \sigma(E) \Omega}{2 \Omega} \cdot \frac{s \cdot n_o \cdot \Delta x}{\sin \theta} = K'(E)/\sin \theta
\]

Fadley(44) has shown that at low angles of photo-ejection, roughness of the surface becomes an important parameter. Taking various degrees of roughness he showed that at every high levels the surface to bulk ratio tends to diminish from a maxima at low \( \theta \) values. This is because at low \( \theta \) values, surface asperities will produce local increases in \( \theta \rightarrow \theta' \) and also cause shadowing, i.e. reduce the overall surface area from which photo-ejection can occur. Whereas electro-polishing can often produce
the best practical smooth surface, adequate mechanical polishing can produce, as Frazer(64) found for the molybdenum work mentioned above, suitable conditions for low angle surface enhancement.

This technique thus makes possible a non-destructive analysis of the outermost atomic layers at varying depths in a sample. In ultra-thin films of the kind produced on stainless steel this form of analysis should also reveal structural information concerning a multilayered or island growth mechanism.

2.4.6 Ion etching

This well known technique of removing atomic layers from a specimen surface has been employed for many years in the thinning of specimens for Transmission Electron Microscopy. An ion-gun typically produces a stream of positively charged inert gas ions which are accelerated down on to the specimen surface. The resultant collision thus causes ejection of atoms from the lattice sites adjacent to the collision, as the accelerated particles give up their kinetic energy to their surroundings.

In the Ion-Tech gun attached to the ESCA II system used in this work, Argon is used, and the Argon ions are produced as a result of the gas first entering the path of accelerated secondary electrons following a circular trajectory. The collision between the electrons and the neutral Argon atoms results in both positively charged Argon ions and ejected electrons. After the initial starting-up of the gun the majority of secondary electrons are produced as a result of some of the Argon ions colliding with the aluminium walls. The $\text{Al}_2\text{O}_3$ film covering the walls has a high secondary electron emission coefficient under ion bombardment.

The acceleration potential of the gun can be controlled along with the discharge current. The landing current is a rough guide to the
etch-rate. However, the emission of electrons from the specimen surface
during ion-etching which, of course, is a function of the secondary
electron emission coefficient for the specimen surface, will tend to
create a disparity in the actual number of positive ions landed and the
number that are apparently neutralized as recorded by the landing
current. Consequently, the discharge or tube current is usually recorded
with the accelerating potential.

2.4.7 Literature review on Argon ion etching

It is intended in this section to review some of the more important
work in which ion-bombardment has been used for chemical or structural
analysis in order to outline some of the potential hazards of using this
technique that have been borne in mind throughout this work.

In a study by Whitcombe\(^{(67)}\) of 18% Cr 8% Ni stainless steel using
etch-rates of 0.05 nm s\(^{-1}\), a scanning electron microscope was used to
show that long time Argon ion sputtering can produce gross changes in
surface topography: this work produced a high density of conical and
cylindrical forms of selectively etched slag particles after 5-30 hrs.

Kim et al\(^{(68)}\) used XPS to show that Argon ion sputtering can result
in oxide reduction. For example, it was found that of a total ion input
at 400 ev accelerating potential, the result was 70% sputtering with 30%
reduction. They showed that the probability of reduction taking place
was directly related to the $\Delta G_f^0$ at room temperature of the oxide. For
example, NiO with $-\Delta G_f^0 = 52$ (Kcal/mole) was reduced back to metal, but
Ni(OH)$_2$ at $-\Delta G_f^0 = 108$ (Kcal/mole) remained stable. Again, Fe$_2$O$_3$ at
$-\Delta G_f^0 = 108$ (Kcal/mole) was reduced, but Cr$_2$O$_3$ at $-\Delta G_f^0 = 250$ (Kcal/mole)
remained stable. A cut-off region between (60-120 Kcal) occurs and
it was thought that this may be related to the fraction of energy required
to generate the quasi-equilibrium state and the fraction lost to
sputtered surface atoms or to Argon species leaving the surface with non-zero kinetic energy.

More recent work by McIntyre et al\(^{(69)}\) on the aqueous formed passive films formed on Monel-400 alloy has shown that whereas the transition $\text{Ni(OH)}_2 \rightarrow \text{NiO}$ may occur, no evidence was found for the $\text{NiO} \rightarrow \text{Ni}$ reduction over a profile depth between 20-100 nm. This apparent discrepancy between the results of Kim et al\(^{(68)}\) and McIntyre et al\(^{(69)}\) indicate firstly the need to describe comprehensively all the etch parameters, and to bring in to question the interpretation of the spectra that has led to the conclusions in each of the papers. This last point is borne out by the evidence of Hedman et al\(^{(70)}\) that non-crystalline carbon shows a broader half-width than crystalline graphite. Asami et al\(^{(71)}\) have shown evidence exists that the $\text{Fe}^{2+} 2p^{3/2}$ half-width from magnetite, may be broader in the non-crystalline state as well. $\text{Fe}^{2+}$ ion in the crystalline state occurs with a half-width of 2.21 ev compared with 2.86 ev for the amorphous state. Whereas there is no question that under certain conditions of extensive Argon-ion bombardment reduction of less stable compounds may occur, it is important to discriminate between peak broadening due to reduction, i.e. addition of lower binding energy peaks, and/or surface damage producing local breakdown of crystallinity.

The gross surface changes produced by extensive bombardment by Whitcombe\(^{(67)}\) (surface topographic changes) and Kim et al\(^{(68)}\) (surface oxide reduction), are unlikely to show up on etching through films of only 1-2 nm. Clearly however, precautions must be taken to ascertain the likelihood of selective etching and oxide reduction especially if certain unstable compounds are present in the passive film.
2.4.8 Quantitative analysis by XPS - Theoretical background

Whereas peak shift data has been widely applied to qualitative analysis, relatively few reports have been published using peak intensity data for quantitative analysis: namely the work of Olefjord and Fischmeister\(^{(72,73)}\) and Castle et al.\(^{(74,75,76)}\)

The photoelectron peak represents a frequency distribution of photoelectrons about the mean binding energy of the sub-shell from which they were ejected. Of course the peak represents only a sample of the total number of photoelectrons ejected from the sub-shells.

The first process of photo-ejection from the sub-shell has a probability function for a given sub-shell per unit volume given by:

\[ N_o = \sigma n F \quad \text{where} \]

\[ \sigma = \text{photoelectron cross-section for a given sub-shell, for a given element} \]
\[ F = \text{X-ray flux} \]
\[ n = \text{concentration of the element in terms of atoms per unit volume} \]

The probability for the electron ejected escaping from the lattice to the vacuum is given by:

\[ e^{-d/\lambda\sin\theta} \quad \text{where} \]

\[ d = \text{sample depth} \]
\[ \lambda = \text{mean free path through the material to the vacuum. This may be the material from which the electron originated or an overlayer} \]
\[ \theta = \text{is the angle between the surface and direction of photo-ejection} \]

\(\lambda\) is found to vary as follows:

\[ \lambda \propto \sqrt{E} \quad \text{over the range of XPS analysis: 100-1000 ev electron energy} \]
This may be compared with the X-ray attenuation range, which is 100 times as large, suggesting that $F$ may be assumed constant.

The probability of an escaped photoelectron being detected by the spectrometer is given as $S$, which is a function of electron energy and is essential to the focussing of the electrons from the Faraday cage (in Retarding Field Analysis) into the spectrometer (see Fig. 18 below). The intensity is therefore given by:

$$dN = N_0 e^{-x/\lambda} dx \, S$$

$$\therefore \quad N = \int_0^\infty N_0 e^{-x/\lambda} dx \, S = \lambda \text{on Ps} \quad (2)$$

![Fig. 18: Schematic representation of problems involved in quantitative evaluation of X-ray photoelectron spectroscopy of solids. If sample is homogeneous without contamination layer, $e^{-d/\lambda'} = 1$. (55)](image)

A comparative study of intensities has been made of some simple molecules utilising the relationship by Carter. (77)

$$\frac{N_1}{N_2} = \frac{\sigma_1 n_1 A_1 S_1}{\sigma_2 n_2 A_2 S_2} \quad \text{where it was assumed that } S_1 = S_2, n_1 = n_2.$$  

Carter, utilizing carbon as the common element throughout, predicted relative intensities by calculations using Scofield's $\sigma$ values (theoretically determined) which related well to observed results.
Carter used the following expression:

\[
\frac{N_{z,n\ell}}{N_{C,1s}} = \frac{\sigma z n\ell \hbar \nu - E(z,n\ell)}{\alpha C,1s \sqrt{\hbar \nu - 285}}
\]

Fig. 19 shows the data calculated for 90 elements.

Fig. 19: Calculated intensities of photoelectron peaks from X-ray photoelectron spectra of solid. Results given are relative to the C\textsubscript{1}s peak for equal atomic concentrations. Calculations are for studies made with Al K\textalpha X-rays, \(\hbar \nu = 1487\) ev. Values are given for each element for different atomic sub-shells.\(^{(77)}\)

The data thus may be used to normalize photoelectron spectra, by dividing into the integral intensity the ratios for each atomic species \(Z\).
This, however, is most accurate for homogeneous samples, whereas some error is bound to be incorporated in such analysis for non-homogeneous samples.

The close agreement seen in Table 4 between Carter's predicted and the observed results gives encouragement to the continuing pursuance of a quantitative analysis of XPS data.

At present the state of progress in this area of XPS analysis is limited by the insufficiency of data to check whether the assumptions made are correct. For example, the photoelectron cross-section for a metal is considered not to change on oxidation. Also λ(metal) and λ(oxide) is considered to remain constant for purposes of simplicity in calculations, due again to lack of experimental information. Clearly, however, the electronic properties of the lattice for a metal (having delocalized metallic bonding and subsequent higher probability of electron inelastic scattering) and an oxide (more localized ionic bonding), would lead one to estimate a higher λ value for the oxide than for the metal. The factor, however, would not be high, and such a scale factor should not prove to be damaging to this kind of analysis. Possibly the lower density of the oxide lattice would also contribute to a large λ oxide value. To any investigation of oxidation or corrosion these are points of very real interest and work relating to them is given in the following chapter.

2.4.9 Concluding remarks

Evaluation of the theoretical background to XPS gives support to Okamoto's(20) view that electron spectroscopy will, in the future, play an important role in defining the chemical composition of the extremely thin passive films formed on stainless steel. Indeed, XPS is at the
Table 4

(Comparison of relative intensities for photoelectron peaks in solids \( h\nu = AK\alpha \))

<table>
<thead>
<tr>
<th>Ratio</th>
<th>Wagner(^{(79)})</th>
<th>Jorgensen(^{(60)})</th>
<th>Carter(^{(77)})</th>
<th>Nefedov(^{(80)})</th>
<th>Ave.</th>
<th>Theory(^{(77)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{1s}/F_{1s} )</td>
<td>0.27</td>
<td>0.27</td>
<td>0.29</td>
<td>0.24</td>
<td>0.27</td>
<td>0.277</td>
</tr>
<tr>
<td>( O_{1s}/Na_{1s} )</td>
<td>0.24</td>
<td>0.3</td>
<td>0.53</td>
<td>0.35</td>
<td>0.36</td>
<td>0.522</td>
</tr>
<tr>
<td>( Na_{1s}/F_{1s} )</td>
<td>2.14</td>
<td>2.00</td>
<td>1.44</td>
<td>1.89</td>
<td>1.87</td>
<td>1.32</td>
</tr>
<tr>
<td>( P_{2p}^{3/2}/Na_{1s} )</td>
<td>0.19</td>
<td>0.15</td>
<td>0.18</td>
<td>0.12</td>
<td>0.16</td>
<td>0.167</td>
</tr>
<tr>
<td>( S_{2p}^{3/2}/Na_{1s} )</td>
<td>0.21</td>
<td>0.18</td>
<td>0.30</td>
<td>0.18</td>
<td>0.22</td>
<td>0.232</td>
</tr>
<tr>
<td>( Cl_{2p}^{3/2}/Na_{1s} )</td>
<td>0.26</td>
<td>0.21</td>
<td>0.43</td>
<td>0.25</td>
<td>0.29</td>
<td>0.312</td>
</tr>
<tr>
<td>( K_{2p}^{3/2}/F_{1s} )</td>
<td>0.94</td>
<td>0.90</td>
<td>1.03</td>
<td>0.83</td>
<td>0.93</td>
<td>0.723</td>
</tr>
<tr>
<td>( Ca_{2p}^{3/2}/F_{1s} )</td>
<td>1.09</td>
<td>0.80</td>
<td>1.06</td>
<td>0.98</td>
<td>0.98</td>
<td>0.903</td>
</tr>
</tbody>
</table>
stages of becoming a quantitative analytical tool: the pioneering work of Wagner(79) and Jorgensen(60) et al in establishing a series of sensitivity factors to normalize peak heights from a variety of compounds has made possible important comparisons of chemical concentrations in such films. In this study it is clear that due to the lack of published data, the chemical species studied here will have their sensitivity factors determined as they are identified throughout this work.

The work of Fadley, (63,66) and others (64,65) has opened up the possibility of carrying out a non-destructive analysis with XPS by varying the angle of electron collection from the specimen surface, thus enabling an analysis of atomic layers of differing depth within a limited sample depth of approximately 1.0 nm to be made. This enables a structural model of island or layered growth to be evaluated.

The more commonly used destructive method of analysing layers of different levels, not restricted to depth limitations, is that of Argon Ion Etching. This technique also appears to be a very suitable method of removing surface films on stainless steel prior to exposure to the corrosive. Consequently, ion etching must be checked to ensure that selective etching of the steel surface does not occur.

The problem of analysing overlapping peaks or multiplets is likely to be a major problem in an analysis of films of thickness equivalent to around the same attenuation length of photoelectrons. Apart from peaks overlapping due to varying degrees of chemical shift related to the oxidation state of the photoelectron emitting species in the film, gradual removal of the film will result in the overlapping of the emerging substrate metal signals and those of corresponding metal ions existing in the film. Peak separation of this kind is essential both to peak identification and peak height measurements.
The factors which have contributed to instrumental broadening of the peaks have been outlined. In any multiplet analysis it is essential that instrumental broadening is kept to a minimum by the correct choice of analyser energy and run time statistics. It will be seen in the next chapter how peak resolution may be artificially enhanced by curve resolving, sometimes known as deconvoluting, which reduces the effect of instrumental broadening, enabling peak identification to be made. In addition, curve synthesis of possible singlets will also be used to determine peak heights for quantitative analysis.
3.0 EXPERIMENTAL AND ANALYTICAL FACTORS EFFECTING THE DETERMINATION OF A CHEMICAL PROFILE

3.1 CHEMICAL PROFILING BY ARGON ION ETCHING - INTRODUCTION

3.11 Introduction

One of the main aims of this work is to understand the distribution of elements throughout the passive layers formed on stainless steel, which are of the same order of magnitude in thickness as the sampled depth. To do this non-destructively with such a limited sample depth, of \( d = \lambda \sin \theta \), either \( \theta \) or the radiation source should be changed so as to change \( \lambda \), the mean free path of electrons. In the fixed geometry single anode system used in this work, this is not practicable, and it is necessary to use the alternative, i.e. to remove the top layers of the passive films homogeneously, with the minimum of damage to the underlying strata, thus allowing a chemical profile to be built up across the film from successive spectra.

3.12 APPARATUS USED IN THIS WORK

In this work an Argon ion gun (Ion Tech Ltd.) was attached to the preparation chamber. This gun was capable of producing a conical beam, completely covering the sample (7 x 7 mm) at 45° incidence. The etch-rate over the central sampled area (as seen by the spectrometer) of 5 x 5 mm is uniform at ca. 0.02 nm s\(^{-1}\) for stainless steel with Argon ions at 3.5 keV, 2 mA discharge or tube current and ~10\(\mu\)A landing current. The gun operates with a continuous passage of high purity Argon which is passed over a titanium sponge furnace at 1123K to remove residual \( \text{O}_2 \) and water vapour, to prevent sputtering induced oxidation. The residual pressure during sputtering is ca. 1.33 x 10\(^{-1}\) N.m\(^{-2}\).

3.13 SURFACE PREPARATION WITH ARGON ION ETCHING

It has already been pointed out in Chapter 1 that for a study of the
initial passive films formed on a specimen, the surface oxides must first be removed, and that the method employed may be critical to the study.\(^{(24,25)}\) Indeed, that the composition of the nude metal surface should first be determined prior to exposure to the corrodenent.

In the ESCA II system used in this study, Argon ion etching may be carried out in the preparation chamber to remove surface oxides, and the surface composition of the specimen can then be monitored by XPS, by passing the specimen attached to a probe into the analysing chamber by a linear drive mechanism. The resultant spectra enables the operator to determine when the surface oxides and contaminants have been removed and a suitably clean surface is prepared for corrosion.

In order to check for selective etching of the steel, a stainless steel sample was ion etched in ESCA at 2 mA and 3.5 keV for one hour. This harsh treatment was intended to reveal any selective enrichment: Fig. 1 is the spectrum of the surface at the end of this period. The notable feature is the high carbon peak which is fully attributable to carbide. In Fig. 2 the peak heights are given, relative to iron, at intermediate periods up to one hour. This shows that the ratio of the peak heights for Cr and Ni to that of iron become relatively constant after approximately 900 s. Oxygen and carbon decrease less rapidly after this period and reach constant non-zero values. Manganese was present in this commercial material as sulphide stringers perpendicular to the etched surface and the signal from this element remains relatively constant during etching. The movement of the relative abundances of the metals in the oxide to that found in the bulk metal can be observed after deconvolution by use of suitable sensitivity factors, and may be used directly once all metals have been etched back to the metallic state, i.e. after about 900 s. The data obtained with eight samples is collected in Fig. 3 and shows that in general once the major
Fig. 1

- % INT.
- B.E. (ev)

Peaks labeled:
- Fe₂p
- Ni₂p
- Fe₃p
- Cl₁s
- Cr₂p
- O₁s
- Mn₂p
- Fe₇M}

Fig. 1
Fig. 2
Little effect of small surface contaminants.

Maximum distortion suggesting preferential sites for contaminants.

Less selective attenuation.

< monolayer coverage.

> monolayer coverage.

Fig. 3
contaminants, carbon and oxygen, are reduced to a value totalling less than 5 at%, the metallic ratios become close to those for the bulk metal, i.e. no selective enrichment of the alloying components appear to have taken place. Swingle has commented on the effect which low levels of surface contamination has in distorting atomic ratios of the bulk metal. An interesting example of this is seen when the oxygen plus carbon value is around 10 at% of the total signal, Fig. 3. However, this cannot be purely a function of the attenuation of electrons of differing kinetic energy as suggested by Swingle since the elemental composition seems to revert to the 'correct' values at even higher contamination levels. Swingle pointed out that differing materials pick up instrumental contamination to different extents and this present result suggests that contaminant molecules selectively adsorb upon iron atoms in the surface. The known affinity of CO for iron suggests one possible reason for this effect. Both the reduction in carbon and oxygen during etching and also a subsequent increase in both their values during exposure to X-rays shown in Fig. 4, indicate a parallel behaviour of the two elements supporting the conjecture that they were combined in some way.

