THE INTERACTION BETWEEN STAINLESS STEEL AND COBALT IONS
IN HIGH TEMPERATURE WATER

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

By

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Activity transport in the water circuit of nuclear reactors is an important problem in the nuclear power industry. The active species (particularly cobalt-60) are transported via particulates or in solution and are readily incorporated into the oxide films on stainless steel and Inconel. This thesis describes research using a novel high pressure water system and sophisticated surface analysis together with ion beam etching to reveal compositional and chemical state information about the incorporation of cobalt into the thin films that form on stainless steel immersed in water at temperatures up to 473 K. The mechanism by which this occurs and the influence of temperature and water chemistry have been examined.

It has been shown that the change in film growth mechanism previously observed to occur between 433 K and 473 K, occurs at or close to 473 K. Dosing small quantities of cobalt into the water resulted in the incorporation of divalent cobalt in the oxide film both at 413 K and at 473 K. The proportion of incorporated cobalt was directly related to solution concentration and was considerably greater at 473 K than at 413 K, with a further increase in cobalt uptake when the water chemistry was modified to simulate reactor chemistry.

The incorporated divalent cobalt is present at the expense of trivalent chromium. This is not explained by current models for film growth, and it has been proposed that it results from cobalt substituted magnetite having a greater stability than the mixed iron/chromium oxide otherwise forming on the surface. This would result in iron, normally lost into solution, being co-precipitated
with cobalt in the film. This incorporated cobalt has no apparent
effect on film thickness, and suggests that the cobalt containing
oxide is as effective as the native oxide in controlling film growth
kinetics.

Advanced computer techniques have been developed in order to
obtain a greater understanding of the chemical environment of the
incorporated cobalt.
ACKNOWLEDGMENTS

The author wishes to express his sincere thanks to his supervisor, Professor J.E. Castle for his valuable advice and encouragement, and to AERE Harwell for funding the research. It is with regret that I have to record the death of Dr. A.J. Tench of Harwell on March 17th 1983, as he was responsible for the initiation of the research contract, and followed the work with great interest. Thanks are also due to Dr. N. Large of Harwell for helpful discussions and to members of the Department of Metallurgy and Materials Technology, and in particular the Surface Analysis Group, for many hours of fruitful discussion.
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<td>AES</td>
<td>Auger Electron Spectrometry</td>
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<td>AISI</td>
<td>American Iron and Steel Institute</td>
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<td>ASEA</td>
<td>Allmanna Svenska Elektriska AB.</td>
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<td>ASTM</td>
<td>American Society for the Testing of Materials</td>
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<tr>
<td>BWR</td>
<td>Boiling Water Reactor</td>
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<tr>
<td>CANDU</td>
<td>CAntadian Deuterium reactor</td>
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<td>CERN</td>
<td>Consieul Europeenne pour la Recherche Nucleaire</td>
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<td>EFFY</td>
<td>Effective Full Power Years</td>
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<td>EIL</td>
<td>Electronic Instruments Ltd.</td>
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<td>EPMA</td>
<td>Electron Probe Micro-Analysis</td>
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<td>ESCA</td>
<td>Electron Spectrometry for Chemical Analysis</td>
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<td>FWHM</td>
<td>Full Width at Half Maximum peak height.</td>
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<td>Low Oxidation state Metal Ions</td>
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<td>PTFE</td>
<td>Poly-Tetra-Fluoro-Ethylene</td>
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<td>PWR</td>
<td>Pressurised Water Reactor</td>
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<td>Reactor Water Clean Up (system)</td>
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<td>UHV</td>
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1. INTRODUCTION

One of the main areas of research into the operation of water cooled reactors concerns the build-up of radioactivity in components of the primary water circuit. This is caused by the transport of activated species from the core of the reactor, and their subsequent incorporation in the oxide films present on out of core components. The main culprit is cobalt-60 but cobalt-58, manganese-54, iron-59, and chromium-51 also contribute to the problem. Cobalt-60 has a long half-life (5.2 years) and emits very penetrating gamma radiation as it decays, hence even very small quantities in a reactor circuit can lead to large radiation fields. It now contributes over 80% to the radiation fields of the Pickering CANDU reactors, and this is typical of many reactors operated for several years. Citing a 1975 survey of light water reactors R.Vanbrabant and P.deRegge reported that the average cumulative dose per plant operating year was 178 man-rem in 1969 and had increased to 427 man-rem by 1974. Temporary personnel must be recruited to enable maintenance and repair activities which could not be accomplished within the exposure limits of the on-site work force. Temporary workers must be transported, housed, trained and returned, the net results being only a short period of effective work within a high radiation field.

This document describes work at the University of Surrey sponsored by the United Kingdom Atomic Energy Authority (Harwell) to use ESCA (Electron Spectrometry for Chemical Analysis) techniques to study the way in which dissolved cobalt-59 is incorporated into the oxide films forming on stainless steel in high temperature water. Using a combination of ESCA analysis and ion beam etching both the
distribution and the chemical state of incorporated cobalt have been studied as a function of depth in the thin oxide films that are formed.

The results have indicated that a change in growth mechanism occurs at or close to 473 K, and that there is a resulting change in both the growth kinetics and the distribution of incorporated cobalt. This has been discussed in relation to proposed mechanisms for cobalt incorporation, and mechanisms of film growth both above and below 473 K.