Following the above preliminary study of surface preparation, all specimens were prepared by 'insitu' ion cleaning, using XPS as a monitor, until the contaminent figure, total C + O, was less than 6 at%. The majority of specimens met this criterion.

3.14 DECOMPOSITION OF OXIDES

In order to determine, under the proposed working conditions of the ion gun used in this work, the likelihood of ion beam induced decomposition of oxides to metals, it was necessary to etch the surfaces of a series of oxides and use ESCA to monitor any resultant changes.
Fig 4: Variation in carbon and oxygen contamination on a stainless steel surface exposed to Kα Al x-rays.

Time in seconds of exposure to 10 kV Kα Al x-ray source.
Etching was carried out at ~3.5 keV accelerating potential, 2 mA discharge or tube current, and ~10 µA landing current. In each case the oxides were prepared on ion-cleaned metal samples and heated in air or CO₂ well into the range where the oxide to be studied is thermodynamically stable.

The 2p⁢³/² spectra of the cation component of the oxide is shown in Figs. 5 to 9. The conditions for the preparation of the oxides is given below.

Both Fe₃O₄ and Fe₂O₃ show an improvement in signal to noise ratio after 60 s etching (see Figs. 5 and 6), coinciding with the complete removal of surface contaminants. No evidence of metallic components were seen in either case.

Fig. 7 shows a comparison of Fe₂O₃ spectra before and after 600 s etch. The main difference is the slight broadening noticed after etching for this prolonged time. The absence again of any noticeable metallic peak confirms Kim et al.'s observation of Fe₂O₃ remaining stable to ion etching. The broadening may be due to surface damage producing a loss of stoichiometry resulting in slight binding energy variations among the cations throughout the surface layer of the oxide; differences in the electron scattering probability for cations occupying interstitial and stable lattice sites and/or consequent changes in the local conduction band affecting the radiative mean life of the vacancy produced by the ejected photoelectrons.

Cr₂O₃, Fig. 8, shows no apparent changes after extensive etch times of 1800 s. However, NiO, in contrast to the other oxide species, shows signs of reduction of the Ni²⁺ to the metallic state after 40 s (see Fig. 9). The metallic component increases in peak height during continued etching, as Ni2p⁢³/² satellite diminishes. Between 200 and
Fig 5a  \((\text{Fe}_3\text{O}_4 \text{ Fe}_{2p}^{3/2})\)  Fig 5b  
BEFORE ION ETCHING  AFTER 60s ION ETCHING

Fig 6a  \((\text{Fe}_2\text{O}_3 \text{ Fe}_{2p}^{3/2})\)  Fig 6b  
BEFORE ION ETCHING  AFTER 60s ION ETCHING
Fig 7a (Fe$_2$O$_3$ Fe$_{2p}^{3/2}$) 
**BEFORE ION ETCHING**

Fig 7b
**AFTER 600s ION ETCHING**

---

Fig 8a (Cr$_2$O$_3$ Cr$_{2p}^{3/2}$) 
**BEFORE ION ETCHING**

Fig 8b
**AFTER 1800s ION ETCHING**
Fig 9a
(Ni O Ni2p$^{3/2}$)
BEFORE ION ETCHING

Fig 9b
AFTER 40s ION ETCHING

Fig 9c
(Ni O Ni2p$^{1/2}$)
AFTER 200s ION ETCHING

Fig 9d
AFTER 500s ION ETCHING
500 s the etching, the rate of decomposition and sputtering seems to level out. There was no question of the film being removed completely during etching as it was clearly in evidence before and after the experiment.

The absence of metallic peaks in the ion and chromium oxides suggests that they are relatively stable to the ion beam under the working conditions of the gun. The broadening evident in the case of Fe$_2$O$_3$ should not lead to measurably large contributions to error during multiplet analysis. However, when NiO is a constituent of the passive films in this study caution must be given to the likely result of the oxide being reduced back to the metallic state.

This study indicated that careful use of Argon ion etching for the recording of chemical profiles through the passive films of stainless steel could successfully be made, provided that Ni$^{++}$ is not a major component to the films.

Indeed, it will be shown in Chapters 4 and 5 that chemical variations throughout the passive films are in most cases far greater than can be attributed to ion-etching.

3.2 QUALITATIVE AND QUANTITATIVE ANALYSIS OF MULTIPLET SPECTRA

3.2.1 Introduction

Multiplet spectra are spectral envelopes consisting of more than one spectral peak or singlet. In the analysis of the passive films on stainless steel three important multiplets arose, namely those of O$_{1s}$, Fe$_{2p}^{3/2}$ and Cr$_{2p}^{3/2}$ spectru. In the early stages of this work, at 315$^0$K and 353$^0$K corrosion temperatures, the O$_{1s}$ multiplet was treated as 100% O$^-$ even though the data suggested (see Section 4.4 ) that OH$^-$ or H$_2$O
components may be present in the film. This was due to the current uncertainty of the exact peak positions of the $\text{OH}^-$ and $\text{H}_2\text{O}/\text{O}_{\text{ad}}\text{ }\text{ }0_{1s}$ singlets. A similar problem with iron was found. The $\text{Fe}_{2p}^{3/2}$ multiplet was resolvable only into the metallic substrate signal of the steel and broad oxide component at about 709.5 eV, considered to be a mixture of $\text{Fe}^{3+}$ (at 710.2 eV) and $\text{Fe}^{2+}$ of uncertain peak position. At this stage disagreement existed in the literature of the exact peak positions of $\text{OH}^-,\text{H}_2\text{O}$ and $\text{Fe}^{2+}$.

The case of chromium $2p^{3/2}$ was more straightforward as the metallic and $\text{Cr}^{3+}$ states were readily known from standards.

During the early stage of the low temperature work ($313^0\text{K}$ and $355^0\text{K}$) a very approximate manual method of multiplet analysis was carried out. However, eventually a PDP-8E computer was installed, able to analyse acquired multiplet spectra stored on magnetic tape. This system enabled multiplets to be curve resolved yielding the possible singlet peak positions and to curve synthesis artificial singlets to enable an estimation of the singlet peak heights to be made.

By the time the higher temperature study ($393-473^0\text{K}$) was carried out, the computer facilities for multiplet analysis had been fully evaluated, and experience gained in this work enabled full advantage to be made of checking the peak positions of the singlets $\text{OH}^-,\text{H}_2\text{O}$ ($0_{1s}$) and $\text{Fe}^{2+}$ ($\text{Fe}_{2p}^{3/2}$) found by other workers at this time. The developments allowed a more comprehensive chemical model to be postulated for the passive films formed in the higher temperature range.

For completeness the very approximate manual method of multiplet analysis used only in a few of the low temperature series will be outlined below, prior to describing the more important computer method.
3.2.2 Manual method

In order to identify the components making up the multiplet, it was necessary to assume first that it consisted of the sum of the singlet peaks of the element or its compounds which could be regarded as standards. Then, taking experimentally observed spectra from samples of known standards in order to determine the relative peak heights in each case, the two spectra were superimposed after first being lined up to take account of charging shifts. Tangents across the base of the peaks were drawn to represent the base-line in each case. As shown in Fig. 10(a), vertical lines were drawn at even intervals down to the base-line. The vertical height of each peak from its base-line was tabulated. The vertical height for each increment along the base-line was summed and the fractional contribution of each constituent peak to any possible multiplet was then calculated, as shown in Fig. 10(b) which attempts to resolve the multiplet into the constituent singlets of the peak position and shape of the standard spectra, which are in this case the Cr $2p^{3/2}$ from the metal and Cr$^{3+}$ states of Cr$_2$O$_3$. Fig. 10(b) shows how, by a similar base-line treatment, the vertical lines may be seen to correspond to those of the superimposed standards in Fig. 10(a). The singlets may then be drawn through points up the vertical scale corresponding to fractional contributions suggested Table 1.

In this work only peaks of equal height were used. In fact, many combinations of peak heights for each component should be used in order to produce a more precise result. The approximate method of using equal peak heights therefore resulted in the greatest inaccuracies occurring when one peak would be less than 20% of the other singlet height, though in such a case the contribution made by the minor peak to entire analysis would be reasonably negligible.
Fig 10a.
STANDARD SPECTRA

Fig 10b.
EXPERIMENTAL MULTIPLET

<table>
<thead>
<tr>
<th>C&lt;sub&gt;r&lt;/sub&gt;</th>
<th>C&lt;sub&gt;r&lt;sup&gt;2+&lt;/sup&gt;&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.50</td>
</tr>
<tr>
<td>2</td>
<td>0.80</td>
</tr>
<tr>
<td>3</td>
<td>0.73</td>
</tr>
<tr>
<td>4</td>
<td>0.40</td>
</tr>
<tr>
<td>5</td>
<td>0.24</td>
</tr>
<tr>
<td>6</td>
<td>0.20</td>
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<tr>
<td>7</td>
<td>0.21</td>
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<td>8</td>
<td>0.21</td>
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<td>9</td>
<td>0</td>
</tr>
<tr>
<td>C&lt;sub&gt;r&lt;sup&gt;max&lt;/sup&gt;&lt;/sub&gt;</td>
<td>0.78</td>
</tr>
<tr>
<td>C&lt;sub&gt;r&lt;sup&gt;2+&lt;/sup&gt;max&lt;/sub&gt;</td>
<td>0.22</td>
</tr>
</tbody>
</table>

See 5
The technique is primarily a curve synthesis of experimentally observed standard spectra. Identification of the component types is made by trial and error of the different standards available. The criterion for an acceptable multiplet analysis is that the two singlets maintain the shape and position of the individual standard spectra. The main limitation to the technique is that only two singlets may be considered. In the case of iron, this was not so important, as Fe\(^{2+}\) iron had not been isolated at this stage as a standard spectra, as mentioned above. For more extensive use of this technique clearly more standard tables should be compiled; however, the tedium involved in such analysis has made way for more efficient computer techniques of the type that were adopted for the bulk of this work, and which is outlined next. A comparison of a multiplet analysis for the techniques is given at the end of the next section.

### 3.2.3 Computer method

This method aims to make possible identification of the binding energy position of the multiplet components by removing instrumental broadening, a process known as curve resolving (sometimes loosely as 'deconvolution'). The method uses a Fourier Transform (after Stokes\(^{(81)}\)) to produce singlets of suitable shape that approximate to the pseudo-Gaussian distributions that symmetrical, background subtracted peaks conform to.

The computer can, subsequent to the determination of the singlet positions mentioned above, be used to sum singlets of selected half-width and height corresponding to the components of the multiplet, until a new multiplet is synthesised corresponding accurately to the original. Thus, the relative proportions of the components of the multiplet may then be calculated.
3.2.4 Curve resolving

Fig. 11(a) shows the spectrum from the \(2p^{3/2}\) sub-orbital of iron. The broad spectrum is known to be a multiplet of three singlets from the substrate iron of the steel, ferrous and ferric ions of the passive film. The spectrum shows a rising background, which the computer automatically subtracts from the spectrum. This results in a more symmetrical multiplet, enabling symmetrical singlets to be used in this analysis. To do this the computer records the highest count value of the multiplet and the two lowest values either side of the spectrum. The two minima are joined by a straight line, and the area bounded by that line and the spectrum is the area to be considered for further analysis.

Perhaps the largest source of error in curve fitting would occur at the base of the spectral peaks. This is because of the variations in the energy loss tails of the spectra mentioned in Chapter 2, due to changes in peak to background and signal to noise ratios, which are dependent on the time of scanning, surface conditions and spectrometer parameters such as the resolution and peak sensitivity dependence on analysing energy. With this in mind, the curve resolving program has a facility that enables tails of the background subtracted multiplet to be 'cut-off'. The term 'threshold' is employed, which refers to the % intensity of the background subtracted peak, below which the spectral tail is removed and a tangent subtended from the peak slope to the binding energy axis. Fig. 11(a) shows these operations in progress. Fig. 11(b) shows the finished multiplet to be curve resolved.

The noise on the spectrum may then be reduced by operating a smoothing sub-program, which produces a least squares fit using a quadratic function enabling a choice of a 0, 3, 5, 7 or 9 point smoothing to be carried out. In this work, acquisition time was reduced to optimise
Fig. 11a.

Fig. 11b.

Fig. 11c.
the final noise level after a constant 5-point smoothing. This will be considered later.

The next stage of the operation is to determine the singlet width to be used. As a rough guide the half-width of the most prominent peak is taken, as shown in Fig. 11(a). Having no idea of singlet characteristics, several solutions will become evident which will produce a good fit when it comes to curve synthesis. One must therefore have some idea of the peak separations, say from reliable standards. Varying singlet width will eventually result in multiples of the original singlets chosen to be produced by the program. These indicate that the program has failed and that these singletts represent harmonics of the Fourier Transform. When a chemically acceptable curve resolution has been performed, a curve synthesis can then be carried out on the singlets to determine their respective heights contributing to the multiplets.

3.2.5 Curve synthesis

(a) Introduction

This technique fits Gaussian singlets with or without tails (optional) under the multiplet in the peak positions suggested from the previous curve resolving operation, or from known standard spectra. All the singlets will have the same width, as in the previous operation, but the peak height may be different. On selecting peak widths and heights the program then performs a least squares fit producing a new multiplet. This synthesised multiplet may be compared visually with the original multiplet by comparing the computer plot-out to the original multiplet on top of the synthesised one (Fig. 11(c)). In addition, for work of greater precision, the program will fit the peaks to 16 different positions and heights to within ±0.1 ev, choosing the least error fit from a root mean square error.
calculation. This was carried out throughout this work.

(b) Experimental conditions: Acquisition time

When acquiring a spectrum it is possible to set the machine to automatically stop collecting data when a specific value of signal to noise ratio S/N is reached. In practice the desired signal to noise ratio may be specified as a power of 2, i.e. 1, 2, 4, 8, 16, etc. The signal to noise ratio of any particular scan is determined by first forming the sum S of the moduli of the differences of the counts in the first seventeen channels (see Fig. 12 below) taken in pairs.

The signal to noise $N_c$ of the current spectrum is then defined as:

$$N_c = \frac{16(\text{MAX}-\text{MIN})}{S}$$

The scan is terminated when $N_c$ is equal to or greater than the specified value. In practice, however, this is not easy to successfully achieve during working hours, owing to the susceptibility of the system to mains spiking, resulting in a premature arrival at what appears to be the specified signal to noise ratio. Consequently, in this work, the scanning time was chosen to optimise the signal to noise and signal to background ratios. It is important in work of this kind to take careful note of the time available for a full laboratory analysis. Chemical profiling can
take up to twenty hours for a careful piece of work, using small etch rates and times. Figs. 13 to 17 illustrate the effect of acquisition time on the success of curve resolving as seen in the curve synthesis, interacting with the peak width factor.

On inspection of Figs. 13 to 17, which are for 500, 1000, 2000, 3000 and 4000 s acquisition time, it would appear that the spectrum does not significantly change after 500 s. The large apparent variations, seen in Fig. 13 to 17 of the suitability of the peak widths 1.8, 2.0 and 2.2 ev for the curve resolving and subsequent curve synthesis, are not due to changes in the experimental peak half-width but to very slight fluctuation in the high binding energy cut-off value. The 500 s peaks show that only 1.8 ev produces a satisfactory result, whereas at 1000, 2000 and 3000 s, the 1.8 and 2.2 ev peak width range is unsuitable, but at 4000 s 1.8 ev again produces a suitable result. Clearly, such fluctuations can only be dealt with by keeping the acquisition time constant throughout the analysis.

(c) Choice of smoothing factor

The choice of the smoothing factor is optional and may be used to remove residual noise peaks. Figs. 18 and 19 are set out to illustrate this. The higher binding energy component is perhaps due to the nearby lower binding energy 0.1s peak energy losses. Here 30%/30% values of threshold were taken. Higher values may have improved the spectra, however, the use of smoothing is seen to actually enhance the higher binding energy peak. It is therefore seen that a high degree of smoothing can distort the multiplet shape. The other variable shown is that of peak width. The best peak positioning is not always readily obtained, as can be seen from the examples below: too high a singlet height can cause penetration of the multiplet and thus a misleading curve synthesis is
Fig 14
SPECTRAL F (mciRo)
$2p_{3/2}$
2.2 eV ACQUISITION TIME 1000S
SMOOTHING FACTORS 0
THRESHOLD: 10% RE 10%
Figs (a), (b), and (c)
Show curve resolving (deconvolution)
Figs (a'), (b') and (c')
Show curve synthesis
FIG 15
SPECTRA OF Cr (Mo50)

2.032
2.24 V
ACQUISITION TIME 30000
SMOOTHING FACTOR 0
THRESHOLD 50% OR 10%
FIGS (a)(b) AND (c)
SHOW CURVE RESOLVING
(DECONVOLUTION)

FIGS (a')(b') AND (c')
SHOW CURVE SYNTHESIS
FIG. 18

SPECTRA OF Cr(III) M"OBA

$2p^3l_2$

ACQUISITION TIME 4000S

SMOOTHING FACTOR 20

THRESHOLD: L=30% R=30%

FIGS. (a)(b) and (c)

SHOW CURVE RESOLVING (DECONVOLUTION)

FIGS. (d)(e) and (c)

SHOW CURVE SYNTHESIS
FIG 19
SPECTRA OF Cr (figs. 2, 3)
Acquisition Time: 4000 ns
Smoothing Factor: 9
Threshold: L=30\%, R=20\%
Fig. 5 (w), (y) and (z)
Show curve resolving (deconvolution)
Figs. (w), (y) and (z)
Show curve synthesis
produced. As with acquisition time, it is best for a series of analyses, to keep the smoothing factor constant, and indeed to a low value to prevent distortion.