The need for detailed analysis of the ESCA spectra from transition elements highlighted inadequacies in the existing data handling system, and as a result a large interactive software package has been written in order to provide facilities previously unavailable. These include sophisticated peak fitting, non-linear background subtraction and area calculation, and automatic peak identification and annotation.
Before discussing the nature of cobalt uptake by the oxides on stainless steel it is necessary to survey the extensive documentation on the behaviour of stainless steel in water between room temperature and 573 K.

2.1 THE AQUEOUS OXIDATION OF STAINLESS STEEL

The study of the oxide that forms on stainless steel falls into two main categories:

i) The thin protective film that forms at room temperature, and gives stainless steel its great resistance to corrosion.

ii) The thicker film that forms when stainless steel is used at higher temperatures (523-623 K) in pressurised water.

The study of both types of oxide was based on earlier experiments on pure iron or mild steel. The very thin protective film that forms on stainless steel at room temperature eluded the best attempts of researchers to understand its composition for many years, until sophisticated surface analysis techniques became available in the early 1970's. The thicker films formed at high temperature were somewhat easier to analyse, though a comprehensive growth mechanism was not proposed until the late 1960's. The background to our present understanding of both types of films is discussed in the next two sections.
2.1.1 THE PASSIVITY OF STAINLESS STEEL

The phenomenon of passivity is reported\(^3\) to have been first noted by J. Keir\(^4\) in 1790. Keir induced the passive state in iron wire by reacting it with concentrated nitric acid in which silver had previously been immersed. Silver immediately precipitated on the wire, and thus stopped further reaction between the wire and the acid. The deposited silver then dissolved leaving the iron wire with a bright surface. In this 'altered' state the wire would not react with nitric acid, unless it was scratched, or coupled to an 'unaltered' piece of wire. Keir thus concluded that this altered state was a surface phenomenon.

In 1807 Hisinger and Berzelius\(^5\) showed that passivity could be induced by anodic polarisation, and in 1836 Schonbein\(^6\) showed that anodic passivation of iron could be achieved in dilute nitric, sulphuric and phosphoric acids, but not in the presence of halides. It was Schonbein\(^7\) who first used the term 'passive' to describe this altered state.

There was considerable research into the passive state in the early 19th century, notably that of Faraday. He showed that the surface film responsible for passivity was not an electrical insulator, and proposed the 'oxide film theory' of passivity\(^8\). This being the generally held theory until the end of the century, when the work of Hittorf\(^9\)-\(^10\) on chromium, and Muller\(^11\)-\(^13\) on the optical reflectance of active and passive iron cast some doubts on the existence of an oxide film. Other theories then gained some headway including those invoking a modification of the metal surface\(^14\)-\(^20\), the reaction velocity theory\(^21\)-\(^24\), and the adsorption theory\(^25\)-\(^28\).
It was in 1911 that Monnartz first reported the passive properties of Fe-Cr alloys containing over a certain chromium level, an observation narrowly missed by Stodart and Faraday some 90 years earlier when they produced iron-chromium alloys that fell short of the critical chromium level. The commercial application of these stainless steels followed rapidly, and in this way passivity was widely applied before the nature of the phenomenon was understood.

In 1927 Evans showed that oxide films could be stripped from metals by immersing the specimen in a solution of iodine in 10% aqueous potassium iodide. He managed to strip an oxide film from passivated iron and this brought the oxide film theory back into favour. The oxide stripping technique was modified by Vernon et al. who employed a saturated solution of iodine in methanol. They first examined iron and mild steel, then progressed to chromium-nickel alloys and stainless steel. Fragments of the stripped oxide were examined by gravimetric analysis, X-ray diffraction, and by transmission electron microscopy. Oxide stripping was a valuable technique and was used by many workers.

Further evidence that passivity was due to the formation of an oxide film came from Tronstad and Borgmann in 1934. They used ellipsometry to show that the air formed oxide film on iron is strengthened or replaced by a thicker and denser oxide when iron is passivated in nitric acid. They also showed that some kind of film exists on stainless steel.

Although film stripping and ellipsometry showed that passive
surfaces were often covered by thin oxide films, the 'adsorption theory' was still supported by many workers. From 1946 to 1959 Uhlig proposed that an adsorbed oxygen film is commonly the primary source of passivity. In 1960 Mueller proposed a link between the adsorption theory and the oxide film theory, suggesting that the formation of an oxide barrier layer might be preceded by the chemisorption of oxygen thus reducing anodic dissolution.

Analysis of passive films continued using ellipsometry, film stripping, electron diffraction, X-ray diffraction and gravimetric analysis until the advent of new methods of surface analysis in the late 1960's. These were Auger electron spectrometry (AES) and X-ray photoelectron spectrometry (XPS). These enabled the composition of very thin passive films to be analysed without removal from the substrate. The arrival of these two powerful surface analytical techniques resulted in a great increase in passive film analysis.

In 1972 Lumsden and Staehle published an AES study of the passive film on stainless steel. Using an ion beam to etch away the film they were able to obtain a chemical profile through the film. They found considerable chromium enrichment over the steel composition, but no nickel enrichment.

Many subsequent papers reported the effect of different anodic potentials, and the effects of different surface preparations on film composition. Of more interest to this study are the effects of increasing temperature on composition and bound water content reported by Saito et al. He showed that the bound
water in the film decreases with increasing temperature reaching a steady level of 5% above 313 K. The chromium content of the film was found to increase slightly up to the maximum temperature investigated (323 K).