(d) Curve resolving: Error check

The curve resolving shown in Figs. 20 and 21 aim to separate the $2p^{3/2}$ signals of chromium metal and Cr$^{3+}$ (Cr$_2$O$_3$) by the known shift of 2.32 ev. The multiplet would, of course, not show this separation accurately due to overlapping. The singlets are plotted at 80% intensity value of the multiplet peak. The curve synthesis re-normalizes the singlets to the multiplet. As a check on the accuracy of the curve resolving carried out here, an analysis was performed on the Cr-Cr$_2$O$_3$ system shown in Fig. 20 for 4000 s acquisition time. The results are summarized in Table 2 below.

| Table 2 |
|---|---|---|
| Ratio of peak intensities of multiplet | Peak width Full width at half max. (FWHM) | Peak separation |
| | | |
| Cr$^0$ | Cr$^{3+}$ | |
| Exp. curve | 15 : 12.3 | 2.3 $\Delta$ev = 0.0 | 2.32 $\Delta$ev = 0.0 |
| Anal. curve | 15 : 10.5 | 2.1 " = -0.2 | 2.4 " = 0.08 |
| " | 15 : 10.3 | 2.3 " = 0.0 | 2.5 " = 0.18 |
| " | 15 : 10.6 | 2.5 " = +0.2 | 2.7 " = 3.8 |

All of the synthetic curves show approximately -20% reduction in Cr$^{3+}$ peak height. The values for half width of 1.8 and 2.0 ev fall within the value ±0.2 ev expected for this type of deconvolution and quoted by V.G. Ltd. In particular the peak width of 1.8 ev gives the most accurate
curve resolution and both peak position and curve synthesis and the FWHM attained by curve synthesis fall within the error margin of ±0.2 ev.

3.2.6 Comparison of manual and computer methods of curve synthesis

As a check on the previous manual method of curve synthesis, the multiplet shown in Fig. 22 was analysed by the computer. The values for the Cr metal to Cr$^{3+}$ peak heights found by the manual method were 96 : 74 and the computer method produced a ratio of 100 : 74. Compare Fig. 10(b) and Fig. 22 below.

The results of the manual and computer methods of curve synthesis clearly agree well in the example taken; greater discrepancy would be expected in a multiplet having one component <20%, however in this case the total contribution of such a small singlet would be reasonably insignificant. The comparison seems to emphasise the respective merits of each technique and indicates the need for a curve synthesis technique to be developed which can offer a choice of singlet width for each of the likely components of the multiplet. More immediate to this work is the conclusion that the application of the approximate manual method to a few of the low temperature results does not seriously affect the rest of the data determined by the described computer method.

3.2.7 Concluding remarks on computer method of multiplet analysis

The greatest limitation to both curve resolving and curve synthesis in the system used throughout the bulk of this work, is the restriction of having to deal with uniform singlet widths, and not the actual peak widths of each of the respective singlets. In addition, the theory behind this form of analysis assumes that most background subtracted photoelectron spectra correspond to Gaussian distributions. In practice
FIG 22 COMPUTER CURVE SYNTHESIS OF CF METAL AND CF$_3^+$ 2p$^3/2$ MULTIPLET
COMPARE WITH FIG 10B
the work in this project has shown that skewness usually does occur and reduces the overall accuracy of an analysis of skewed multiplets. In this work, for example, the determination of the Fe$^{2+}$ 2p$^{3/2}$ peak position could not confidently be made from curve resolving the skewed multiplet. The results could only be checked against the work of others when such data became available.

Bearing in mind the errors involved in curve resolving, one can, with careful choice of the program parameters, successfully curve resolve complex shaped multiplets. One has, of course, to discern between chemical and physical effects, such as peak broadening due to changing gradients. Curve resolving at its present stage of development in the field of XPS is, like curve synthesis, an art, with the guidelines being the chemistry of the systems being analysed.

3.3 DERIVATION OF SENSITIVITY FACTORS RELATIVE TO THE $F_{1s}$ SIGNAL FOR THE SHIFTED PEAKS

3.3.1 Theory

The integral intensity is given by the following equation:

$$N = N_p \sigma_Z |Z| \lambda_E K_E \sin \theta \cos \phi$$  \hspace{1cm} (1)

$E \rightarrow E + dE$

$N_p$ = X-ray flux

$\sigma_Z$ = photoelectron cross-section for a given sub-shell of element Z

$|Z|$ = concentration of species Z in solid

$\lambda_E$ = mean free path for electrons of energy E

$K_E$ = spectrometer factor

$\theta$ = angle of take-off of photoelectrons

$\phi$ = angle of incident X-ray flux
The instrumental measurement of the integral intensity is given by the following equation:

\[ I \cdot W_Z \cdot H \cdot T = N \cdot \sigma_z \cdot |Z| \cdot \lambda_e^K \cdot \sin \theta \cdot \cos \phi \]  \hfill (2)

where

- \( I \) = scalar factor, i.e. full-scale deflection of the curve plot (cps/mm)
- \( W_Z \) = full width at half-maximum (ev) FWHM
- \( H \) = full peak height (mm)
- \( T \) = time in secs/ev of counting for each channel

Therefore by (1) and (2):

\[ W_Z \cdot H = \frac{|Z| \cdot \lambda_e^K \cdot \sigma_z \cdot \sin \theta \cdot \cos \phi}{I \cdot T} \]  \hfill (3)

Using peak height normalization to the \( F_{1s} \) signal after Jorgensen and Berthou, we have:

\[ J_z = \frac{\sigma_z \cdot |Z| \cdot f(\lambda_z) \cdot W_F}{\sigma_F \cdot |F| \cdot f(\lambda_F) \cdot W_Z} \]

The assumptions implied in the work of Jorgensen and Berthou are the following, that

\[ f(\lambda_z) = f(\lambda_F), \quad W_Z = W_F \]

and that

\[ \frac{|Z|}{|F|} = \text{unity} \]

Then

\[ J_z = \frac{\sigma_z}{\sigma_F} \]  \hfill (4)
For quantitative analysis we may use for non-shifted peaks:

\[
\frac{\frac{H}{J_z}}{\lambda_{E_F}} = |Z| \lambda_{E_F} \left| \frac{K_{E_P}}{I\cdot T} \right| \sin \theta \cos \phi
\]  

(5)

Assuming

\[
\frac{K_{E_P} \cdot \sin \theta \cos \phi}{I\cdot T} \text{ const}
\]

The photoelectron peaks conform well to Gaussian distribution curves. It is a property of such curves that as peak height changes, the FWHM value remains constant.

The measured integral intensity of a non-shifted peak and a shifted peak of the same elemental species and sub-shell should only vary if the \( \lambda_{E_F} \) or \( |Z| \) values change. For most compounds the change in \( |Z| \) may be accounted for from known or estimated values of \( |Z| \). The mean free path for electrons in a metallic lattice is, however, assumed to be shorter than for an oxide lattice having the more localised ionic bonding and lower density. The resultant larger sampled volume for an oxide is therefore expected to compensate to some extent for the lower concentration of metal ion emitting centres in the oxide compared with the metal lattice. In the light of the present shortage of electron mean free path data, it is assumed for the purpose of this work that these two factors totally compensate one another in ionic oxides. Any such flaw arising in this assumption should result in a systematic error.

The half-width varies with chemical shift but not with elemental concentration. The peak height or sensitivity does, however, vary with concentration to satisfy eqn.(2).

In order to apply eqn.(5) to shifted peaks, we have first to
calculate the new peak sensitivity factor of the shifted peak relative
to the non-shifted peak. This is derived from eqn. (6):

\[
J_{z'} = \frac{J_z W_z}{W_{z'}}
\]  

(6)

where

\[
J_{z'} = \text{sensitivity factor for shifted peak of same}
\]

\[
\text{species } Z \text{ and sub-shell as for } J_z
\]

\[
W_z \text{ and } W_{z'} = \text{respective half width}
\]

Thus, for a given concentration \( Z' \) we can determine the value of that
concentration, by applying the easily measured value of peak height \( H \).

\[
\frac{H}{J_{z'}} \propto |Z'|
\]  

(7)

The method described above offers the most reliable one for
determining the sensitivity factors for shifted peaks. However, it cannot
be used on peaks which possess a satellite. For such spectra a peak
height calculation has to be performed, making certain assumptions about
the ratio of the peak height to that of the satellite. It is because
\( K(E) \) is determined by the type of energy analysing system used that we
cannot use a universal set of sensitivity factors \( (J_z) \). However, the
spectrometer used by Jorgensen and Berthou conform closely to our
own V.G. spectrometer and hence the sensitivity values determined by
Jorgensen and Berthou have been used throughout this work.

Finally it should be noted that the practice of deriving sensitivity
factors related to the \( F_{1s} \) level can only be used with compounds. The
factors for the elements themselves cannot be derived in this way, but
must always be determined indirectly from the appropriate compounds.
3.3.2 Calculation for atomic %

So far, only the integral intensity $N$ has been considered. However, this would in practice require that the area under the peak be measured after removing the background from the spectral line, which is a task not easily achieved. In addition, as pointed out by Jorgensen and Berthou, the degree of undulation of the sides of the peaks may lead to substantial error. In practice, because the photoelectron peak is usually very nearly Gaussian, the peak height will be a consistent measure of the photoelectron population. Thus, throughout this work the term peak height intensity $I_p$ will be used.

The method of calculating atomic % is outlined below:

$$\text{At\% of } A = 100 \times \frac{\frac{P_A(n,\lambda)}{J_A(n,\lambda)}}{\frac{P_A(n,\lambda)}{J_A(n,\lambda)} + \frac{P_B(n,\lambda)}{J_B(n,\lambda)} + \frac{P_C(n,\lambda)}{J_C(n,\lambda)}}$$

where

$P_x(n,\lambda) = \text{peak height of the most intense spectral line from element } x \text{ having been excited from the } (n,\lambda) \text{ quantum sub-shell}$

$J_x(n,\lambda) = \text{peak height normalization or sensitivity factor relative to the } F_{1s} \text{ peak}$

Diagrammatically,
The diagram shows the basic value of peak height taken. The tangent x-y enables an approximate background subtraction to be carried out. However, this is usually carried out by the computer.

### 3.3.3 Practical application of sensitivity factors

To date very little work has been published using sensitivity factors in an XPS quantitative analysis. Consequently, few attempts have been made to determine sensitivity factors for the important compounds which commonly form as corrosion products. Indeed only the work of Olefjord and Fischmeister\(^{(72,73)}\) can be cited, other than work that has been carried out in this laboratory.\(^{(74-76)}\) This may be due to the lack of standard spectral data which has been published. Indeed, as will be seen in Section 3.3.5 of this chapter, the most exact binding energy positions of the peaks of OH\(^{-}\) and H\(_2\)O/O\(_{2ad}\) O\(_{1s}\) and Fe\(^{2+}\) 2p\(^{3/2}\) were only established at the beginning of the second stage of this work concerning corrosion in the range 393-473\(^{0}\)K. In addition, factors for the elements themselves are required in order for phenomena such as selective oxidation to be discerned.

In the low temperature study (313-353\(^{0}\)K), sensitivity values from the paper of Jorgensen and Berthou\(^{(60)}\) were applied. The values for the relative peak intensities for each of the sub-orbital levels of the elements quoted and that of the F\(_{1s}\) orbital, were assumed to approximate to the ratio of the respective photoelectron cross-sections (\(\sigma\)). Therefore, it was assumed that the ratios of these sensitivity factors for elements in the compound could be applied to elements in the metallic state, provided that the unpublished peak widths (FWHM) of the spectra in the compound state were in the same ratio as those in the metallic state. In order to check the validity of this assumption, peak heights of the 2p\(^{3/2}\) spectra for metallic iron, chromium and nickel were recorded from several specimens or surface cleaned (ion etched) stainless steel. The average
peak heights were then compared with the total % concentrations of the respective elements determined by the alternative method of spectrographic analysis.

The spectrographic analysis gave the Fe : Cr : Ni content in the ratio 72.1 : 18.6 : 9.3. XPS analysis at low contamination levels gave the peak heights for the 2p\(^{3/2}\) as follows:

\[ \text{Fe : Cr : Ni} = \frac{1278}{189} : \frac{189}{186} : \frac{153}{93.1} = 1278 : 189 : 153 \]

Peak height sensitivity with respect to the metallic state was calculated from eqn. (7) as follows:

\[ \text{Fe} : \frac{1278}{721} = 1.78 \]
\[ \text{Cr} : \frac{189}{186} = 1.01 \]
\[ \text{Ni} : \frac{153}{93.1} = 1.64 \]

The ratio of the metallic peak heights are in the same ratio for the 2p\(^{3/2}\) signals as shown below:

<table>
<thead>
<tr>
<th>Metallic State</th>
<th>Combined state with respect to F(_{1s})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>Fe ( K_4\text{Fe(CN)}_6 ) 1.8</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr ( \text{NaCrO}_4 ) 1.1</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni ( K_4\text{Ni(CN)}_6 ) 1.7</td>
</tr>
</tbody>
</table>

The agreement between these two sets of ratios suggested that the assumption above was valid. The values quoted by Jorgensen and Berthou were used, therefore, as they were very nearly the same values calculated by the previous method and were now standard data.
3.3.4 Sensitivity factors for low temperature study (313-353°K)

As indicated above, the peak heights of the metallic components of the alloy and the elemental impurities on the surface may be normalized to atomic percent using factors relating the sensitivity of particular peaks to that of the fluorine ls level. In order to estimate the composition of the oxides, factors must be obtained relating the relative sensitivities of the metallic ions in their appropriate compounds. These differ from those of the pure elements because of their differing line shape which is often most easily appreciated by the changes in the half height width of the line. It has been the practice in this laboratory to obtain the sensitivity factor for important oxides, relative to that for the parent metal and thus to that for fluorine, by in situ oxidation of the evaporated metal to a thermodynamically controlled final state. Unfortunately this proved impossible for the oxidation of Cr to Cr$_2$O$_3$ which always formed a protective oxide of lesser thickness than the mean escape depth of the electrons. The possibility of obtaining factors by the aqueous phase oxidation of chromium was investigated but these erred seriously on the low side (e.g. 0.40 for Cr$^{+++}$ in Cr(OH)$_3$) because of surface contamination by water molecules. The values used for the calculation of the depth profiles presented in the following results section, viz. Cr$^{+++}$ = 1.05 and Fe$^{II}$ (the maximum of the Fe$_3$O$_4$ multiplet) = 0.7 fluorine ls units respectively, were obtained by comparison of the initial and final maximum peak heights, such as those in Fig. 24, in a sequence of spectra obtained during the ion etching of an air formed oxide on an iron/chromium alloy. It is probable that the values obtained in this way err on the high side for chromium and on the low side for iron: the value obtained by the change in the half width of the chromium line is 0.88 and the value obtained for iron by oxidation of the pure metal is 0.96.$^{(48)}$ These latter values have been used for all
Fig. 2.4
computations leading to the data presented in Chapter 3.

3.3.5 Sensitivity factors for high temperature study (393-473\(^{\circ}\)K)

(a) Introduction

At this stage a more detailed quantitative analysis could be undertaken because the photoelectron peak positions and FWHM had been established for peaks of \(\text{OH}^-\) and \(\text{H}_2\text{O}/\text{O}_{\text{ad}}\) \(\text{Fe}^{2+} 2p^{3/2}\). A table of such data is given in Table 3.

Asami (49) had devised a computer method of subtracting standard photoelectron spectra from multiplets, thus producing a peak profile of the remaining peaks. The method suggested a position for \(\text{Fe}^{2+} 2p^{3/2}\) at 2 ev shifted to a higher binding energy from the metallic state. This result confirmed the very approximate method of resolving out the difference in the \(2p^{3/2}\) peaks of \(\text{Fe}^{3+}\) from \(\alpha\text{Fe}_2\text{O}_3\) and the \(\text{Fe}_3\text{O}_4\) multiplet, shown in Fig. 25. The peaks are normalized to the same peak height so as to determine the difference in concavity of the lower binding energy side of the two peaks. The figure shows a plot of the peak separations between 706 and 710 ev binding energy. The greatest separation at 708 ev suggests the position of the \(\text{Fe}^{2+}\) maxima.

Asami also determined the FWHM value of the \(\text{Fe}^{2+} 2p^{3/2}\) peak at 2.2 ev. These results enabled a curve synthesis analysis to be carried out on a standard \(\alpha\text{Fe}_2\text{O}_3\) \(\text{Fe}2p^{3/2}\) spectrum, producing the approximate singlet heights for the two spectra of \(\text{Fe}^{2+}\) and \(\text{Fe}^{3+}\) respectively. From the \(\alpha\text{Fe}_2\text{O}_3\) sample, the peak sensitivity of the \(\text{Fe}^{3+}\) peak could be determined against the \(0^+\) 1s signal intensity and known sensitivity value of 0.6 from Jorgensen and Berthou's work. A similar calculation would thus yield for \(\alpha\text{Fe}_3\text{O}_4\) a sensitivity value for \(\text{Fe}^{2+}\), to enable the relative concentration of this component of the passive films formed on stainless steel to be calculated.
**FIG 25**

Comparison of Fe$^{2+} 3p^{3/2}$ for Fe$_2$O$_3$ and Fe$_3$O$_4$ to determine the possible position of the Fe$^{2+} 2p^{3/2}$ in the Fe$_3$O$_4$ multiplet.
<table>
<thead>
<tr>
<th>Spectral peak</th>
<th>Chemical species</th>
<th>Peak BE position (ev)</th>
<th>Chemical shift E (ev)</th>
<th>FWHM* (ev)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_{1s})</td>
<td>Dif. pump oil</td>
<td>283.7</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>O(_{1s})</td>
<td>O(^{2-})</td>
<td>529.8</td>
<td>-</td>
<td>2.1</td>
</tr>
<tr>
<td>O(_{1s})</td>
<td>OH(^{-})</td>
<td>531.5</td>
<td>1.7</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>H(<em>{2}O/O</em>{2ad})</td>
<td>533.0</td>
<td>3.2</td>
<td>3.5</td>
</tr>
<tr>
<td>Fe(_{2p})(^{3/2})</td>
<td>Fe metal</td>
<td>706.5</td>
<td>-</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Fe(^{2+})</td>
<td>708.5</td>
<td>2.0</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Fe(^{3+})(Fe(<em>{2}O</em>{3}))</td>
<td>710.7</td>
<td>4.2</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>Fe(^{3+})(FeOOH)</td>
<td>712.2</td>
<td>5.7</td>
<td>4.2</td>
</tr>
<tr>
<td>Cr(_{2p})(^{3/2})</td>
<td>Cr metal</td>
<td>573.7</td>
<td>-</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td>Cr(^{3+}) Cr(<em>{2}O</em>{3})</td>
<td>576.0</td>
<td>2.3</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>Cr(^{3+}) Cr(OH)(<em>{-4H</em>{2}O})</td>
<td>576.6(\dagger)</td>
<td>2.9</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Cr(^{3+}) CrOOH</td>
<td>577.0(\dagger)</td>
<td>3.3</td>
<td>N/A</td>
</tr>
<tr>
<td>Ni(_{2p})(^{3/2})</td>
<td>Ni metal</td>
<td>853.6</td>
<td>-</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Ni(^{2+}) NiO</td>
<td>856.1</td>
<td>2.5</td>
<td>2.7</td>
</tr>
<tr>
<td></td>
<td>Ni(^{2+}) Ni(OH)(_{2})</td>
<td>857.0</td>
<td>3.4</td>
<td>3.1(\ddagger)</td>
</tr>
</tbody>
</table>

* after background subtraction
\(\dagger\) Asami
\(\ddagger\) McIntyre
(b) Calculation of peak sensitivity values \((F_{1s} \text{ units})\)

for: \(\alpha\text{Fe}_2\text{O}_3\), \(\text{Cr}_2\text{O}_3\), \(\text{Fe}_3\text{O}_4\) and \(\text{NiO}\)

The intensities of the signals \(M_{2p} 3/2 (M^{3+})\) and \(O_{1s} (O^{2-})\) may be measured by XPS for a compound with the minimum of surface contamination. This method of determining sensitivity factors is an approximation method used in this case where no alternative data is available. It is assumed that changes of \(\lambda(E)\) with chemical compounds of differing structure are negligible and that the oxides in this work are entirely ionic. The calculation of the sensitivity factors for \(\alpha\text{Fe}_2\text{O}_3\), \(\text{Fe}_3\text{O}_4\), \(\text{Cr}_2\text{O}_3\) and \(\text{NiO}\) will be given below.