The study of changes in the film on stainless steel with increasing temperature was more extensively investigated by Castle and Clayton between 313 K and 353 K, using XPS and argon ion bombardment to etch the surface. They carefully investigated the time related effect of transferring thin films in humid air from the aqueous medium in which they were formed to the ultra high vacuum (UHV) of the spectrometer (1 to 5 X 10\(^{-9}\) N/m\(^2\)). This showed that little change occurs in the first 300 seconds either to the oxygen/iron ratio or the chromium/iron ratio. The oxide films formed were found to be enriched with chromium with respect to the steel composition (AISI Grade 304), with an overlayer of organic molecules and bound water. Those formed at 353 K were thicker (2.5-3.0 nm) than those formed at 313 K (1.0-2.0 nm), but had very similar chemical profiles.

In later work Clayton extended this investigation to 473 K using a PTFE corrosion cell to eliminate metals. At 393 K and 433 K the films formed were observed to have an iron-rich, possibly spinel region in the outer region of the film, and an inner chromium rich region, possibly of corundum structure. This structure persisted at 473 K, though the growth rate of the film was considerably faster and exhibited an almost linear rate of growth over the 1 and 3 hour exposure periods examined (fig.1). The bases of the films appeared to have an interfacial zone of oxidised
Fig. 1 Effect of temperature on oxide growth rate
chromium and metallic iron and nickel. This was thought to be due to the internal oxidation of chromium by magnetite, though the possibility that this was an effect induced by ion beam profiling was not discounted. The films observed between 313 K and 433 K were thought to form by a field induced growth mechanism\textsuperscript{59}, whereas at 473 K further growth occurred due to the high rate of cation diffusion. It is of interest to note that the pickup of copper and nickel contamination from solution was observed at 473 K, probably being incorporated into the film as it grew.

The change in mechanism between 433 K and 473 K was further discussed at the Fourth International Symposium on Passivity\textsuperscript{60}. Fig. 2 shows the effect of temperature on film thickness and separation of iron and chromium compounds in the film. The film was thought to be composed of hydrated spinel type oxides which form a barrier layer at 313 K to 433 K, but continue growing due to enhanced cation diffusion, possibly through an aqueous phase, at 473 K.

Work on this higher temperature growth mechanism is more fully discussed in the next section.

2.1.2 THE OXIDATION OF STAINLESS STEEL IN HIGH TEMPERATURE WATER

Plant observations show that in a reactor environment (558-573 K) duplex oxide scale forms on stainless steel surfaces. The outer layer is composed of coarse crystals of magnetite or nickel ferrite, and the inner layer is a spinel rich in alloying elements. The inner layer grows with zero volume change, as the inner/outer layer interface maintains the same position as the original unoxidised metal surface.
The thickness of the oxide as a function of temperature, as determined by the point at which oxygen drops below 40 a/o. The position of the interface zone derived from the total signal is shown by horizontal bars. The vertical hatched bars illustrate the trend for chromium and iron compounds to separate with increased temperature.
The understanding of this form of film growth dates back to the early 1960's, when Potter and Mann were investigating the oxide formed on mild steel in high temperature water. They observed the growth of duplex films (fig. 3), at a parabolic rate and concluded that the oxidation was controlled by the rate of oxygen diffusion within the lattice. However, the work of Kingery, Hill and Nelson showed that oxygen diffusion in the spinel lattice was too slow to account for the observed film growth rate. It was thought that the oxygen diffusion rate might be enhanced by the presence of hydroxyl ions.

At the same time Bloom and co-workers had corroded iron under very similar conditions and had formed a continuous film, rather than the duplex film formed by Potter and Mann (fig. 3). It was found that the continuous film would revert to the Potter-Mann type film if damaged.

From 1963 to 1966 evidence was produced to show that there were interconnecting pores in the duplex oxide. It was further shown that the oxygen diffusion argument was not valid, thus making pore diffusion a likely mechanism.

In 1966 Castle and Mann showed that whether a Bloom type film or a Potter-Mann type film grew was determined by the rate of transport of dissolved iron away from the corroding surface. If dissolution is suppressed the continuous Bloom type film forms, encourage iron dissolution and a porous duplex oxide forms. In 1969 Castle, Foster and Masterson proposed a mechanism for the growth of the duplex film based on the diffusion of soluble iron through interconnecting pores in the oxide, and a competition between
FIG 3. TYPICAL METALLOGRAPHIC SECTION OF DUPLEX FILM
oxidation and dissolution at the metal/oxide interface. This competition leads both to the interconnecting porosity and the zero volume change of the inner layer oxide (fig.4). This model, developed on the behaviour of mild steel in water at 323-423 K, gave reasonable agreement with the observed rate law, and correctly predicted the behaviour of nickel/aluminium alloys under conditions leading to duplex layer formation. The model did not however explain why magnetite is not precipitated in the pores, thus blocking them and slowing growth.

Fig.5 shows in detail the mechanism proposed to explain the zero volume change of the inner layer. Oxide crystals nucleate at the metal/solution interface, and grow by the solid state diffusion of metallic ions to the crystallite surface, where new oxide forms. The rate of growth of the crystallite slows as the diffusion path gets longer, and growth halts whenever the crystallite touches another, as the solution is excluded. While the crystal is growing there is continual dissolution of the unoxidised substrate, until the crystal is eventually isolated from its source of metal ions, and ceases to grow.

In 1972 Bignold, Garnsey and Mann showed that the above mechanism does not lead to pore blocking if there is a stoichiometry gradient in the oxide. This allows there to be a diffusion gradient for dissolved ion species whilst still maintaining solubility equilibrium throughout the oxide. The rate controlling step is the physical process of diffusion through the solution filled pores. The stoichiometry gradient required in the oxide is such that the oxide nearer the metallic substrate will contain a higher proportion of
Fig. 4 A representation of the overall corrosion process
(Movement of H⁺ ions and electrons are omitted)

IONIC TRANSPORT
Na₂FeO₂

INTERFACE REACTIONS

OXIDATION
Fe + 2H₂O → Fe(OH)₂
+ 2H⁺ + 2e⁻

3Fe + 4H₂O → Fe₃O₄
+ 8H⁺ + 6e⁻

DISSOLUTION.
Fe(OH)₂ → FeO₂⁻ + 2H⁺

Fig. 4 The mathematical model for the overall corrosion process
FIG. 5 SCHEMATIC MODEL OF GROWTH AT METAL/OXIDE INTERFACE
ferrous iron. It is well documented that magnetite, and other spinels are capable of changing their stoichiometry over quite a wide range $77-80$.

Some years later Berge$^{81}$ proposed an alternative process by which iron species could diffuse through the inner layer without depositing and blocking the pores. This was based on the effect of a hydrogen concentration gradient across the oxide on the solubility of dissolved iron species. The possibility of hydrogen evolved at the metal/oxide interface creating such a gradient was considered by Bignold et al$^{76}$, but rejected because a variation in hydrogen concentration implied a potential drop across the oxide. This was not detected by measurement of the response to transient charging, so the possibility was rejected. Berge$^{81}$, however, showed that Bloom type films could be grown on his specimens if hydrogen diffusion through the metal was encouraged, whereas Potter-Mann type films grew on identical specimens if hydrogen was forced to diffuse through the oxide. Which, if any, of the two proposed mechanisms predominates is still a matter for conjecture.

So far we have considered only the formation of duplex layers on iron or carbon steel, but the same type of film was found on stainless steel. In 1965 Warzee et al$^{82}$ reported duplex layer formation on grade 304 stainless steel after oxidation for 1000 hours at 773 K in steam. The outside layer was highly crystalline magnetite, free of chromium or nickel whereas the inner layer was rich in these elements. In 1967 Warzee$^{83}$ found similar films on specimens of AISI 410 and AISI 304 steels corroded in water under varying conditions, between 473 and 623 K.
Duplex film formation is found on stainless steel under a wide variety of conditions, and is essentially the same as the films Potter and Mann observed on iron. The main difference being the presence of nickel and chromium in the inner layer spinel. The outer layer is predominantly magnetite, but may include some nickel. The growth mechanism proposed by Castle, Foster and Mann has proved to be equally applicable to duplex film formation on carbon steel and on stainless steel in high temperature water.

2.2 NUCLEAR PLANT OBSERVATIONS

As mentioned in chapter 1 a tendency towards increasing radiation levels has been noted in all water cooled reactors. Fig.6 shows this for Westinghouse 'U-tube' steam generators on several PWR's, and fig.7 shows this for recirculation pump suction piping on several BWR's.

The radiation levels vary widely between plants and are undoubtedly influenced by the reactor design, water chemistry, reactor water clean-up (RWCU) system, and shutdown/decontamination procedures.

As early as 1961 there was sufficient concern about this topic to warrant an international tripartite conference (Canada, UK, and USA) to discuss the 'Transport of Materials in PWR Systems'. By the end of the 1960's some 4 effective full power years (EFPY) of BWR and PWR operation had been accumulated, and the problem of increasing radiation fields was confirmed. The problem has been, and still is, being approached from many angles.

A solution that might immediately spring to mind is to remove
FIGURE 6

Dose Rate (R/hr)

Time—Effective Full Powered Years (EFPY)

PWR STEAM GENERATOR CHANNEL HEAD RADIATION FIELDS
FIG. 7 Shutdown radiation levels on BWR recirculation pump suction piping
all possible cobalt sources from the water circuit and feedtrain. The hardness of some cobalt alloys, however, makes them essential for some applications where wear resistance is required. The use of other materials such as Nitronic 60, and Inconel X750 in place of the conventional Haynes 25 and Stellite 6 alloys is currently being tested at Millstone-1 BWR in the USA. The steels used in the water circuit and the Inconel alloys used in the steam generators may also contain cobalt as an impurity, and the economics of specifying very low cobalt contents for these materials may not be justified in terms of the saving in radiation dose from the plant.

It seems likely that activity transfer can be reduced by using the correct water chemistry, though to model this requires an understanding of the fundamental mechanisms of activity transportation. The majority of models proposed to date fall into the same general pattern and certain mechanisms are now achieving worldwide acceptance.

Most of the models for activity transfer support the idea that crud (i.e. suspended oxide particles) is mainly responsible for the transport of activity. For this reason there are many research groups working on the possibility of filtering crud from the water circuits. These filters must work at operating temperature (573 K) and must have a high throughput. One of these on which considerable interest rests is the electromagnetic filter, which has been in worldwide use in conventional power plants for some time.

Another possible answer to the problem of activity transport is periodic decontamination. This has widespread usage and usually
involves the individual decontamination of system components. It is obvious that there is considerable interest in the development of a method for decontamination of the entire system, using a low concentration reagent which can subsequently be removed together with dissolved active material by ion-exchange filters. Typical of this is the LOMI reagent developed in this country and currently being tested on the Winfrith SGHWR.

Plant observations show that the oxides that form inside stainless steel primary water circuit tubing are basically of the 'Potter-Mann' type discussed in section 2.1.2. The inner layer is a mixed spinel, rich in chromium and nickel. The outer layer is nickel ferrite, and may also contain considerable haematite, mainly in BWR's as these are run with a more oxidising water chemistry than PWR's. The outer layer is generally loosely adherent and appears to be formed partly by the deposition of crud. The inner layer is much more continuous, seems unaffected by the water chemistry, and adheres strongly to the steel substrate.