**Compound (1) - \(\text{Fe}_2\text{O}_3\)**

Produced on pure iron at 1273°C for 30 minutes in air.

\[
\begin{align*}
O_{1s} & \quad \text{I} = 4880 \text{ (cps)} \quad J_0 = 0.6 \\
\text{Fe} \ 2p^{3/2} & \quad \text{Fe}^{3+} \quad \text{I} = 2509 \text{ (cps)} \quad J_{\text{Fe}^{3+}} = ?
\end{align*}
\]

For \(\text{Fe}_2\text{O}_3\) the ratio of ions is given by:

\[
\frac{|\text{Fe}^{3+}|}{|\text{Fe}^{3+}| + |O^{2-}|} = \frac{2}{5}
\]

By (7) we have that

\[
\frac{\text{Fe} \ 2p^{3/2} (\text{Fe}^{3+})}{J_{\text{Fe}^{3+}}} \quad \frac{O_{1s} (O^{2-})}{J_0} = \frac{2}{5}
\]

\[
J_{\text{Fe}^{3+}} = \frac{0.6 \times 2509 \times 0.6}{0.4 \times 4880} = 0.463 \sim 0.46
\]
An alternative route to determine the sensitivity factor is to compare the FWHM values of Fe$^{3+}$ and Fe metal 2p$^{3/2}$ peaks.

From Table 3 we have that:

<table>
<thead>
<tr>
<th></th>
<th>FWHM (ev)</th>
<th>$J_z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe metal</td>
<td>2.2</td>
<td>1.8</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>3.6</td>
<td>?</td>
</tr>
</tbody>
</table>

\[ J_{\text{Fe}^{3/2}} = \frac{2.2 \times 1.8}{3.6} = 1.1 \]

This is much larger than the value of 0.46 calculated above because it ignores the loss of electrons into the broad satellite between the 2p$^{3/2}$ and 2p$^{1/2}$ peaks.

A similar calculation was used in the low temperature study (313-353 K) for the determination of Cr$^{3+}$ sensitivity peak which yielded a value 0.88. Cr$_2$O$_3$ does not have a satellite broadening the 2p$^{3/2}$ peak, and a comparison of this value is made below from observed peak height data.

**Compound (2) - Cr$_2$O$_3$**

Produced at 1123 K under CO$_2$ atmosphere in an autoclave for 1 hour.

\[ O_{1s} = 11012 \text{ (cps)} \quad J_{\text{Cr}^{3+}} = ? \]

\[ \text{Cr } 2p^{3/2} \quad \text{Cr}^{3+} \quad I = 9645 \text{ (cps)} \quad J_{O_{2-}} = 0.6 \]

The compound is of the form Fe$_2$O$_3$, so by a similar calculation we arrive at:

\[ J_{\text{Cr}^{3+}} = \frac{0.6 \times 9645 \times 0.6}{0.4 \times 11012} = 0.788 \sim 0.79 \]

The value of 0.79 compares well with that of 0.88 because satellites are less important with chromium compounds.
From the value of 0.46 derived for the sensitivity factor for Fe\(^{3+}\) above, the sensitivity value for Fe\(^{2+}\) may be determined from the multiplet spectra of magnetite Fe\(_3\)O\(_4\).

**Compound (3) - Fe\(_3\)O\(_4\)**

Produced at 1123\(^0\)K under a CO\(_2\) atmosphere in an autoclave for one hour.

\[
\begin{align*}
0_{1s}^0 & \quad I = 2336 \text{ (cps)} & J_0^+ &= 0.6 \\
\text{Fe } 2p^{3/2} \quad \text{Fe}^{2+} & \quad I = 807 \text{ (cps)} & \text{Determined} & \quad J_{\text{Fe}^{2+}} = ? \\
\text{Fe } 2p^{3/2} \quad \text{Fe}^{3+} & \quad I = 1345 \text{ (cps)} & \text{from curve} & \quad J_{\text{Fe}^{3+}} = 0.46
\end{align*}
\]

\[
\frac{|\text{Fe}^{2+}|}{|\text{Fe}^{2+}| + |\text{Fe}^{3+}| + |O^=|} = \frac{1}{7} = \frac{J_{\text{Fe}^{2+}}}{J_{\text{Fe}^{2+}} + J_{\text{Fe}^{3+}} + O_{1s}(O^=)}
\]

From the expression above:

\[J_{\text{Fe}^{2+}} = \frac{6 \times 807}{6217} = 0.71\]

**Compound (4) - NiO**

Produced by heating nickel in air at about 1300\(^0\)C.

\[
\begin{align*}
\text{Ni } 2p^{3/2} \quad \text{Ni}^{2+} & \quad I = 5705 \text{ (cps)} & J_{\text{Ni}^{2+}} = ? \\
0_{1s}^0 & \quad I = 9020 \text{ (cps)} & J_0^+ &= 0.6
\end{align*}
\]

\[
\frac{|\text{Ni}^{2+}|}{|\text{Ni}^{2+}| + |O^=|} = 0.5 = \frac{J_{\text{Ni}^{2+}}}{J_{\text{Ni}^{2+}} + O_{1s}(O^=)}
\]
\[ J_{\text{Ni}^{2+}} = \frac{5705 \times 0.6}{9020} = 0.394 \sim 0.39 \]

The 2p\(^{3/2}\) Ni photoelectron peak of NiO has a satellite which is ignored in this calculation, as it is in a constant height ratio to that of the main peak.

Finally, the sensitivity values for OH\(^-\) and H\(_2\)O/O\(_{\text{2ads}}\), were determined by comparison of the FWHM data available from standard spectra which were experimentally observed. By applying eqn. (6) the following results were produced:

<table>
<thead>
<tr>
<th>SPECIES (O(_{1s}))</th>
<th>FWHM (ev)</th>
<th>SENSITIVITY FACTOR (J)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(^=)</td>
<td>2.1</td>
<td>0.60 (Jorgensen &amp; Berthou)</td>
</tr>
<tr>
<td>OH(^-)</td>
<td>2.5</td>
<td>0.50</td>
</tr>
<tr>
<td>H(<em>2)O/O(</em>{\text{2ads}})</td>
<td>3.5</td>
<td>0.36</td>
</tr>
</tbody>
</table>

3.4 TRANSFER TECHNIQUE AND FILM THICKNESS CALCULATIONS

Transfer of specimens from the spectrometer to the aqueous phase and vice versa requires a brief exposure to air. A set of simple experiments were therefore carried out in which ion cleaned specimens which had been briefly exposed to aqueous conditions were compared with control specimens which had not been immersed. In all cases except the dried air exposure, the specimens were transferred through the laboratory air.

The specimens were subjected to 3 x 300 s exposures, with XPS analysis during the intervening periods, to the following condition:

1. Distilled water
2. De-aerated, distilled water
3. Air
4. Dried air in the preparation chamber

Peak to peak ratios of intensities of O/Fe and Cr/Fe are plotted with exposure times in Figs. 26(a) and 26(b). These figures show that the transfer through humid air does not obscure very important changes in the nature of the surface layers on the steel which become apparent during the second 300 s exposure. Thus the possible absorption of water from air which appears to occur to a small extent does not obscure the massive increase in oxygen from adsorbed water, which occurs on immersion.

There also occur interesting changes in the apparent ratio of iron and chromium showing that the effect of immersion is not obscured by air transfer. However, full interpretation of such relative peak heights requires their deconvolution from the peaks arising from the underlying metal, their normalization with appropriate sensitivity factors, and in addition some consideration of the possible thickness and depth of the emitting material. It is possible to estimate thickness by considering the absorption of the photoelectrons to obey the Beer-Lambert relationship. The intensity will depend, for a given species and concentration, on the thickness of the photoemitting layer, the thickness of any absorbing layer, and the angle of collection of the electrons. For clarity in the following equations these parameters are written, as required and in the order given above, as subscripts to the intensity symbol I. There are four important cases, as follows:

$I_\infty$ is the signal from an infinitely thick, clean, layer or substrate. Except at very low angles, this value will be independent of the collection angle $\theta$.

$I_{d_1\theta}$ is the signal from the infinitely thick layer when covered with an absorbing layer of thickness, $d_1$. 
Fig. 2.6(a) and (b) illustrate the peak ratio of oxygen to iron and chrom. to iron, respectively, as a function of exposure time in seconds for water, deaerated water, air, and dry air.
Id\_2^\theta is the signal from a clean layer of thickness, d\_2.

Id\_2 d\_1^\theta is the signal from a layer of thickness, d\_2, when covered with an absorbing layer of thickness, d\_1.

By relating any one of the latter three intensities to the reference value, I\_\infty, we eliminate the dependence of the signal strength on concentration, photoelectron cross-section and instrumental factors and highlight the thickness relationships thus:

\[
\frac{I_{\infty} d\_1^\theta}{I_{\infty}} = \exp \left( -\frac{d\_1}{\lambda \sin \theta} \right) \tag{1}
\]

where \( \lambda \) is the characteristic absorption length of the electron\(^{(44,45)}\)

\[
\frac{I d\_2^\theta}{I_{\infty}} = 1 - \exp \left( -\frac{d\_2}{\lambda \sin \theta} \right) \tag{2}
\]

and

\[
\frac{I d\_2 d\_1^\theta}{I_{\infty}} = \exp \left( -\frac{d\_1}{\lambda \sin \theta} \right)(1 - \exp \left( -\frac{d\_2}{\lambda \sin \theta} \right)
= \exp \left( -\frac{d\_1}{\lambda \sin \theta} \right) - \exp \left( -\frac{(d\_1 + d\_2)}{\lambda \sin \theta} \right) \tag{3}
\]

The derivation of (3) has been discussed by Fadley.\(^{(66)}\)

For the purpose of the present discussion of transfer techniques the fact is used that nickel does not appear to enter as an ion into any of the oxide films formed in the test exposures. The attenuation of the nickel signal by the absorbing layer, in eqn.\,(1), can be used to estimate the thickness of the oxide, plus that of any contaminants or bound water molecules, which is formed or picked up during the exposure. \( I_{\infty} \) is the Ni\_2\_p^{3/2} electron intensity from the ion cleaned surface and \( I_{\infty} d\_1^\theta \) is the corresponding signal after exposure. The collection angle, \( \theta \), for the spectrometer is \( 45^o \) and the absorption length, \( \lambda \), is taken as \( 1.5 \) nm.\(^{(45)}\)
The thickness of the product layers, d₁, obtained by this method are given in Table 4. They show that the difference in specimens which is detected by means of the elemental ratios after 600 s is already occurring in terms of thickness after only 300 s exposure. The necessity therefore is to work with transfer times of no more than 300 s duration.

Figs. 27 and 28 show the spectra of Fe, Cr, Ni, 2p\textsuperscript{3/2} and O\textsubscript{1s} before and after 300 s exposure to air. The spectra show the formation of iron and chromium oxides. The nickel is seen not to oxidise. The time of 300 s is a suitable time for transfer of specimens to and from the spectrometer and corrosion cells. The passive film so formed appears to be a mixture of oxidised iron and chromium with a contamination layer of adsorbed oxygen and water totalling a thickness of ca. 0.8 nm. It was decided at this stage that if such a film was able to seriously alter the nature of the resultant passive film in water at the various temperatures of interest, then a preliminary study at low temperature should reveal any such effect. This will be described in the next chapter.
### TABLE 4: PASSIVE LAYER THICKNESS (nm).

<table>
<thead>
<tr>
<th>TIME OF EXPOSURE (SECS)</th>
<th>DRIED AIR 298 K</th>
<th>NORMAL HUMIDITY AIR 298 K</th>
<th>AERATED WATER 298 K</th>
<th>DEAERATED WATER 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>0.49</td>
<td>0.78</td>
<td>2.0</td>
<td>&gt;2.0</td>
</tr>
<tr>
<td>600</td>
<td>0.73</td>
<td>0.78</td>
<td>&gt;2.0</td>
<td>&gt;2.0</td>
</tr>
<tr>
<td>900</td>
<td>0.87</td>
<td>1.0</td>
<td>&gt;2.0</td>
<td>&gt;2.0</td>
</tr>
</tbody>
</table>
BEFORE ION ETCHING

**OIs VACUUM CONTAMINANT**

**Cr$_{2p}^{3/2}$ METAL**

**FIG. 27**

**OIs $O^2, OH^- + H_2O|O_{2ad}$**

**Cr$_{2p}^{3/2}$ METAL + OXIDE**

**AFTER 3005 ION ETCHING**
BEFORE ION ETCHING

**Figure 2.8**

Fe$2p^{3/2}$ METAL

Ni$2p^{3/2}$ METAL

Fe$2p^{3/2}$ METAL + OXIDE

Ni$2p^{3/2}$ METAL SIGNAL ATTENUATED

AFTER 300s ION ETCHING
4.0 XPS ANALYSIS OF THE PASSIVE LAYERS FORMED ON A COMMERCIAL GRADE STAINLESS STEEL EXPOSED TO HIGH PURITY DEOXYGENATED WATER AT 313 AND 353°C

4.1 INTRODUCTION

As indicated by the previous discussions of Chapter 3 on the practical and theoretical procedures for carrying out a quantitative or semi-quantitative XPS analysis, the study of the aqueous phase oxidation of stainless steel is as much a study of the potential use of XPS as of the subject itself.

For this purpose it has been chosen to study the development of the oxide on a commercial-grade 18-8 stainless steel in low conductivity, deoxygenated water as a function of time, temperature and solution refreshment rate. The conditions used covered a wide enough range for systematic variation in the surface composition to be expected and thus to provide a test of the ability of XPS to reveal such responses to environmental factors. It was hoped that such a study would delineate the useful range of the XPS technique as a preliminary to the study of the corrosion of stainless steel in high pressure, high temperature water to be reported in Chapter 5.

4.2 EXPERIMENTAL DESIGN

The main experiment was designed to show if loss of material from the surface by selective dissolution would modify the composition of the passive layer over a period of time. Organic contamination of water presents problems in XPS analysis and in this respect de-ionised water is less satisfactory than distilled water. XPS was able to detect organic contamination from the water, suggesting traces of organic rosin or its by-products. A simple test was set up to compare distilled
Deionized water and deionized water. The results are shown below.

<table>
<thead>
<tr>
<th>Conductivity (x 1.28 μS)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deionized water exposed to air for one hour</td>
<td>0.45</td>
</tr>
<tr>
<td>Boiled deionized water exposed to air for one hour</td>
<td>1.45</td>
</tr>
<tr>
<td>Deionized water triple distilled (NaOH/KMnO₄) and exposed to air for one hour</td>
<td>0.78</td>
</tr>
</tbody>
</table>

Exposure to air allowed for dissolusion of atmospheric carbon dioxide forming a slight acidity. However, the higher acidity and conductivity found in the boiled deionized water was considered to be due to the breakdown of traces of organic resin to weak acids. Distilling the deionized water in the oxidising medium enabled the resin to be completely converted to the acid form whereupon sodium hydroxide neutralized the acid to a salt, which enabled the water distilled from this mixture to be collected free of resin. This removed the possibility of the resin interfering with the pH of the water, which was to be neutral for this preliminary work.

Arrangements were therefore made for the water supply to be drawn directly from a loop in which deionized water was multipli-distilled from alkaline potassium permanganate solution. The water was deoxygenated with oxygen free nitrogen, which was scrubbed as shown in Fig. 1(b), until its oxygen level was ≤ 1 ppm O₂ (μg/l) measured by a Mackereth cell (E.I.L. 1510 oxygen meter). The conductivity of the water was < 1 μS and the pH value = 6.7 The water was fed by a multichannel peristaltic pump to the test cells (Fig. 1).

The refreshment rates and cell volumes were set in relation to the saturation concentration of Fe⁺⁺ ion in equilibrium with Fe(OH)₂ at
Fig. I (a) Distillation System

Fig. I (b) Deaeration and Feed to Corrosion Cells
pH 7. The cell volume was 5 ml and, taking a solubility of $5 \times 10^{-5}$ g l$^{-1}$, the thickness of Fe(OH)$_2$ dissolved from a sample of 1 cm$^2$ in reaching saturation would be $\approx 0.5$ nm. This is comparable with the film thicknesses determined by XPS and thus some response to refreshment rates should be detectable. Values of 1, 3 and 6 ml/h were chosen. These small rates would be capable of removing Fe(OH)$_2$ at a rate commensurate with probable film growth rates at low temperatures.

All specimens were ion etched as described above, immersed in the test cell for 1 or 3 hours at 313 or 353$^0$K, transferred rapidly to the spectrometer and examined, first without etching and then at intervals as the films were etched back to the metallic spectrum. Spectrographic analysis of the stainless steel used is given below in weight percent.

<table>
<thead>
<tr>
<th>Si</th>
<th>Mn</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Ti</th>
<th>Nb</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>1.22</td>
<td>&lt;0.15</td>
<td>18.2</td>
<td>9.1</td>
<td>0.11</td>
<td>&lt;0.05</td>
<td>&lt;0.2</td>
<td>Balance</td>
</tr>
</tbody>
</table>

Carbon is not detected by this instrument.

4.3 RESULTS

This initial programme of work produced 540 individual photoelectron peaks of which a further 200 were split into their constituent chemical states by deconvolution (using the data system and software supplied by Vacuum Generators). These data have been used to determine the total oxide thickness and the iron to chromium ratio in its outer 33% of oxide (Table 1): only representative samples of the individual spectra and composition profiles are reproduced here. It can be seen from Fig. 2 that the difference in chemical profiles determined by the two sets of sensitivity factors for the Cr$^{3+}$ 2p$^{3/2}$ and the Fe$_3$O$_4$ Fe 2p$^{3/2}$ max., mentioned in Section 3.3.4, are very slight, and in particular the calculation of the oxide thickness is in no way affected. Figs. 3 to 6
Fig. 2(b)

- 0.6 O
- 1.7 Ni
- 1.1 Cr
- 0.88 Cr$^{3+}$
- 1.8 Fe
- 0.96 Fe$^{2+}$/Fe$^{3+}$max.