In a recent report A.B. Johnson et al examined the duplex films formed on several BWR's and PWR's. On stainless steel in BWR's a loosely attached outer layer was found, over a dense inner layer up to 2 microns thick. The inner layer was found to contain 80% to 90% of the radioactive nucleides, this was assumed to be due to Co-60 cations which have substituted into the spinel lattice. This preference of the activated cobalt for the inner layer has also been observed by other workers, who have also noted that the cobalt/iron ratio in the outer layer is similar to that of the water borne crud (≈0.1%), whereas that of the inner layer is higher (0.1 to
A linear relationship between the Co-60 surface concentration and the water conductivity has also been observed by Comley and Bird\(^8\) (fig.8), and this has been attributed to the dependence of cobalt pickup on the corrosion rate.

Another report on the oxides on out-of-core components\(^9\) separated Ni-rich and Cr-rich spinels as two components of the inner layer. The outer layer haematite was less active than either spinel and was the same as that of the crud suspended in the reactor water. The nickel content of both spinels was close to that of the stainless steel. Here cobalt was thought to be able to reach equilibrium with the reactor water in a short time due to the high diffusion rates of cobalt in the spinels.

In Swedish BWR's the oxides on out-of-core components have been studied over several years\(^4\). Again the oxides are found to be two layered. The inner layer is reported to be more dense and to contain a higher concentration of alloying elements than the outer layer, and has the ability to absorb ionically dissolved alloying elements from the reactor water. The outer layer has a lower proportion of alloying metals and contains a relatively large amount of haematite. The haematite particles may be deposited then partially embedded in the growing oxide. In typical reactor water 90% of the cobalt is dissolved or in the form of fine particles below 0.45 microns diameter, typical concentration is 20-50 ppt.

Under steady state operating conditions the water chemistry is fairly well known and the methods of activity transport can be
Fig. 8. A comparison of $^{60}$Co retention rates in blowdown line over two operating periods

Based on data from 7 BWRs at 830-1600 EFPDS by W.R. Dehollander of GE(USA)

Variation of $^{60}$Co activity retained on coolant pipework and reactor coolant conductivity
roughly modelled, however during shutdown dramatic changes occur (figs 9 and 10)\(^2\). The amounts of radioactive species increases considerably, and the levels of all dissolved material changes considerably from the norm. Little is known of the mechanisms in operation, and a few groups\(^95\) are now turning their attentions to these lower temperatures in order to shed light on the oxide/solution interactions.

2.3 ACTIVITY TRANSPORT STUDIES

A small number of test loops have been set up around the world to look into the problems of activity transport. The simulation of reactor water conditions is, however, not very easy as the loops must be operated at high temperature and pressure whilst maintaining control of water purity to very fine limits. Wherever the problem is being studied models are being developed to predict the influence of different parameters on radiation fields. These models are based both on the results from test loops and plant observations. Most of them remain, however, semi-empirical. There are still too many aspects of the corrosion process about which we have little knowledge. One of the areas is the mechanism by which activation of out-of-core surfaces occurs, and the influence exerted on this by the reactor water chemistry. This is the area of concern to this project and is considered below.

In a recent paper\(^96\) Anstine and Naughton reviewed the possible mechanisms for cobalt deposition on out-of-core surfaces. There are two main ways in which this can occur :-
FIG. 9 CHANGES DURING REACTOR SHUTDOWN
VARIATION OF THE ACTIVITY OF THE PRIMARY COOLANT DURING SHUTDOWN

CW = COOLING WATER
F = FILTRATE

FIG. 10 CHANGES IN COBALT LEVELS DURING SHUTDOWN
i) deposition of insoluble particles, 'crud'.

ii) incorporation of soluble cobalt-60 into the indigenous corrosion film.

The second of these accounts for the majority of activation, and 90% of the cobalt-60 is typically present in the inner layer (Section 2.2). There are three possible mechanisms by which Co-60 may get there:

i) incorporation into the crystal structure as the oxide is formed

ii) chemical exchange of Co-60 for other elements in the oxide.

iii) isotopic exchange of Co-60 for Co-59 in the oxide.

The fraction of cobalt in the film has been seen to be a function of the concentration of cobalt in solution, though this is not supported by all workers. Dehollander has proposed that only a certain small proportion of the atomic sites in the spinel lattice may be available for cobalt substitution. Anstine and Naughton concluded that chemical and isotopic exchange are probably the two most important mechanisms, and are continuing tests to look into this in a test loop in the RWCU system of Unit 2 of the Edwin I Hatch nuclear plant. The chemical exchange mechanism is supported by Hemmi et al who have assumed that this can be achieved by solid state diffusion of cobalt within the oxide. From the distribution of
specific activity in the oxides formed in a BWR, they have calculated the diffusion rates of cobalt in Ni-rich spinel and Cr-rich spinel to be $1.3 \times 10^{-16}$ and $2 \times 10^{-17} \text{ cm}^2/\text{sec}$ respectively. This mechanism is also supported by Walton and Hesford\textsuperscript{98}.

Lin et al\textsuperscript{92} have included this mechanism in their mathematical model of the corrosion process, but place more emphasis on the incorporation of cobalt during oxide formation. They too have noted that the cobalt content of films formed on type 304 stainless steel was nearly proportional to the cobalt content of the water in laboratory tests (temperature unspecified).