Fig. 2(a)

- 0.6 O
- 1.7 Ni
- 1.1 Cr
- 1.05 Cr$^{3+}$
- 1.8 Fe
- 0.7 Fe$^{2+}$/Fe$^{3+}$max.
Fig. 3 (a)

(1 HR 313 K 1 ml/hr)

Etch Depth (nm)

Fig. 3 (b)

(1 HR 353 K 1 ml/hr)

Etch Depth (nm)
Fig. 4 (a)

Fig. 4 (b)

- Fe
- O
- Cr
- Ni

(1 HR 313 K 6ml/hr)

(1 HR 353 K 6ml/hr)
Fig. 5(a) and Fig. 5(b) show the etch depth (nm) for different elements with varying etch conditions. The plots illustrate the at% of Fe, Cr, O, and Ni as a function of etch depth for (3HR 313 K 1ml/hr) and (3HR 353 K 1ml/hr) conditions.
show the composition profiles obtained for samples exposed at 1 ml/h and 6 ml/h respectively. The curves for 3 ml/h did not differ significantly from those at 1 ml/h and one representative only is included as Fig. 2. Each composition profile was examined and the interface region identified by the change of slope where the oxygen concentration reached its plateau (Point A, Fig. 3). The nickel signal at this point was then measured and used as the values for $I_{\infty}$ in eqn. (1) of Section 3.4. The initial value for the nickel signal obtained prior to etching gives $I_{0}$ and hence total film thickness is rapidly obtained from eqn. (1). Fig. 7 gives the thickness values as a function of the operational variables.

This thickness value was then used to normalize the etch rate scale and to yield the thickness scale used in Figs. 3 to 6. The samples which were exposed at 353°K formed a film of a thickness which obscured the initial nickel signal completely. In this case the difference between the nickel value after 10 s etching and that at the oxygen plateau was used to calibrate the etch rate. The material removed in the initial 10 s was estimated by using the change in the carbon and the Cr$^{3+}$ signals over this period. The reduction in the carbon signal (75) gave a value of 0.6 nm and the increase in the Cr$^{3+}$ gave 0.75 nm. These values would not be expected to be identical since water will also be removed in addition to carbon and there may also be a genuine increase in Cr$^{3+}$ unrelated to the decrease in surface contamination. However, a figure of around 0.6 nm should be added to that determined by the increase in the nickel signal to yield the total thickness estimates for 353°K and this has been done in Table 1 and Figs. 7 and 10.

From the profiles the relative concentrations of chromium and iron are obtained. The outermost region of the oxide is likely to reflect most strongly any dependence of selective dissolution as a function of refreshment rate and hence in Table 1 is listed the values for the outer
Fig. 7
### Table 1

<table>
<thead>
<tr>
<th>TEMP °C</th>
<th>FLOW-RATE ml/hr</th>
<th>TOTAL R/Cr IN OUTER 33% OF PASSIVE LAYER</th>
<th>Cr MAX (at%)</th>
<th>Ni MIN% - MAX%</th>
<th>TIME OF ETCH (secs)</th>
<th>PASSIVE FILM THICKNESS [m]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>1 Hr 313 K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.1</td>
<td>12</td>
<td>3 - 9</td>
<td>0 - 240</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.5</td>
<td>15</td>
<td>3 - 10</td>
<td>0 - 180</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.3</td>
<td>19</td>
<td>2 - 10</td>
<td>0 - 120</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td><strong>1 Hr 363 K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.6</td>
<td>13</td>
<td>3.9 - 7.2</td>
<td>10 - 60</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.4</td>
<td>20</td>
<td>1 - 7</td>
<td>12 - 90</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>8.7</td>
<td>11</td>
<td>1 - 7</td>
<td>20 - 120</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td><strong>3 Hr 313 K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.4</td>
<td>16</td>
<td>3 - 10</td>
<td>0 - 120</td>
<td>1.3</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>3.2</td>
<td>16</td>
<td>1 - 5.6</td>
<td>0 - 240</td>
<td>1.8</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>9.1</td>
<td>15</td>
<td>1 - 7</td>
<td>0 - 240</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td><strong>3 Hr 383 K</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>4.3</td>
<td>20</td>
<td>1 - 7</td>
<td>11 - 90</td>
<td>2.7</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>8.9</td>
<td>15</td>
<td>1 - 6.5</td>
<td>0 - 90</td>
<td>2.6</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>2.3</td>
<td>22</td>
<td>1 - 9</td>
<td>10 - 120</td>
<td>2.9</td>
<td></td>
</tr>
</tbody>
</table>

**GENERAL DATA**
33% of the film thickness. These values also have the advantage of less interference from the signal arising from the underlying metal. The scatter at 1 and 3 ml/h is slight and no systematic dependence on flow rate can be discerned. The ratios, in Table 1, are grouped around the value expected for the bulk metal suggesting that the oxide composition is close to that of the metal. The scatter at the 6 ml is so large that it appears an uncontrolled factor may be important at the higher flow rate.

4.4 DISCUSSION

From the extensive number of spectra recorded during this work two variables have been extracted, 'film thickness' and 'outer film composition'. These summarize the behaviour of 18-8 stainless steel in water as a function of time, temperature and flow-rate. The only subjective judgement was the identification of the oxide/metal interface from the oxygen profile; together with the assumption that nickel was excluded, on thermodynamic grounds, from the oxide itself. Otherwise the 'thicknesses' were calculated using the best estimate of $\lambda$ currently available. However, other interpretations of these data are possible and need to be considered. For example, the steady decrease in the nickel signal could arise from a progressive increase in the area of the overlying oxide rather than in its thickness. In principle this question can be resolved by investigating the dependence of the signal from the substrate on the angle of collection of the electrons, i.e. confirming that the change in intensity is that expected for the model of a substrate covered with a uniform, absorbing layer. The appropriate equation, which is readily derived from eqn.(1) of Section 3.4, is:

$$\frac{I_{\text{ox}} \theta_1}{I_{\text{ox}} \theta_2} = \exp - \frac{d}{\lambda} (\cosec \theta_1 - \cosec \theta_2)$$
where \( d \) is the total thickness of the product layer masking the substrate. A specially prepared specimen with steps machined to give take off angles of 75° and 15° respectively, according to orientation, \(^{(66)}\) was used to investigate this possibility. After ion etching in both orientations the sample was exposed in the standard way to water at 313°K flowing at 3 ml/h for 3 hours. After this treatment nickel was just visible in the spectrum obtained at 75° but could not be seen in the 15° spectrum. A uniform layer (d) of thickness \( \geq 0.6 \) nm would be sufficient to cause such attenuation and the experiment is not a very sensitive test of the model. The attenuation of the chromium signal, Fig. 8, could, however, be measured accurately: the ratio of the peak heights was 3.1 which yields a value of \( d = 1.2 \) nm when inserted in eqn. (1). By contrast with the behaviour of chromium metal the signal from Cr\(^{+++}\) remains unchanged on going to the greater collection angle. There is no way in which such a result can be reconciled with the requirements of eqn. (1) but it is to be expected from eqn. (3) of Section 3.4, derived for the case in which a thin layer of emitting material (Cr\(^{+++}\)) is covered with a layer of absorbing material. The dependence of \( I_d d_1 \theta \) on \( \theta \) will vary the individual values of \( d_2 \) and \( d_1 \), the emitting and the absorbing layers respectively and is represented for the two angles in question by the curves given in Fig. 8. The signal strength is independent of angles within the hatched zone on the field relating total film thickness, \( d (= d_1 + d_2) \) to the absorbing thickness, \( d_1 \). The value of \( d \) is known to be 1.2 nm from observation of the signal from metallic chromium and thus \( d_1 \) is approximately 0.6 nm. It is thus concluded that the film is duplex in structure with only the inner layer containing the chromium ions.

The method just described in which a variation of collection angle is used to obtain structural information is a novel and potentially valuable technique for very thin films, particularly so since it is
non-destructive. However, in the present case, it was used for one specimen only and neither analysis of the nickel signal, nor that of the iron, gave conclusions which were as clear cut as those of chromium. For this reason the conclusion regarding the duplex structure needs checking against the bulk of the data which was obtained in the conventional way by ion etching. The analysis of the outer third of the depth profile (Table 1) showed that the mean film composition with respect to chromium and iron may not be very different from that of the bulk metal.\(^{(23,82)}\)

However it is apparent from the actual profiles that there are sharp concentration gradients within this part of the film and a more sensitive analysis of the composition profile upon the film would be based on a point by point analysis of the stoichiometry. Such an analysis is set out in Table 2 for a typical specimen (3 h, 6 ml/h, 353°K). The peak heights of the charged species are given (after normalization with the appropriate sensitivity factors) and from these the anion and cation charges are calculated assuming the ions to have the full charge given in the column heading. The net charge in the final column clearly supports the conclusion that the outermost layer differs from the rest of the film by being rich in OH\(^{-}\). This result was well supported by the angular experiment which gave a pronounced OH\(^{-}\) peak at low angles. In particular the peak heights of both OH\(^{-}\) and H\(_2\)O/O\(_{2ad}\) are seen in Fig. 9 to become smaller compared with the O\(^{=}\) peak as the ion etching proceeds.

The final analysis which can be made is that of the kinetics of the film growth, Fig. 10. In this case the influence of the water flow rate becomes clearer when the film thickness is plotted against the total volume of water to which the sample was exposed. The plot in Fig. 10 shows that a linear relationship is obeyed at 313°K and corresponds to growth to 1.15 nm followed by water volume dependent growth of 0.15 nm/cm\(^2\)/ml. The data for 353°K are more scattered but show a similar
TABLE 2

<table>
<thead>
<tr>
<th>ETCH TIME (SECS)</th>
<th>At%</th>
<th>NORMALISED (fluorine PEAK HEIGHTS units)</th>
<th>CHARGE</th>
<th>TOTAL</th>
<th>NET CHARGE</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O1s</td>
<td>Cr2p3/2</td>
<td>Fe2p3/2</td>
<td>OH−</td>
</tr>
<tr>
<td>0</td>
<td>56.7</td>
<td>78</td>
<td>9</td>
<td>14</td>
<td>78</td>
</tr>
<tr>
<td>10</td>
<td>16.1</td>
<td>66</td>
<td>10</td>
<td>19</td>
<td>66</td>
</tr>
<tr>
<td>30</td>
<td>8.5</td>
<td>47</td>
<td>14</td>
<td>15</td>
<td>47</td>
</tr>
<tr>
<td>60</td>
<td>14.0</td>
<td>34</td>
<td>11</td>
<td>29</td>
<td>34</td>
</tr>
</tbody>
</table>
O is multialet. \( \theta = 15^\circ \)

A METAL-OXIDE INTERFACE.

B INTERMEDIATE REGION.

C OXIDE-SOLUTION INTERFACE.

Fig. 9.
Figure 10

Thickness (nm) vs. Volume of Water (ml)

Slope = 30 ppb

353 K
313 K

Symbols:
- @ 1 ml/hr
- X 3 ml/hr
- ○ 6 ml/hr
pattern: initial growth to 1.95 nm followed by steady accretion of material at the same rate.

Thus there are quite definitely two parts in the growth curve to match the conjectured duplex film. Assuming that the outer part of the film, i.e. that absorbing the Cr\superscript{+++} radiation, is a 'contaminant' layer picked up from the water, it is necessary to discuss its source. There is of course no reason why the pick-up of water itself should depend on water volume and thus some other species must also be involved: organic carbon and oxygen must be the main suspects. Unfortunately the total thickness of the growth in the second phase corresponds to only a 3 x 10\textsuperscript{-8} part of the water and, as has been shown, much of this is either OH\textsuperscript{-} or water itself. Thus the contaminant species is at a level much too small for detection in the aqueous phase. Hercules\textsuperscript{(83)} has demonstrated how well suited is XPS to the detection of surface species concentrated from sub-analytical levels in solution. Of the two suspects, organic molecules seem to be most likely to account for the stabilization of a surface 'bound water' layer. The analyses show that the outermost layers are rich in organic carbon and the water molecules would be stabilized by hydrogen bonding. It is interesting to speculate that the layers of bound water detected by electro- and radiochemical techniques could result from this phenomenon.

4.5 CONCLUSIONS

In the introduction to this work it was indicated that the programme of work was in part an examination of the XPS technique itself. It has been attempted to show that each of the expected points of difficulty can be met and overcome, both in the specimen preparation and in the exposure and analysis stages of the experiment. It has been shown that proper interpretation of the spectra leads to the view that the surface
product formed by immersion of stainless steel in water has a duplex layer structure of which only the inner layer is rich in chromium. The outer layer is rich in OH⁻ ions and may in fact be the layer of bound water reported by Okamoto.¹ This outer layer increases in thickness when the sample is exposed to greater volumes of water and does contain organic molecules. These two conclusions may be linked. Finally it has been demonstrated that the layer structure of very thin films (3 nm) may be investigated by examining the spectra as a function of collection angle.

This study has shown that the procedure for carrying out an analysis of this nature by XPS does not appear to interfere with the final results. The slight oxidation of the samples during transfer from the spectrometer to the corrosion cells and vice versa is not found to seriously mask the changes in the nature of the final passive layer for each of the various sets of experimental conditions. Finally, the approximations made both in multiplet analysis and in the determination of the sensitivity factors used in this analysis have not prevented a meaningful and perhaps novel chemical model being constructed. The technique of XPS, despite the deficiencies found at this stage, seems eminently suitable for the further study of the passive layers formed at high temperatures.
5.0 XPS ANALYSIS OF THE PASSIVE LAYERS FORMED ON A COMMERCIAL GRADE STAINLESS STEEL EXPOSED TO HIGH PURITY DEOXYGENATED WATER AT \(393^\circ\), \(433^\circ\) and \(473^\circ\)K

5.1 INTRODUCTION

In Chapter 3 an attempt was described to remove many of the deficiencies in multiplet analysis and the determination of sensitivity factors which had been highlighted by the low temperature study. As a consequence of the experience gained in the low temperature study, a more comprehensive chemical analysis of the passive products formed in the range \(393-473^\circ\)K was undertaken. In this range of temperature, selection of materials for the construction of the corrosion cell is critical, to avoid contamination of the corrodernt, which in this case is water. Bearing this in mind, it will be described how some of these problems were overcome in the design of a suitable corrosion cell.

5.2 EXPERIMENTAL

The conventional technique for studying reactions in high temperature water utilises an autoclave which is heated together with the aqueous solutions and reaction assembly. This method has two disadvantages when studying the formation of the very thin passive layer: (a) the solution must be separated from the steel pressure vessel to avoid contamination, and (b) the heating systems are relatively large, hindering rapid heating-up and cooling-down which is essential to the short corrosion tests of 1-3 hours carried out in this work in order to determine the initial kinetics of film formation. These problems were circumvented in this work by use of a pressurised enclosure rather than an autoclave. This vessel which is shown in Fig. 1 can be filled with 'oxygen free nitrogen' to provide an inert atmosphere up to \(2070 \text{ kNm}^{-2}\). The boiling point
of water at this pressure is 500°K and this measurement can be made using individually heated glass or PTFE cells.

The pressure vessel can be seen from Fig. 2 to have a large door, in principle large enough to enable the basic experimental apparatus used in the low temperature study to be placed inside the vessel. In practice a modified design of a corrosion cell, heater, peristaltic pump and a water reservoir, as well as effluent trap, were adequately set up inside this vessel. The vessel accommodated the need for a variety of electrical terminals for such items as the peristaltic pump, heater and electric bulb by conduiting electrical wire through one of the side ports. Thermocouple compensating wires were separately conducted in a similar fashion.

A 160 mm diameter viewing port was conveniently situated at the top surface of the vessel, and with the aid of a 'pygmy' bulb lamp, able to sustain pressures of up to 2070 kN m⁻², the experimental set-up could be observed. A pressure gauge was mounted on a T-section piping along with the main gas stopcock and a safety valve. The pressure gauge was attached to an automatic relay cut-out which turned off the electrical supply to the vessel if the pressure dropped to a predetermined level. This prevented the consequent excessive boiling off of the water as well as stopping the experiment.

5.2.1 Corrosion cell material

The choice of corrosion cell material is a critical one. Mercer et al.⁸⁴ have pointed out that silicon pick-up may occur from silica corrosion cells, which may alter very radically the nature of the corrosion product. Unpublished work from this laboratory, in which samples were exposed at 433°K for extended periods up to 200 hours, showed that indeed such alterations to the corrosion product may be related to silicon pick-up
which made evident by XPS analysis. In the low temperature range of 313-353°K, and short corrosion times of 1-3 h silicon pick-up was considered unlikely, indeed XPS analysis of the passive layers formed on stainless steel revealed no traces of silicon pick-up, and therefore silica vessels were used. At the elevated temperature of the next stage of this work, 393-473°K, an alternative corrosion cell was used, which was manufactured to an appropriate design from PTFE supplied by Dalal Plastics Ltd. and heat-treated at 653°K to improve both thermal stability (and machinability), thus reducing contamination of the corroden.

5.2.2 Heater design

Two attempts were made to design a PTFE corrosion cell with a built-in water heater. The first design is shown in Fig. 3. In order to prevent contamination of the water, the heater, a Watlow Fire-rod of 10 mm diameter, was surrounded by a PTFE sleeve or closed end tube of thickness 1 mm. A chromel-alumel thermocouple, sheathed in PTFE was placed in the water to control the temperature, via a Eurotherm heater control. It was found that the thermal conductivity of the PTFE sleeve was so high that a large thermal gradient between the water-sleeve interface and the heater-sleeve interface was set up. Consequently, when the temperature recorded in the water reached 463°K, the PTFE sleeve decomposed. The decomposed sleeve is shown in Fig. 4.

The second design was quite different from the first as can be seen in Figs. 5 and 6. The heater was contained in a close-fitted copper tube, closed at the top end by a copper disc larger than the tube and having a diameter of 20 mm. This formed the basis of a heater plate and base for the corrosion cell. To prevent copper contamination of the water, a 0.1 mm thick gold foil disc covered the copper disc. The thermocouple was brought down upon the heater plate and the temperature at the
Fig. 3
Fig. 4
Fig. 5

Side view of corrosion cell and heater assembly.
Fig. 7

Plan view of corrosion cell showing gold heater plate.
heater plate/water interface was efficiently controlled by a Eurotherm device. The small, 5 ml volume of water reduced the likelihood of temperature gradients permanently remaining in the water.

The cell was fitted with an inlet and outlet for water pumped from a reservoir by a peristaltic pump at the appropriate flow-rate. The tubing used was PTFE and Neoprene which are commonly used for their stability to water at room temperature. A gold specimen was placed in the corrosion cell for three hours at 473 K, 6 mL/h flow-rate to enable a test to be made as to whether contamination would be picked up on the gold surface, and analysed by XPS. The carbon peak that was detected was characteristic of organic contamination, and no fluorine or other possible contaminant signals were observed. Consequently, the design was considered a satisfactory answer to the problem of contamination of the corroder.