In Sweden Hermansson et al\textsuperscript{95} recently reported results from their 'Maggan' test loop, where data is being acquired for mathematical modelling. They were not specific about the mechanisms by which deposition was thought to occur. Another computer model named 'CRUD' being developed by ASEA-ATOM in Sweden, assumes out-of-core oxides to be single layer and to have a constant base metal corrosion rate. The cobalt incorporation mechanism is again unspecified.

Another computer simulation program 'RADTRAN' recently reported by Horvath\textsuperscript{99}, tries to encompass previous models, and appears to favour the activation of surfaces by incorporation during growth, as proposed by Lister\textsuperscript{100}, rather than the ion exchange mechanism.

Lister used a stainless steel test loop containing recirculating water at 573 K\textsuperscript{101} to study deposition, and came to the conclusion that it is the corrosion of the surface that controls the activation. He found that the use of first order deposition and release coefficients was unsuitable to describe this form of activation.
and went on to propose his own mathematical model\textsuperscript{100}. This is based on the oxide growth mechanism shown in fig.4, as discussed previously for the growth of duplex films on mild steel in high temperature water\textsuperscript{75}. Cobalt is incorporated at the base of the inner layer and also deposited in the outer layer. The amount of cobalt is thus proportional both to the rate of film growth and the cobalt concentration in the reactor water.

A similar model was proposed by Dehollander\textsuperscript{97}, however this assumes that cobalt can only substitute into the growing spinel at a fixed number of iron sites. From plant observations he deduced that the amount of cobalt in the oxide does not appear to change with the cobalt concentration in solution, and that the iron/cobalt ratio in reactor oxides is fixed at around 200:1.

In summary, it can be seen that the out-of-core deposition model used for activity transportation modelling varies considerably between different groups of workers. The formation of a duplex film in which the majority of activity is found in the inner layer is generally recognised. A majority of models assume that the level of cobalt in the oxide depends on the solution concentration, however there is considerable disagreement over the mechanism of incorporation. It is still not known whether cobalt is able to diffuse sufficiently quickly within the film to achieve equilibrium or whether it is incorporated during growth then fixed due to lower diffusion rates.

An understanding of the mechanisms of incorporation will aid control of uptake and the development of 'soft' decontamination techniques such as the use of the LOMI reagent discussed previously.
2.4 OBJECTIVES OF THIS INVESTIGATION

The computer models used to predict the rate of cobalt incorporation only consider the activity level of the entire film. Information is still required on the distribution of cobalt through the oxide, and how this varies with time, water chemistry and temperature. Research in this area will lead to a better understanding of the mechanisms of cobalt incorporation, thus not only enabling better activity transport models to be created, but will also benefit those investigating the decontamination of reactor components by the removal of the active oxide film. This understanding is likely to be achieved by the pursuit of the following objectives:

i) To study the growth kinetics and composition of cobalt free films at high temperatures.

ii) To find the effect of cobalt on film composition and kinetics.

iii) To etch through cobalt containing films and thus reveal the cobalt distribution.

iv) To find the relationship between cobalt concentration in solution and cobalt incorporation, and the effect of temperature and water chemistry on this relationship.

v) To reveal the chemical state of cobalt within the film

vi) To study the effect of modifying the water chemistry on the relationships above.

The combination of surface analysis by photoelectron spectrometry and ion beam etching has provided a technique capable of producing composition profiles of the thin oxide films formed on
stainless steel in high temperature water. It is the aim of this investigation to use this technique to study the uptake of cobalt-59 by stainless steel exposed to cobalt dosed water. To minimise the possibilities for metal-ion transport in the experimental system a non-metallic, low volume cell within a nitrogen pressurised vessel will be used. It is recognised that the attendant disadvantage of this method is the upper temperature limit of 473 K.
3. SURFACE ANALYSIS

The surface analytical techniques mentioned at the end of the last chapter analyse only the top few nanometres of a surface, and are thus quite distinct from electron microscopy techniques such as EPMA, which have an analytical depth of the order of one micron, a factor of a thousand greater. The reason that AES and XPS are so sensitive is that they depend on the ejection of low energy electrons from the specimen being analysed. These electrons have only a short escape depth due to the high probability of them being stopped by inelastic collisions within the specimen.

X-ray photoelectron spectrometry (XPS) is the preferred technique when chemical state information is required and spatial resolution is not essential. This technique is discussed in the following sections of this chapter, whilst the use of ion beam thinning to obtain chemical depth profiles is discussed in the next chapter.

3.1 HISTORICAL BACKGROUND

Photoelectrons are electrons liberated from a surface by incident electromagnetic radiation. The photoelectric effect was first reported by Hertz\textsuperscript{102} in 1887, who observed that a spark occurs more readily between two electrodes if the negative electrode is illuminated by ultra-violet radiation. Some 10 years later Thompson\textsuperscript{103} discovered the electron, and over the next few years the effect was shown to be due to the emission of electrons by metals while illuminated.

The photoemission process could not be explained by the
classical electromagnetic theory of light until, in 1905, Einstein\textsuperscript{104} put forward an explanation based on an extension of Planck's quantum theory of thermal radiation. This was based on the following assumptions:-

i) Electromagnetic radiation of frequency $\nu$ consists of quanta of energy called photons, which have energy $E=h\nu$ and travel at the speed of light.

ii) In the photoemission process one photon is completely absorbed by one electron, which thereby gains the quantum of energy and may be emitted from the metal.

If the quantum absorbed by the electron is greater than the binding energy of the electron then it is released from the metal and takes up the balance of the energy in the form of kinetic energy. Thus the kinetic energy is given by :-

$$\frac{1}{2}mv^2 = h\nu - E.E. - W$$

Where the work function ($W$) is the minimum energy required to release an electron from the surface of the metal.

By 1912 Einstein's theory was generally accepted, and in 1921 he was awarded the Nobel Prize in Physics "for the photoelectric law and his work in the domain of theoretical physics".

The work function term in Einstein's equation attracted much interest and between 1915 and 1940 considerable effort was expended on the acquisition of work function values for different metals.
However, poor vacuums and insufficient care in the surface preparation has meant that many of the results obtained are only roughly approximate by today's standards.

The use of X-rays as the exciting radiation (XPS) dates back to 1914 and 1921. The kα lines of silver or molybdenum were used to excite photoelectrons, and these were passed through a magnetic analyser to give a spectrum, which was recorded on a photographic plate. Broad bands could be seen in the photoelectron spectrum which were attributed to the atomic shells. Resolution was however poor due to the broad X-ray linewidth and poor analysers. The technique soon lost favour to the newer techniques of X-ray absorption and X-ray emission spectroscopy.

XPS did not re-emerge until 1951 when Seigbahn and co-workers in Uppsala embarked on a program to get high resolution XPS spectra. The first spectrum was obtained in 1954, and it was soon realised that the bands observed previously by Robinson and de Broglie ended with a sharp line at the high energy threshold. This was correctly interpreted as photoelectrons emitted according to Einstein's law without suffering any other energy losses. These lines were then used in a comprehensive redetermination of the binding energies of electrons.

Seigbahn's research group pioneered many developments including monochromated X-radiation, new X-ray sources, and the use of multi-channel analysers to reduce the time taken to acquire a spectrum. It was this research group that first observed changes in the binding energy of core levels according to chemical state, and consequently introduced the term ESCA - electron spectroscopy for chemical
Since the late 1960's ESCA equipment has been available from many different companies. The use of ion beam thinning has enabled greater depths to be analysed, thus making it possible to construct chemical depth profiles. Data is now usually handled by computer in a digital form, enabling more sophisticated interpretation of the qualitative and quantitative attributes of an ESCA spectrum. These developments have changed ESCA equipment from a very useful scientific technique, to a powerful technological tool. It is now used throughout the world in areas such as corrosion, adhesion, catalysis, coatings, wear, and electronics.

3.2 ESCA THEORY

Any electromagnetic radiation with energy greater than the work function may excite photoelectrons from a metal. In order to acquire information about the electron energy levels in the specimen it is necessary to use a radiation source of well defined energy. Classical photon sources fall into two categories. There are those based on rare gas discharge lamps in the range of 10 to 50 eV. They have a linewidth of only a few meV, but can only excite photons from the outermost atomic orbitals. These sources fall into the ultra-violet range, hence their use is referred to as ultra-violet photoelectron spectroscopy (UPS). Where core electrons need to be analysed a higher energy source is needed, and the two most used are Al kα and Mg kα. The most common sources together with their energies and linewidths are listed in the following table.
<table>
<thead>
<tr>
<th>SOURCE</th>
<th>ENERGY (eV)</th>
<th>LINewidth (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>He I</td>
<td>21.22</td>
<td>3</td>
</tr>
<tr>
<td>He II</td>
<td>40.82</td>
<td>17</td>
</tr>
<tr>
<td>Mg kα</td>
<td>1253.6</td>
<td>680</td>
</tr>
<tr>
<td>Al kα</td>
<td>1486.6</td>
<td>830</td>
</tr>
</tbody>
</table>

The greater linewidth of the X-ray sources limits the resolution of XPS spectra to 0.1 to 0.2 eV. This can be improved upon, at the expense of a considerable reduction in count rate, by the use of a monochromator such as a bent quartz crystal. The use of this technique can reduce the X-ray linewidth to 160 meV, and totally remove X-ray satellites and Bremsstrahlung radiation.

Fig. 11 shows the process of photoelectron emission diagramatically. As the energy of the incoming photon is well defined, then measurement of the kinetic energy of the photoelectron will give us the binding energy of the orbital from which it was expelled, thus:

\[ E_{KE} = h\nu - E_{BE} - W - E_R \]

Where:

- \( E_{KE} \) = Measured kinetic energy of photoelectron
- \( E_{BE} \) = Binding energy of electron before emission
- \( h\nu \) = Photon energy
FIG. 11 EXCITATION PROCESS RESULTING IN INNER SHELL VACANCY AND EJECTED PHOTOELECTRON
$W$ = Work function of spectrometer

$E_R$ = Recoil energy

The last term, $E_R$, results from the conservation of momentum. Seigbahn et al$^{107}$ showed that this is negligible in this work (Table 2).

### TABLE 2 MAXIMUM RECOIL ENERGIES [eV]

<table>
<thead>
<tr>
<th></th>
<th>Z</th>
<th>Ag$_{k\alpha}$</th>
<th>Cu$_{k\alpha}$</th>
<th>Al$_{k\alpha}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H</td>
<td>1</td>
<td>16</td>
<td>5</td>
<td>0.9</td>
</tr>
<tr>
<td>Li</td>
<td>3</td>
<td>2</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Na</td>
<td>11</td>
<td>0.7</td>
<td>0.2</td>
<td>0.04</td>
</tr>
<tr>
<td>K</td>
<td>19</td>
<td>0.4</td>
<td>0.1</td>
<td>0.02</td>
</tr>
<tr>
<td>Rb</td>
<td>37</td>
<td>0.2</td>
<td>0.06</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The work function term is that of the spectrometer and not the specimen. When the photoelectron leaves the surface of the specimen it has the kinetic energy as expected from Einstein's relationship:

$$E_{KE} = h\nu - BE - W_{SPECIMEN}$$

However, to reach the analyser the specimen must not only travel through the imposed retarding field, but also through a small field arising from the contact potentials between specimen, holder and components of the spectrometer. These contact potentials arise when two metals are joined because their Fermi levels assume the same potentials, but the metals have different work functions. Hence the contact potential between the two metals is equal to the difference
between the work functions. In this case the contact potential affecting the photoelectron is given by:

\[ C_p = W_{\text{SPECTROMETER}} - W_{\text{SPECIMEN}} \]