5.2.3 Experimental: Method

The specimen preparation followed the procedure described in Chapter 4. The only difference in experimental method was in the procedure of using the pressure vessel, which will be described below.

The water was prepared in the same way as described in Chapter 4, in this case the reservoir was continually flushed with 'oxygen free nitrogen', whilst the pressure vessel was being prepared. The PTFE corrosion cell and heater were placed in the autoclave and the pump, water reservoir and effluent bottle were then connected by the appropriate tubing (see Fig. 2). The pressure vessel was then continually flushed with nitrogen. The specimen was rapidly transferred in a specimen bottle to the pressure vessel, where it was mounted on a PTFE specimen holder attached to the thermocouple sheathing shown in Fig. 5. The cell was then filled with
water direct from the reservoir and the pump was manually operated to fill all the inlet tubing with water. The pump was then switched on. The cell top and thermocouple were then finally fitted. Temporarily turning off the nitrogen and disconnecting the nitrogen supply to the water reservoir, the pressure vessel door was bolted. Whilst the pressure vessel was being filled with nitrogen to the appropriate pressure to prevent boiling off of the water in the corrosion cell, the heater was switched on. To speed up the time to obtain the desired temperature, the heater was controlled so as to keep pace with the rate of filling with nitrogen; the corrosion cell was observed through the viewing port to ensure that release of dissolved nitrogen or boiling off did not occur during this process. The mean heating time was about 15 minutes in each case, which corresponded to the time required to obtain the working pressure of nitrogen. After the maximum temperature had been reached, the time of exposure was then measured. The pressure gauge was pre-set to activate a relay cut-out switch, mentioned above, on drop of pressure due to leakage.

After maximum temperature had been reached, the time of exposure was then measured. After the total exposure time had been achieved, the heater was turned off and the gas removed via a stopcock on the pressure vessel. The turbulence created by the escaping gas and the slight boiling off of a fraction of the water and the saturating nitrogen, aided the rapid cooling of the corrodent. The pressure vessel door was then opened when the pressure of the nitrogen was reduced to atmospheric pressure. The specimen was rapidly transferred to the preparation chamber of the spectrometer. The time taken for releasing the pressure was about fifteen minutes. The total period of about twenty minutes required to reach operating temperature, to cool and recover the specimen for analysis, compares well with the common practise of using an autoclave, which often
have higher turn-around times due to the method of heating employed and
the mass of the correldent, and autoclave.

5.2.4 Experimental design

The experimental design remained unchanged from the low temperature
work. In practice, the two flow-rate levels of 1 and 6 ml/h were set and
the temperature levels used were 393, 433 and 473°K at 1 h and 3 h.

5.2.5 XPS analysis

The spectrometer was programmed to scan five spectra: C_1s, O_1s,
Cr_2p^3/2, Fe_2p^3/2 and the Ni_2p^3/2. The occasional wide scan to search for
surface contaminants and other elements, perhaps from the steel, was
carried out.

Narrow scan statistics

Three scans were made per spectra across 200 channels, at a count
rate of one second per channel, taking a total of 600 s per spectra.

Wide scan statistics

One scan was made across 4000 channels, at a count rate of 0.25 s
per channel, taking a total of 1000 s per spectra.

5.2.6 Ion etching

The outer layer of the sample was analysed, and then a short etch
of about 10 s was made at 3.5 keV acceleration potential and 2 mA tube
current at \(1.33 \times 10^{-1}\) N m\(^{-2}\) background pressure of Argon. This was sufficient
to remove the surface adsorbed air, water and carbonaceous contamination.
The next ten steps of ion etching procedure were made at 30 s intervals, between analysing times. The etch times were made longer when interesting changes in spectra were no longer occurring.

The etching was stopped when the metallic spectra were sharp and preferably where no traces of the higher binding energy oxidised states were present.

5.30 Results

5.31 Introduction

Compared with film thickness studies by ellipsometry and structural studies by electron diffraction, a chemical compositional study of this type demands a more exacting approach in order to reveal not only the slightest chemical variation occurring throughout the depth of each of these passive layers, but also to reveal any effects that may be induced by the influence of the levels of the flow-rate, temperature and time of exposure. For each of a succession of etch steps this study compiled the 1 s level spectra of carbon and oxygen, and the 2p$^{3/2}$ level spectra of iron, chromium and nickel. Subsequent multiplet analysis yielded the following species $\text{O}^-$, $\text{OH}^-$, $\text{H}_2\text{O/O}_{2\text{ad}}$, $\text{Fe}$, $\text{Fe}^{2+}$, $\text{Fe}^{3+}$, $\text{Cr}$, $\text{Cr}^{3+}$, $\text{Ni}$ and $\text{Ni}$. The length of acquisition time to obtain suitably well-defined multiplets to facilitate multiplet analysis and the number of individual etch steps made throughout these passive layers have been optimised to suit the requirements of this work. The series of spectra shown in Figs. 7-11 illustrate the level to which these demands have, in practice, been met.

5.32 Presentation of Data

By applying the respective sensitivity factors to account for variations in photoelectron cross-sections for each element and FWHM
Cl₆ MULTIPLET
(SAMPLE: 435°K, 6 miln, 1h.)

--- Vacuum Contam. ⬇️
--- Carbide.

Fig. 7
O15 MULTIPLET

(SAMPLE: 433 °K, 6 ml/h, 1h)

\[
\begin{align*}
\text{O}^+ & \\
\text{OH}^- & \\
\text{H}_2\text{O/O}_2\text{ads.} & 
\end{align*}
\]
Cr₂P₀₁₅ Multiplet

(Sample: 433°C, 6mL/h, 1h.)

--- Cr Metal
--- Cr³⁺

Fig. 4
Fe\textsubscript{2}P\textsubscript{3/2} Multiplet
(Sample: 493\textdegree}K, 6\text{mI/h/h})

---
Fig. 10
characteristics for each oxidation state of that element, the normalised peak heights for each of the emitting species were calculated and are tabulated in Tables 1-12, along with the observed peak height values.

To aid interpretation, the data and selected extracts are presented graphically with a common x-axis in Figs. 12-23. The order of graphical presentation for each stainless steel sample is given below. Fig. (a) gives a plot of the total normalised signals together with the normalised $1_s$ signal for carbon which was the major contaminant derived from the spectrometer vacuum system. The $C_{1s}$ signal conformed to the binding energy position of the vacuum contaminant $C_{1s} = 283.7$ eV was assumed to be not included in the film. The less significant water or adsorbed oxygen spectra was also assumed to be a contaminant and was not included in the main analysis.

Fig. (b) gives the total signal derived from the ionised states in the film together with (c), the relative proportions of the individual ions. Fig. (d) gives the total signal derived from elemental states together with (e), the relative proportions of the metals.

The extracts have been chosen for the following reasons:

1. The total signal (a) is related to the sampled depth which may be different in oxides and metals. It also gives warning of any abnormality in X-ray intensity;

2. the carbon contaminant is a largely instrumental variation and alterations in its intensity may lead to complementary changes in the signal from the sample;

3. the total ion signal curve illustrates the extent of the chemically altered zone whilst the $\text{At}\%$ curves give some indication of the distribution of the respective ions.
4. the Ar% curves for the metals illustrate the depletion zones for the elements which have diffused into the passive layer.

Inspection of the extracts a to e for each of the samples reveals some common features. Firstly, the rapid decrease in the C_is signal is seen to correspond to the rapid increase in the total ion signal curve (b). This supports the conjecture that the C_is signal is from an outer contaminant layer. After removal of the initial contaminant layer, the total ion signal curve (b) appears to reach a maxima or plateau region followed by a gradual decline, corresponding to an increase in the substrate metal signals of (d). The two curves suggest firstly that there is evidence of a passive film overlaying the steel substrate. However, the absence in all cases of a sharp drop-off of the total ion signals expected of a discrete interface between film and substrate, suggests an interfacial zone. Correspondingly (d) shows a change in the rate of emergence of the substrate signals in this region. The constant low level of residual ion signals shown in all cases in extract (b) suggests the presence of a residual level of oxide expected for this commercial grade steel. The nature and cause of the interfacial zone will be discussed later.

The Figs. 12-23 therefore show four main regions: a contaminant zone, a passive film with an intermediate zone between the film and the substrate. These regions are labelled in the schemata shown in Fig. 24.

The previous method of determining etch-rate and consequent determination of film thickness could not be carried out in this work as there was no clearly defined interface present. The thickness of the interfacial zone and passive film can be best related to the time to etch through these regions assuming a constant etch-rate. The relative thicknesses were therefore plotted against the time of exposure, flow-rate and the temperature of the corrosion test, and shown in Fig. 25.
Table 1. 393°K 1 ml/h, 1 h

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<th>Cr(^{3+})</th>
<th>Fe(^{2+})</th>
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Tables 1 - 12 are the normalized peak heights for each of the species, which were calculated from the recorded peak heights. The sensitivity factors used to calculate these values are as follows:

\[
\begin{align*}
C_{1s} \quad C & = 0.27 \\
O_{1s} \quad O^{2-} & = 0.60 \quad OH^{-} = 0.50 \\
Fe_{2p}^{3/2} \quad Fe \text{ metal} & = 1.8 \quad Fe^{2+} = 0.71 \quad Fe^{3+} = 0.46 \\
Cr_{2p}^{3/2} \quad Cr \text{ metal} & = 1.1 \quad Cr^{3+} = 0.79 \\
Ni_{2p}^{3/2} \quad Ni \text{ metal} & = 1.7 \quad Ni^{2+} = 0.39
\end{align*}
\]
Table 2: 393°K, 6 ml/h, 1 h

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Table 3. 393°K, 1 ml/h, 3h

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### Table 12. \(473^\circ\text{K, 6 ml/h, 3 h}\)

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Passive film  Interfacial Steel substrate zone

Total normalised signals

Cl\textsubscript{2} Normalised signals

Total normalised signals from cations and anions

Atomic % of cations and anions

O\textsuperscript{-}

OH\textsuperscript{-}

Fe\textsuperscript{3+}

Cr\textsuperscript{3+}

Fe\textsuperscript{2+}

Total normalised signals from metallic substrate

Atomic % of metals

Fe

Cr

Ni
Fig. 13(a)  
Total counts per sec. Total counts per sec.

Fig. 13(b)  
Total normalised signals

Fig. 13(c)  
Atomic % of cations and anions

Fig. 13(d)  
Total normalised signals from cations and anions

Fig. 13(e)  
Total normalised signals from metallic substrate

Etch time (s)
- 170 -

393°K 1ml/h 3h.

Passive film
Interfacial zone
Steel substrate

Total normalised signals

Total normalised signals from cations and anions

Atomic % of cations and anions

Total normalised signals from metallic substrate

Atomic % of metals

Etch time (s)
Fig. 15(a) - Passive film | Interfacial zone | Steel substrate
Total normalised signals

Fig. 15(b) - Total normalised signals from cations and anions
Cl²⁻ Normalised signals

Fig. 15(c) - Atomic % of cations and anions
Atomic % of metals

Fig. 15(d) - Total normalised signals from metallic substrate
Fe³⁺
Cr³⁺
Fe²⁺

Fig. 15(e) - Atomic % of metals
Fe
Cr
Ni
433°K 1 ml/h 1h.

Fig. 16(a) Total normalised signals

Cl\textsubscript{2} Normalised signals

Fig. 16(b) Total normalised signals from cations and anions

Fig. 16(c) Atomic % of cations and anions

Fig. 16(d) Total normalised signals from metallic substrate

Fig. 16(e) Atomic % of metals

Etch time (s)
Fig. 17(a)  Total normalised signals

Fig. 17(b) Total normalised signals from cations and anions

Fig. 17(c) Atomic % of cations and anions

Fig. 17(d) Total normalised signals from metallic substrate

Fig. 17(e) Atomic % of metals
$433^\circ \text{K} \ 1 \text{ml/h} \ 3 \text{h.}$

**Passive film**  
**Interfacial zone**  
**Steel substrate**

**Fig. 18(a)**  
Total normalised signals

**Fig. 18(b)**  
Total normalised signals from cations and anions

**Fig. 18(c)**  
Atomic % of cations and anions

**Fig. 18(d)**  
Total normalised signals from metallic substrate

**Fig. 18(e)**  
Atomic % of metals

Etch time (s)
433°K 6ml/h 3h.

Fig. 19(a)
Total normalised signals

Fig. 19(b)
Total normalised signals from cations and anions

Fig. 19(c)
Atomic % of cations and anions

Fig. 19(d)
Total normalised signals from metallic substrate

Fig. 19(e)
Atomic % of metals

Etch time (s)
Fig. 20(a) - Passive layer Interfacial zone Steel substrate

Total normalised signals

Cl_s Normalised signals

Fig. 20(b) - Total normalised signals from cations and anions

Fig. 20(c) - Atomic % of cations and anions

O^= 40

OH^- 20

Fe_{3+}^+ Ni_{2+}^+

Cr_{3+}^+

Total normalised signals from metallic substrate

Fig. 20(d)

Total normalised signals from metallic substrate

Fig. 20(e) - Atomic % of metals

Fe 100

Cr 50

Ni 25

Etch time (s)
Fig. 21(a) Total normalised signals from metallic substrate

Fig. 21(b) Total normalised signals from cations and anions.

Fig. 21(c) Atomic % of cations and anions

Fig. 21(d) Total normalised signals from metallic substrate

Fig. 21(e) Atomic % of metals
Interfacial zone

473°K 1ml/h 3h

Passive film

Steel substrate

Total normalised signals

Cl$_s$ Normalised signals

Total normalised signals from cations and anions.

Atomic % of cations and anions

Total normalised signals from metallic substrate

Atomic % of metals

Etch time (s)
Passive film \[ \rightarrow \text{Interfacial zone} \rightarrow \text{Steel substrate} \]

**Fig. 23(a)**

![Graph showing total normalised signals.](image)

**Fig. 23(b)**

![Graph showing Cls normalised signals.](image)

**Fig. 23(c)**

![Graph showing atomic % of cations and anions.](image)

**Fig. 23(d)**

![Graph showing total normalised signals from metallic substrate.](image)

**Fig. 23(e)**

![Graph showing atomic % of metals.](image)
There appears to be little significant difference in film thickness at 393°K and 433°K irrespective of the time of exposure and flow-rate. At 473°K the film thickness is seen to increase rapidly, and whereas no significant flow-rate dependence is seen, the films appear to increase in thickness almost linearly with time between 1 and 3 h exposure.

The interfacial zone thickness is seen to increase slightly with time and temperature between 393 and 473°K but is independent of flow-rate.
The zone thickness is also seen to increase markedly at 473°K. However, whereas at 393 and 433°K the film and zone thickness are about the same, at 473°K the film thickness is double that of the film.

5.33 **Chemical characteristics of the interfacial zone**

The interfacial zone is marked by the appearance of a region enriched in metallic nickel reducing with etch time to the usual proportions found for this composition of stainless steel, and by a rapid reduction in the Fe$^{2+}$ content with a corresponding increase in the Cr$^{3+}$ content tending to reduce the iron-chromium ratio of the oxide. The cause of the interfacial zone will be discussed later.

5.34 **Chemical characteristics of the passive film**

Between 393°K and 433°K, Fig. 25 shows no evidence of an increase in film or interfacial thickness. However, the extract (c) showing the chemical profile of the passive layer, suggests that in each case there exists an outer iron-rich layer and an inner chromium-rich layer, extending into the interfacial zone.

An arbitrary guide to the relative growth of the iron-rich outer layer compared to the chromium-rich inner layer is given in Table 13 below, indicating the time to etch (in seconds) through the iron-rich layer to reach a concentration of about 5 At% Cr$^{3+}$ - thus defining the iron-rich layer as that portion of the film having <5 At% Cr$^{3+}$.

<table>
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<th>Flow-rate</th>
<th>1 h 393°K</th>
<th>3 h 393°K</th>
<th>1 h 433°K</th>
<th>3 h 433°K</th>
<th>1 h 473°K</th>
<th>3 h 473°K</th>
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<td>48</td>
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<tr>
<td>6 ml/h</td>
<td>36</td>
<td>60</td>
<td>100</td>
<td>100</td>
<td>180</td>
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**Table 13. Time to etch through iron-rich layer (seconds)**
Inspection of Table 13 reveals the increasing depth of the iron-rich layer with increase of temperature. From Fig. 25 it appears that film thickness remains constant at 393°K and 433°K, but growth accelerates at 473°K. At 393°K and 433°K the iron-rich layer appears to increase with flow-rate more markedly than with the increase of the time of exposure. At 473°K, flow-rate appears to have no significant effect upon the development of film composition except to pick up more Ni^{++} in the outer layer. Fig. 26 shows extensive growth at 473°K between 1-3h.

The Ni^{++} was observed in the extreme outer region of the passive film formed at 473°K only. The enrichment of Ni^{++} was seen to increase with both flow-rate and time, as seen from extract (c) of Figs. 20-23.

A check was made to ensure that the Chromel-Alumel thermocouple used in this test was not responsible for the pick-up of Ni^{++} in the outer layer of the passive film at 473°K. The composition of the two wires are:
Chromel: Ni 90%, Cr 10%; and Alumel: Ni 98%, Al 2%. A gold specimen was substituted for a stainless steel specimen for 6 h at 473°K at 6 ml/h flow-rate. This was twice as long as the original test mentioned in 5.2.2, which showed no contamination. The resulting XPS analysis of the gold sample was a definite Ni^{2+} signal, suggesting that the thermocouple selectively dissolved out Ni^{2+}, chromium not being present on the gold surface. The choice of Chromel-Alumel was made in preference to platinum-rhodium as it has a larger emf range, needed for accurate measurement. Solubility data assembled by McDonald et al (85) suggests that nickel has a marked increase in solubility at 473°K in solution approaching neutrality. The galvanic cell created by the contact made between the thermocouple and the gold heater-plate would not be effective in anodically dissolving nickel: for the resistivity of the electrolyte would normally be too low. However, the nickel dissolution might be accelerated by the galvanic effect when sufficient Ni^{2+} had dissolved in the water to increase the
conductivity of the water. The consequent effect of this contaminant upon the composition of the passive film will be discussed later.

In addition to the pick-up of nickel, traces of Cu$_2$O, barely detected by the LMM Auger spectra having greater peak intensity than the Cu2p$^{3/2}$ signal, were also found in the outermost layer of the passive steel at 473°K. This cation was not included in the profile owing to the low peak intensity and the nearness of the more intense Cr$^{3+}$ 2p$^{3/2}$ signal. This was suspected to come from the copper disc, underlying the 0.1 mm thick gold heater plate cover. Indeed, Electron Micro-probe Analysis of the gold heater plate found traces of copper in the gold foil. Copper is a common contaminant of gold and the diffusion rate of copper through gold at around 473°K appears to be large enough to reach the gold/water interface and to dissolve out into the water. Though the copper content of the gold may have built up gradually during the 393°K and 433°K experiments.

5.40 Discussion of Results
5.41 Factors Influencing the Total Photoelectron Yield

On inspection of the results of Figs. 12-23 it can be seen that from extract (a), showing the total normalized signal included in the analysis for each etch step, a gradual reduction in photoelectron yield occurred with etch time. The only exception was the 473°K, 6 ml/h, 1 h specimen (Fig. 15) where a sharp reduction in photoelectron yield could be easily distinguished from other minor variations in the curve profile. Four possible causes for this reduction in photoelectron yield are considered here: (1) that the X-ray flux intensity varied with time, (2) an unaccounted species may be present in the metallic phases that is not included in the oxide phases, (3) an unaccounted species is present in both phases, but is enhanced in the metallic phases, such as implanted argon, and finally (4) that the total emitting species present in the sample volume is higher in the oxide phase, compared with the metallic phase.
Each analysis was carried out over two days. If the X-ray intensity had been dependent on time, one might expect to see sharp variations in X-ray flux intensity at the point of recommencing the analysis on the second day; however, this is not observed. The X-ray flux intensity was therefore thought to remain uniform, and variations which may have occurred were considered to be represented by the small fluctuations in the points making up the curves, or by other obvious large variations such as that in Fig.15.

The metallic phase is known to have traces of stringers containing manganese and sulphur as well as carbides, as often found in commercial-grade stainless steels. The constituents were not present in the passive layer and were therefore excluded from these analyses. The resultant reduction in photoelectron yield from the sample volume of the metallic phase is thought to be partly responsible for the variations in the % reduction of photoelectron yield found for the metallic phases ranging from 12- 23 in the samples analysed.

Argon ion implantation may occur, but the photoelectron peak was not detected in this mode, and therefore it is likely only to make a minor contribution to the reduction in photoelectron yield with continued etching.

An important contribution to the reduced photoelectron yield may be the difference in the number of emitters found in the sampled volume. The ratio of the number of emitters in the sample volume of the oxide and metal phase is given below:

\[
\frac{N_{ox}}{N_{m}} = \frac{x_{ox} \cdot d_{ox}}{x_{m} \cdot d_{m}}
\]

where
$x$ is the effective sampled depth ($x = f(\lambda)$)

$N$ is the number of emitting species in the sampled volume of a given phase.

$d$ is the atomic density of the phase.

Thus, the observed intensity is an exponential function of $\lambda$ and is not, therefore, proportional to $N$. A much more important variable is the number of emitters in the surface plane and the intensity would be proportional to this term, which is normally contained in the pre-exponential term of the Beer-Lambert equation. Taking the simplest case of a close-packed oxide lattice formed on a close-packed face of metal, the appropriate ratio is found to be:

$$\frac{n_{\text{ox}}}{n_m}$$

where $n$ is the plane concentration of emitters

The number of unit cells/cc = $\frac{10^{24}}{A^3}$ $A$ = unit cell size in Å

... number of emitters/cc = $\frac{m \times 10^{24}}{A^3}$ $m$ = no. of atoms per unit cell

... $n = \frac{2}{3} \sqrt[3]{\frac{m \times 10^{24}}{A^3}} = \frac{10^{16}}{A^2} \ m^{2/3}$

$n_{\text{Fe}} = \frac{4^{2/3} \times 10^{16}}{(3.637)^2} = \frac{2.517 \times 10^{16}}{13.22} = 1.89 \times 10^{15}$

$n_{\text{Fe}_3\text{O}_4} = \frac{56^{2/3} \times 10^{16}}{(8.391)^2} = \frac{14.6 \times 10^{16}}{70.5} = 2.07 \times 10^{15}$

The signal intensity from the oxides will, therefore, be greater than for metals if the value of $\lambda$ is the same. Thus, the mean enhancement of
the total signals recorded from the oxide phase because of its higher density of emitters is 10%.

It is therefore concluded that slag and carbide inclusion in the steel surface, and differences in the plane atomic densities, are the main reasons for the observed variations in photoelectron yield in these analyses.

5.42 The Nature and Formation of the Interfacial Zone

The interfacial zone is marked by the rapid fall in ferrous iron concentration and an enhancement in chromium ions, together with a gradual rather than a sharp drop-off of the total ion signal. The metallic nickel signal is also seen to be enhanced with respect to iron and chromium in this region, and to revert to the usual concentration level for this steel at the end of the zone.

This zone may be either the product of ion-beam knock-in damage (knocking into the material a portion of the surface ions) and/or of internal oxidation (selective oxidation of some of the alloy components). Ion-beam damage arguments must answer the apparent selective penetration of Cr$^{3+}$, the net reduction in Fe$^{2+}$ concentration and selective enrichment of metallic nickel. Firstly, the most likely ion to penetrate a surface would be the one requiring the lowest activation energy to leave its lattice site. This would correspond to the ion most likely to be ejected or sputtered from the surface, and the ion with the greatest diffusivity at a given temperature. Cr$^{3+}$ does not have such a high diffusivity as Fe$^{2+}$ or Fe$^{3+}$, and forms the most stable oxide. Fe$^{2+}$ ions have the highest diffusivity and least oxide stability of the three cations and yet is not enriched in this zone. Secondly, selective etching has not been evident over the entire range of the compositions studied throughout this
work and, therefore, no evidence of selective knock-in damage is revealed from the profiles of the film, with the possible exception of NiO, which is only applicable at 473°K. As seen from Chapter 3, there is no evidence of iron or chromium oxides being reduced by selective removal of $O^-$ and therefore one would not expect selective knock-in damage to occur with $O^-$ anions. It is therefore considered that ion-beam damage is less important than the processes of internal oxidation by diffusion of $OH^-$ and $O^-$ in the range of temperature 393-473°K.

From Fig. 25, it is clear that at 473°K, the interfacial zone appears to increase in thickness with the time of exposure. At 393 and 433°K, the interfacial zone is the same order of thickness as the overlying film, but a weak dependence on time of exposure is reflected in the results. Internal oxidation is a common occurrence in alloys having a continuous oxide layer, where the diffusion rate of oxygen in the metal phase is greater than that for cation diffusion in the oxide phase. The thickness of an internally oxidised zone is determined by the relative rates of these two transport processes. It is virtually unchanged over the interval 393 to 433°K, but at the higher temperature represents a much lower proportion of the passive layer thickness. This arises because of a much increased effective rate of transport of cations within the oxide phase at 473°K. The fact that internal oxidation is seen, indicated that the high $Cr^{3+}$ concentration observed in the concentration profiles in the vicinity of the passive film/interfacial zone interface, cannot represent a continuous $Cr_2O_3$ barrier film. This is because the oxygen potential at a $Cr_2O_3$/metal interface would be insufficient to oxidise chromium within the alloy itself.
5.43 A Model of Film Growth in the Temperature Range 313-433°K

In section 3.53 it was seen that the passive films showed distinct iron rich and chromium rich regions. Cr$^{3+}$ was enriched in the innermost part of the film as well as the interfacial zone. Between 393°K and 433°K exposure there is little evidence to suggest that film or interfacial zone thickness increases.

Unlike the 313 and 353°K samples, where a considerable build-up of a contaminant layer was seen to increase with flow-rate, no such behaviour was found in the samples exposed to 393-473°K. This layer, which was a characteristic of the low temperature range, was believed to consist of organic molecules stabilizing bound water by hydrogen bonding. The exceptional levels of carbon found for one sample only in the high temperature study (Fig. 16) are believed to be the result of a slight leak in the analyser chamber which was also observed from the ion gauge.

Film thicknesses at 313 and 353°K appeared to be of the same order of magnitude, prior to pick-up of water in the outer layer. Direct comparison of the film thickness produced at 313, 353, 393 and 433°K cannot easily be made. This is because the formation of an interfacial zone at 393 and 433°K does not allow the film thickness to be estimated from the attenuation of the Ni2p$^{3/2}$ signal, as was carried out at the low temperature range of study. However, the relatively early appearance of metallic nickel does suggest that the films formed at 393 and 433°K are of the same order of thickness as those formed at 313 and 353°K.

Neglecting the outer boundlayer of water, and considering the passive film thicknesses only, it can therefore be assumed that at each of these four levels of temperature a barrier film was grown of constant thickness. This rate of growth suggests that a 'logarithmic' rate law is being obeyed. Indeed the mechanism of film growth may be analogous to the model postulated
by Mott and Cabrera\textsuperscript{(17)} for the dry oxidation of metals at low temperatures, where a strong field is set up in the oxide film due to a contact potential difference between the metal and adsorbed oxygen, which enables the metal ions to move through it with little help from temperature. The consequent inverse logarithmic growth rate formed was given by

$$\frac{1}{x} = A - B \log_e t$$

$x =$ thickness of film at time $t$

A and B are constants

In the case of the passivation of stainless steel it is possible that the field may be built up by adsorption of anions from the water or to the metal surface. The presence of the anion field could explain why both Ni\textsuperscript{++} and copper species are so readily picked up when the temperature is great enough to permit their aqueous phase transport as noted on the 473\textdegree K samples.

Such an anion field would enable iron and chromium to diffuse out into the resulting oxide film, more or less in proportions equivalent to those found in the steel. Selective oxidation or diffusion would be ruled out in this initial film as the field would be so strong as to reduce diffusion differentials. In Mott and Cabrera's\textsuperscript{(17)} early paper such values as 1 volt were calculated to be acting across films of 1 nm, resulting in an intense field of $10^7\, \text{V/cm}$. The steady state film thickness would be reached when the field strength, reducing with film thickness, is too low to enhance cation diffusion. In such films electron tunnelling should ensure that efficient transfer of electrons to the cathodic outer region of the film occurs in order to accommodate the cathodic reaction.

In the presence of $\lesssim 1$ ppm $O_2$ at pH 7, the likely cathodic reaction
is as follows:

\[ \text{O}_2^{\text{dissolved}} + 4e + 2H_2O \rightarrow 4OH^- \]

The initial film would be expected to grow rapidly as has been found in the case of iron \(^{(13)}\) and stainless steel, \(^{(36)}\) and despite flow-rate and temperature the film will initially tend to have the same composition. However, subsequent changes in composition may occur with flow-rate, time and temperature, resulting in a film of more stable composition to these conditions. In the range 313 to 433°K, the obedience to the suggested logarithmic growth law implies that at these temperatures diffusion rates are so slow as to prevent further film growth.

Compositional changes are seen to occur with time, at all temperature levels, and the final films had distinct iron-rich and chromium-rich regions. The major change in the range 313 to 353°K is a slight increase in the concentration of the Cr\(^{3+}\). At 393°K and 433°K marked changes occur in the respective thicknesses of the two regions. However, the most striking changes occurred at 473°K and these are dealt with in a later section.

5.44 The Presence of Bound Water

The 0\(_{1s}\) spectra of water and adsorbed oxygen have the same binding energy position, so that it is not possible to state whether the high level of this peak from analysis of the outer layer is due to oxygen contamination picked up during specimen transfer, or bound water. However, the hydroxyl ion peak is clearly distinguished from the other oxygen species. It is seen from the A t% plots of OH\(^-\) in Figs. 12-23 that the concentration of hydroxyl ions is higher than for oxygen anions in the outer layer. This suggests that the first structure formed is hydrated.
However, following the first few seconds of etching, a more or less constant ratio of $[\text{OH}^-]:[\text{O}^\text{m}]$ is maintained throughout the passive layer and interfacial zone. This evidence supports Okamoto's\cite{20} model of the passivation of stainless steel, described in Chapter 1, where an initially hydrated structure was thought to age into a more stable oxide structure.

5.45 Phase Distribution and the Passive Layers: 313-433°K

The low temperature and oxygen levels considered in this work favour, thermodynamically, the formation of spinel structures in the passive film. The iron maximum position of the unresolved Fe$_2$P$^{3/2}$ multiplet, found at 313 and 353°K suggest the presence of ferrous ions and, therefore, the likelihood of spinel phase. The chemical profiles of the outer iron-rich portion of the films at 393 and 433°K (see Figs. 12-19) show the ferric and ferrous ions in the approximate ratio of 2:1, typically found for magnetite. Moreover, neither Fe(OH)$_2$ nor FeO are stable compounds: Fe(OH)$_2$ has a high solubility in water and FeO is only formed at much higher temperatures, so these compounds are unlikely to account for the presence of ferrous ions. The low concentration of Cr$^{3+}$ ($<5$ At%) in the iron-rich layer suggests that a range of chromite is formed, having the basic FeCr$_2$O$_4$ structure. On further etching through the iron-rich outer layer, the level of Cr$^{3+}$ is seen to increase until the Cr$^{3+}$ rich inner layer is reached. This may suggest an intermediate range of Fe$_3$O$_4$ - FeCr$_2$O$_4$ solid solution: Francis et al\cite{86} have shown that these spinels may form solid solutions as suggested by the range of lattice parameters found for the iron-chromium spinel formed at high temperatures in stainless steel exposed to CO$_2$.

The chromium-rich inner layer corresponds to a region of low ferrous ion concentration, which implies that in this region, as with the interfacial zone, the hydrated oxides are in the form of the corundum structures:
\( \gamma \text{Fe}_2\text{O}_3 \) (owing to the presence of hydroxyl ions the \( \alpha \text{Fe}_2\text{O}_3 \) structure is unlikely) and \( \text{Cr}_2\text{O}_3 \). The appearance of a chromium-rich inner layer at the higher temperature is not surprising as it is a common product of the oxidation of stainless steel exposed to \( \text{CO}_2 \), air and \( \text{H}_2\text{O} \). This layer is ascribed to the trapping of \( \text{Cr}^{3+} \) during growth. However, in this work it is likely that growth has already occurred within the first few seconds of exposure to water. Thus, ageing of the passive film or redistribution of the constituents has to be considered.

5.46 Factors Influencing the Ageing of the Films Formed at 393 and 433°K

As shown in Table 13, the main variations in the proportions of the iron-rich and chromium-rich regions within the films are strongly dependent on flow-rate and weakly dependent on times of exposure. The oxygen content of the water was \( \leq 1 \text{ ppm O}_2 \). How important the maximum level of \( 1 \text{ ppm O}_2 \) can be to oxidation is seen from the calculation given below, which determines the required level of oxygen to oxidise a 2.0 nm film of magnetite to \( \gamma \text{Fe}_2\text{O}_3 \).

The volume occupied by 2.0 nm of passive layer on a surface of 1 sq cm = \( 2.0 \times 10^{-7} \text{ cc per sq cm} \).

For a density of \( \text{Fe}_3\text{O}_4 \) of 5.18, the mass of passive layer on 1 sq cm is:

\[
5.18 \times 2 \times 10^{-7} \sim 10^{-6} \text{ g}
\]

In the reaction \( 2\text{Fe}_3\text{O}_4 + \frac{1}{2} \text{O}_2 = 3\text{Fe}_2\text{O}_3 \)

\[16 \text{ g of O}_2 \text{ reacts with 464 g of Fe}_3\text{O}_4\]

The mass of oxygen needed to convert passive film to \( \text{Fe}_2\text{O}_3 \):

\[
= \frac{16}{464} \times 10^{-6} \text{ g} \sim 3 \times 10^{-8} \text{ g}
\]
If all this oxygen was supplied in 1 ml passage of water over the specimen surface the concentration of oxygen in the water would be 0.003 ppm which is well into the expected range of dissolved oxygen for this experiment. Such a relatively high level of oxygen would suggest that the increased supply rate affected by an increase in flow-rate from 1 ml/h to 6 ml/h would have little influence on the oxidation rate of the film.

The second possible effect of flow-rate is that of the original role assumed likely at the outset of this work, namely to refresh the passive film surface, by removing dissolving cations. Table 13, as well as the profiles in Figs. 12-19, suggest that the most likely element to be refreshed in order to account for the increased thickness of iron-rich layer is that of the dissolution of \( \text{Cr}^{3+} \). However, the solubility of \( \text{Cr}^{3+} \) ions is far lower than that of \( \text{Fe}^{2+} \), and one would expect the reverse behaviour of that actually found.

If it is assumed that the outer layer of iron and chromium corresponds to the initial composition and structure of the barrier film, then it would seem at first paradoxical that the ferrous ion concentration should be lowest in the inner zone of this film. Cohen's\(^{(12)}\) work, described in Chapter 1, showed that for the passivation of iron in deoxygenated water, an inner spinel structure formed with an outer ferric oxide layer, where the oxygen concentration was highest. The inner chromium-rich layer may therefore be due to two possible reactions, (a) a solid state reaction involving the reduction of magnetite at the barrier film/steel interface by metallic chromium, or (b) the internal oxidation of the steel by anion diffusion through the passive film.

The reaction between chromium metal and magnetite may be expressed as follows:
\[ 8\text{Cr} + 3\text{Fe}_3\text{O}_4 = 4\text{Cr}_2\text{O}_3 + 9\text{Fe} \]

The formation of iron metal would tend to erode away the film/metal interface creating an interfacial zone of the type that is observed. A similar reaction was observed in the oxidation of a 70-30 cupro-nickel alloy, using XPS analysis by Castle and Nasserian-Riabi.\(^{(74)}\) This reaction is expected to occur when the film has first formed. The distances needed for chromium metal to diffuse to the film/metal interface is much shorter than the pathway of diffusing anions that will have to traverse the close-packed oxygen structure of the film, in order to internally oxidise the metal at the film/metal interface. It is therefore likely that the predominant reaction will be that of the reduction of magnetite, followed by the oxidation of the steel by oxygen anion diffusion. The onset of anion diffusion would tend to reduce the rate of the former reduction reaction, for in the presence of oxygen anions, chromium metal is likely to react directly with the oxygen rather than by a thermodynamically less favourable reaction with spinel. Indeed, the diffusion rate of oxygen through austenite is expected to be greater than for chromium.

The distance away from the original film/metal interface affected by internal oxidation and the low density of resulting cations and anions, suggests that internal oxidation may be along grain boundaries and imperfections in the steel. The diffusion of chromium metal, however, is less likely to depend on grain boundary diffusion because of the close proximity of the original film/metal interface, thus resulting in a more dense structure.

A schematic representation of the reaction sequence is given below in Fig.27.
The identification of the composition and possible structure of the entire passive film has been discussed; however, no explanation can be found for the flow-rate dependence upon the development of the ageing process at present.

5.47 Passivity of Stainless Steel in Water at 473°K

The films formed on the samples at 473°K showed similar chemical and structural properties to those formed at 393 and 433°K. However, nickel was present in the extreme outer layer, and traces of Cu⁺ were also observed which were not included in the profiles because of the low level of concentration observed and the difficulty in obtaining suitable spectral definition.

Cation diffusion appears to be high enough in this region to enable extensive film growth to occur beyond the initial barrier film formation. Comparing the film thickness values (see Fig. 25) for after 1 h and 3 h, it would appear that the film growth rate is almost linear. Flow-rate appears to have no significant effect upon the growth of these film, or to their composition.
The chemical profiles of the films formed at 473°K (see Figs. 20-23) show that the build-up of nickel in the outer layer is seen to increase sharply between 1 and 3 h. One would expect that the rate of supply of the nickel ions to the film surface would remain constant with time, after an initial stage where the passive film upon the thermocouple surface breakdown. The proportion of nickel ions incorporated in a developing passive film surface must be a function of the rate of film growth.

If the Mott-Cabrera model is assumed to describe the rate of growth, then:

\[
\frac{dx}{dt} = K e^{-x/K'}
\]

where

\( x \) = the thickness of the film at time \( t \)

\( K \) and \( K' \) are constants

The flux of iron ions \( J_{(Fe)} \) at any instant is given by:

\[
J_{(Fe)} = \frac{K'}{\Omega} e^{x/K'}
\]

where

\( \Omega \) = volume of oxide per metal ion

Assuming that iron and nickel ions have an equal chance of incorporation into the film, and that \( J_{(Ni)} = \text{const.} \), then the concentration of \( \text{Ni}^{2+} \) in the film is expressed in the following way:

\[
[Ni] = \frac{J_{(Ni)}}{J_{(Fe)}} = \frac{\Omega \text{ const.}}{K e^{K'/x}} = \text{const.} \frac{1}{e^x}
\]

The thickness of film remaining after an etch-time \( t_x \) is given by:
\[ X = R \left( t_0 - t_x \right) \]

where

\[ R = \text{etch-rate, which is assumed to be constant} \]
\[ t_0 = \text{time to etch through the entire film} \]

Therefore:

\[ [\text{Ni}] = \text{const} \cdot e^{-\left( \frac{1}{t_0 - t_x} \right)} \]

or

\[ \log_e[\text{Ni}] \propto \frac{1}{t_0 - t_x} \]

A curve is plotted of this function for the 473°K, 6 ml/h, 3 h specimen and is shown in Fig. 28 below.
The points which have been plotted included both the Ni$_2^+$ and Ni metal concentrations, as the Ni metal plots of Fig. 23 suggest that the early appearance of nickel may correspond to nickel ions which have been reduced by the ion-beam. The initial region of the plot shows a good fit but the two lowest plots of Log$_e$[Ni] imply that all of the nickel metal component is attributable to the substrate signal, which is to be expected at this etch-depth.

Whereas this curve shows a good fit in the initial region, the points for the corresponding 1 h exposure do not superimpose onto this plot. It can be seen from the relative levels of Ni$_2^+$ in the outer layer of Fig. 21, that the level of the 3 h specimen is less than would be expected from the 1 h plots. This means that either, (a) part of the surface nickel deposit is not time-dependent, i.e. some precipitation on cooling may occur, (b) the value of J(Fe) increases with time, or (c) the concentration of Ni$_2^+$ is not constant but decreases with time. Of these possibilities, (b) would appear to be in accordance with the observed results, i.e. that the total film thickness is seen to increase markedly between 1 and 3 h. However, further work is required to examine (a) and (c).

Whereas nickel ions are clearly observed in the extreme outer portion of the film, it would appear from the profiles of nickel metal and nickel ions that a portion of Ni$_2^+$ picked up in the early stages of rapid film growth may have been reduced by the Argon ion etching. By adding both species together a general agreement of the dependence of log$_e$ t is seen for both film thickness and time of exposure. This point is borne out by the parallel but lower concentration gradient of Cu$^+$. The Auger spectrum is seen in Fig. 29 below. This ion is observed to a deeper level than the Ni$_2^+$ ions. The parallel nature of the concentration of these contaminants suggests that the rate of deposition is a function of the film growth rate.
- 202 -
Cr$^{3+}$ 2p$_{3/2}$

Cu$^+ L_{MM}$

ETCH TIME

B.E.(eV)

FIG. 29
It would appear, therefore, that the steep concentration profile found for the film formed at 3 h exposure indicates the slowing down of the film growth rate.

The pick-up of nickel ions in the outer layer of the film may or may not have a significant effect upon the resulting passive layer. It is therefore important to investigate more fully the effect of nickel deposition on the iron-rich layer. The figures for the relative atomic % of the cations Fe$^{2+}$, Fe$^{3+}$, Cr$^{3+}$ and Ni$^{2+}$ for the 473°K samples have been expanded to a common etch-time axis in Fig. 30. The shaded portions represent the apparent concentration depletion or enhancement during the etch period 10 to 70 s.

The enhancement of Fe$^{3+}$ in the first 10 s etch period at 1 h is contrasted with a more constant level found at 3 h. This suggests that at 1 h the Ni$^{2+}$ layer is less than one mono-layer in thickness. Transfer of the specimen from the corrosion cell to the spectrometer vacuum enables atmospheric oxidation of the surface Fe$^{2+}$ ions to Fe$^{3+}$ producing the depletion of Fe$^{2+}$ and enhancement of Fe$^{3+}$ observed.

At 1 h exposure the incorporation of nickel results in a marked reduction in the ferrous ion concentration. The ferric concentration does not appear to be reduced. At 3 h exposure the ferrous ion concentration decreases but with corresponding reduction in the ferric ion content. This suggests that the nickel deposition may be selective in the choice of atomic site for deposition. The 3 h exposure suggests that the nickel tends to deposit upon the Fe$^{2+}$ and Fe$^{3+}$ ion sites and therefore attenuate their respective signals, as the Cr$^{3+}$ concentration seems to remain constant. At 1 h, the reduction in the ferrous ion concentration may suggest either selective deposition on ferrous ion sites or substitutes for ferrous ions in the outer structure of the film.
Nakayama et al\(^{(24,25)}\) found that NiFe\(_2\)O\(_4\) spinel formed in the passive film of 18% Cr, 8% Ni austenitic stainless steel when a specimen initially electropolished was exposed to deoxygenated neutral water at 573\(^{\circ}\)K. This spinel was so stable that even heating the film for 3 h at 1273\(^{\circ}\)K in air did not produce the corundum oxide structure. This demonstrates that nickel can have a stabilizing effect upon the spinel structure. This may be in evidence in this work, especially in the film formed at 1 h where evidence is found of nickel ion substitution for ferrous ions.

In nuclear power plant, the incorporation of Co into Fe\(_3\)O\(_4\) layer is also found to give spinels which are resistant to chemical cleaning acids.\(^{(88)}\)

Castle and Thompson\(^{(11)}\) have shown that the presence of nickel foil in a solution of Fe(OH)\(_2\) at 573\(^{\circ}\)K catalyses the Shikorr reaction to form magnetite. The possible catalytic effect of nickel ions upon the solid-state growth of these iron-rich films cannot be ruled out. However, there is no evidence to suggest that film growth occurs by back-deposition, a mode of growth where the Shikorr\(^{(7)}\) reaction might be expected to be catalysed by the dissolved nickel.

The presence of the chromium-rich inner layer is believed to be due to the same solid state reaction suggested for the lower temperatures. Clearly, the cation diffusion at this temperature is sufficiently high to reduce the level of internal oxidation. The composition and rate of growth of the passive film appear to be sufficient to lower considerably the relative thickness of the internal oxidation zone, compared to that of the passive film.
5.50 Conclusions

The development of multiplet analysis and the determination of a range of sensitivity factors led to an extensive improvement in the qualitative and quantitative analysis of the passive layers formed on stainless steel at 393, 433 and 473°K. The data revealed a passive film overlaying an interfacial zone. The absence of a distinct film/metal interface prevented the determination of the etch-rate and total film thickness by the method previously used in the lower temperature study. Nickel from the steel surface did not enter the passive film at any of the temperatures studied.

Whereas the initial passive film formed at 313 and 353°K was seen to increase in thickness with flow-rate, which was attributed to the accretion of an outer contaminant layer, no such behaviour was observed at the higher temperatures of exposure. The specimens exposed to temperatures below 473°K appeared to grow to a limiting thickness, which was attributed to field induced growth, in agreement with Mott and Cabrera's (17) film growth model of the low temperature oxidation of metals.

Although an increase in the chromium level of the 313 and 353°K specimens was observed, the more comprehensive analysis of the specimens exposed to 393 and 433°K revealed what appeared to be an outer iron-rich spinel structure overlying an inner chromium-rich corundum structure. The limited growth suggested low cation diffusion. In the absence of any evidence of selective cation dissolution occurring with the change of flow-rate, it was assumed that the outer region of the film probably conformed to the initial barrier film composition. The chromium-rich inner layer was thought to be the result of the chromium metal of the steel reacting with the magnetite at the metal/film interface, producing \( \text{Cr}_2\text{O}_3 \) and Fe. Thus, modifying the film structure and initiating the
breakdown of the interface. It was thought that, after anion diffusion to the steel surface had occurred, the former reaction rate was reduced, as the chromium metal of the steel reacted directly with the oxygen anions. The preferential oxidation of chromium and the selective attack along the faster diffusion paths of the grain boundaries and imperfections in the austenite lattice was thought to be responsible for the extent of the interfacial zone.

At 473°C cation diffusion was sufficient to sustain continued field growth beyond the initial barrier film. The film showed an inner chromium-rich layer and an extensive iron-rich outer layer. In addition, pick-up of Ni²⁺ from the thermocouple and a trace of Cu⁺ from the heater plate appeared, from their concentrations in the film layers, to indicate that between 1 and 3 h exposure the film growth rate reduced. The nickel ion profile particularly illustrated this reduction in growth rate. The nickel ions were thought to be incorporated in the film as a spinel of the form NiFe₂O₄ which is likely to stabilize the structure of the film. There is insufficient evidence to suggest that the nickel ions may catalyse what appears to be a predominantly solid state film growth of the iron-rich layer.

All the films showed evidence of an initial hydrated structure ageing to a structure having a predominance of oxygen anions.

The presence of Ni⁺⁺ and Cu⁺ contamination suggests that a design modification be made to prevent the ions from interfering with the experiment. The presence of the ions brings into question the conventional use of unlined autoclaves for studies of repassivation.
6.0 GENERAL DISCUSSION

As a result of this study it has been shown that there are various components to the passive layers formed on a commercial grade stainless steel exposed to deoxygenated water, in the range of temperature 313 to 473°K:

(1) An outer water rich contaminent layer
(2) A passive film consisting of hydrated chromium and iron oxides
(3) An interfacial zone, between the passive film and the steel substrate.

XPS was instrumental in detecting a hitherto unsuspected contaminent layer which was present in all of the films but which was most prominent in the 313 and 353°K samples. The thickness of this layer at the lower temperatures was seen to increase with flow-rate. The contaminent layer was thought to be built-up by the acretion of organic molecules, able to bind water to the passive film surface by hydrogen bonding.

At 313 to 433°K the film thickness could be estimated by XPS to be about 2.0 nm, and the film growth was considered to follow the Mott-Cabrera model of "field induced" growth. At 473°K, further film growth occurred which was attributed to a higher rate of cation diffusion at this temperature. Assuming a constant etch-rate, the film thickness at 473°K was estimated to be about 7 nm after 1 h compared with 18 nm formed after 3 h.

The film formed on a 313°K, 3 ml/h, 1 h sample was formed by varying the sample depth with θ, the electron collection angle, to be composed of an iron rich film interspersed with a thinner chromium rich film. This was attributed to the inhomogeneity of the composition of the underlying steel.
The structure of the films formed in the range 313 to 433°K, appeared from stoichiometric considerations to be extensively an iron rich iron-chromium spinel. The less comprehensive analysis of the 313 and 353°K samples only revealed an increase in the level of chromium in the film, with increase of temperature. However at 393 and 433°k the more comprehensive analysis revealed a distinct iron-rich iron-chromium spinel outer layer, and an inner chromium rich layer. As changes in flow-rate did not reveal any selective dissolution of the film throughout the entire temperature range, the iron rich outer layer was thought to correspond to the composition of the initial barrier film, formed by field induced growth. The inner chromium rich layer was probably formed by the reduction of magnetite at the metal/film interface by metallic chromium. This would result in Cr$_2$O$_3$ and metallic iron, resulting in some deterioration of the metal/film interface. Such a reaction could be responsible for the enrichment of chromium in the films formed at 353°K. This reaction would be arrested on diffusion of oxygen and hydroxyl anions to the metal/film interface. The anions would diffuse through breaks in the chromium-rich layer to react directly with chromium and iron. This internal oxidation would therefore extend the interfacial zone by selective attack along grain boundaries and surface imperfections.

At 473°K, the composition of the film and interfacial zone were very similar to those formed at the lower temperatures. However, significant quantities of nickel ions and traces of Cu$^+$ ions were picked up from the solution during film growth. The nickel was probably incorporated in the film as NiFe$_2$O$_4$ spinel, which is extremely stable. A preliminary investigation into the nickel ion profiles revealed that the concentration of the nickel in each of the atomic layers of the growing film was likely to be a function of the rate of film growth. The evidence therefore suggested that film growth in the 1 h period was generally lower than
indicated for the 1 to 3 h period, where a higher growth rate was followed by a sudden fall. At this stage, however, it is apparent that further work is required to evaluate this hypothesis.

The internal oxidation reaction was not apparent at 313 and 353°K, which suggested that the diffusion rates for the anions at these temperatures were considerably lower than at 393 and 433°K, where the interfacial zone was of comparable thickness to that of the passive film. At 473°K, the rate of cation diffusion was greater than for the anions which resulted in an interfacial zone having a depth, a fraction of the thickness of the passive film.

In the study of the initial passive films formed on a stainless steel it is essential that the time of exposure be of the order of a few hours. For such work use of the conventional autoclave is unsuitable as they commonly have extensive heating and cooling times. This problem was overcome in this work by using a pressure vessel housing a corrosion cell and the ancillary equipment. The corrosion cell was made of PTFE to minimise contamination of the water. The built-in heater unit efficiently maintained the desired temperature. The volume of the water contained in the cell was 5 mls, sufficient to cover a standard size XPS sample. This design enabled more rapid heating and cooling to be carried out, as well as reducing the likelihood of thermal gradients being set up in the water.

Contamination of the water was not observed below 473°K, but at this temperature nickel and copper ions were observed. These sources of the contaminants are easily removed as suggested in the text. However, this level of contamination brings into question how much contamination is picked up in the corroden of the conventional unlined metal autoclaves. Indeed it would appear from this study that the observations of contamination is best made by a sensitive surface analysis such as XPS,
in the initial passive films rather than in thicker films where contaminants may be more finely dispersed.

The XPS analytical technique has been evaluated throughout the course of this study, and four main areas requiring further work have become apparent:

(1) In order to improve the accuracy of both quantitative and qualitative analysis, the multiplet analysis operation must enable singlet peaks to be selected having half-widths conforming to the actual values for that species, as well as an appropriate degree of skewness to conform to the normal peak shape. This would increase the accuracy of both curve resolving and curve synthesis.

(2) Extensive work is required to determine the mean free paths of electron through a variety of suitable media. This would particularly aid the determination of sensitivity factors of spectral species emitted from different media and from different oxidation states.

(3) Argon ion etching has been found to be a suitable tool for cleaning steel surfaces, and for the gradual removal of the passive layers to obtain a chemical profile through these films. However, a more extensive study of chemical interfaces would require further knowledge of the kinds of ion etch damage that may occur and indeed the distribution of this damage over the sampled area and within the film depth.

(4) Non-destructive "in-depth" analysis, by varying the electron collection angle $\theta$ and by varying the X-ray source energy should be evaluated more fully to facilitate the study of ion-etch damage as well as to determine between island and layered growth morphology in passive films.
XPS seems eminently suitable to a study of this type, revealing compositional, structural and stoichiometric information. However, the greatest disadvantage of this form of analysis is the length of the analysis time. In a commercial laboratory it may be expedient to combine A.E.S. and X.P.S. for determining chemical profiles of this sort. The faster analysis time of A.E.S. is otherwise out-weighed both by the more comprehensive chemical information available from X.P.S. and the greater suitability of XPS to quantitative analysis. However, it would be reasonable to obtain a chemical profile with AES carrying out intermittent XPS analysis in order to enable a more comprehensive interpretation to be made of the AES data, especially where interesting changes in the chemical profile are apparent.

Whereas the corrosion of stainless steel in high purity water in the temperature range studied is of specific interest to the power industry, it is hoped that the general evaluation of XPS analysis as a suitable analytical technique to work of this work will be of wider interest to laboratories concerned with this kind of work. It has been shown that there is a need to further develop multiplet analysis to enable more exacting quantitative and qualitative analysis to be made. However, at this stage of development of this technique a considerable amount of information has been determined by this study concerning the composition of the passive layers on stainless steel that has not been detected by any other technique.
7.0 CONCLUSIONS

The object of this thesis, as defined at the conclusion of Chapter 1, was to evaluate the use of XPS for surface analysis in corrosion. A relatively simple but industrially important system was defined: the formation of the passive layer on stainless steel in high purity water.

As a result of this study four conclusions have emerged which can be ascribed directly to the use of XPS in this context:-

(1) At ambient or slightly elevated temperatures an outer layer consisting of organic and water molecules is formed on the surface.

(2) At all temperatures up to 473°K the passive film consists of hydrated oxides.

(3) In the temperature range 393 to 473°K the passive film is separated from the bulk metal by an interfacial zone consisting of mixed metal oxides.

(4) At high temperatures ≥ 473°K aqueous phase transport of metallic species is sufficiently important for trivial and sometimes unavoidable metal components in the systems, e.g. thermocouple wire, to be a source of contamination. These ions are apparently incorporated in the passive layer.

The use of XPS is, however, time consuming and may be too expensive for some studies. For example in the present work approximately 1000 multiplets were analysed into singlets. Moreover, as the study developed it was clear that much of the information required for quantitative interpretation of the singlet intensities is not available. The following conclusions concerning the use of XPS as an analytical technique may be stated:-
(5) Escape depths may be taken from the literature, using the commonly held assumption that the surface phase is relatively unimportant. However, the variation of the total signal with phase, which was discussed in Chapter 5 shows that escape depth and species concentration are both important in quantitative analysis. Therefore, further work must be done in this area.

(6) An exploratory study showed that structural information can be derived from angular resolved spectroscopy, but the curves required for analysis of the intensity variation with angle are complicated and would need to be constructed for individual oxide/metal systems.

(7) Concentration profiles can be obtained by ion etching but evidence showed that the use of an assumed etch rate could give inconsistent results. In certain cases etch-rates may be determined by use of a calibration signal from the substrate, but this will not always be possible. In any case it is difficult to use this method once the oxide exceeds a certain thickness, and thought should be given to the inclusion of deliberate markers within the oxide layer.
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