Hence the measured kinetic energy of the photoelectron is given by:

\[ E_{KE} = h\nu - BE - W_{\text{SPECIMEN}} - C_p \]
\[ E_{KE} = h\nu - BE - W_{\text{SPECTROMETER}} \]

These relationships only hold however if the specimen is in good electrical contact with the specimen holder, otherwise an indeterminate amount of specimen charging may occur. This is usually only of the order of a few volts.

To overcome the problems of charging and to estimate the value of the spectrometer work function a means of calibration is required. Primary standards include the Fermi edge of a spectrum (not always resolvable), and the gold 4f^7/2 line, which occurs at a binding energy of 84.0 eV. These two primary standards are used to calibrate secondary standards such as the carbon 1s peak. This is always present due to a small amount of carbonaceous contamination in the vacuum system (classically thought to be due to traces of pump oil), and is found at 284.0 eV. This has been used as the main standard throughout this work, and the alternative practice of evaporating gold onto the surface has been avoided due to recent doubts concerning the suitability of this method\textsuperscript{108,109}.\]
Mention should briefly be made of the de-excitation processes occurring in the specimen (fig. 12). The photoelectron process leaves an atom in an excited state, with an electron missing from one of its inner electron orbitals.

De-excitation may occur by a process discovered by Pierre Auger in 1925\textsuperscript{10,11}, which gained practical use in surface analysis in 1967\textsuperscript{12}. An electron drops from an orbital of lower binding energy to fill the inner orbital, and thus releases energy characteristic of the transition. This is acquired by a loosely bound electron which is ejected from the atom. These Auger electrons are analysed together with the ejected photoelectrons and give rise to Auger peaks in the spectrum. These peaks are readily identified because they remain at the same kinetic energy irrespective of changes in the incoming photon energy, e.g. a change from Al to Mg radiation. Auger electrons have not been used in this work as they yield less chemical state information than photoelectrons and are more difficult to quantify.

The same de-excitation between levels may result in the emission of a X-ray. The energy of this is again characteristic of the atom from which it came. If the atom was excited using an electron beam then this is the principle used in Electron Probe Micro-Analysis (EPMA), whereas if the excitation was from an X-ray source then the process is termed X-ray fluorescence (XRF). This technique has not been used as the ESCA 3 spectrometer is not fitted with an X-ray analyser.
FIG 12. DE-EXCITATION PROCESSES
3.3 ESCA EQUIPMENT

The equipment used for all the ESCA analysis discussed in this report is a Vacuum Generators Ltd. ESCA 3 spectrometer. This is fitted with two chambers connected by a linear drive mechanism. The preparation chamber houses a small furnace for heating specimens, an evaporator, a mass spectrometer head, and has additional porting available for other additions such as a fracture stage.

The analyser chamber is made out of mu-metal to screen out the earth's magnetic field and is fitted with X-ray and electron sources, an ion gun, a secondary electron detector, and the photoelectron analyser. Both chambers operate at a vacuum better than 1.3 X 10⁻⁶ Pa (10⁻⁸ Torr), and may reach 1.3 X 10⁻⁸ Pa (10⁻¹⁰ Torr) when the system is freshly baked.

The X-ray gun has a double anode, so that either Mg kα or Al kα X-rays can be generated. Normal maximum power is 1 kW for aluminium and 480 W for magnesium. The radiation is filtered by an aluminium window.

To clean or etch specimens an AG 2 ion gun is provided. This has its own feed of argon purified by passing over titanium granules in a small in-line furnace. The gun is normally operated at an argon pressure of 1.3X10⁻⁴ Pa (10⁻⁶ Torr). The use of the ion gun is further discussed in chapter 4.

The heart of the instrument is the spherical sector analyser (fig. 13). This is operated with a fixed pass energy of 2, 5, 10, 20, 50, 100, or 200 eV according to the resolution required. Before reaching the spectrometer the photoelectrons are slowed by a retarding field, then pass through variable entrance slits. Electrons
FIG 13. SCHEMATIC OF PHOTOELECTRON ANALYSER
of the correct energy after going through the retarding field pass through the analyser, and exit via a second set of variable slits into the channeltron. The entry of an electron into the channeltron causes a cascade of electrons, thus resulting in an electrical pulse. The retarding field voltage is controlled by a ramp generator which may be driven by the controls on the ESCA or by the datasystem.

The resolution of the spherical sector analyser is given by :

\[ dE = \frac{wE}{2R} \]

Where

- \( dE \) = Full width at half maximum height (FWHM) for peak in ESCA spectrum
- \( E \) = Pass energy
- \( w \) = Slit width
- \( R \) = Mean radius of hemispheres (10 cm)

For this work a pass energy of 50 eV and a slit width of 0.2 cm was used, giving a nominal analyser resolution of 0.5 eV.

The actual spectral resolution in XPS is also governed by the natural X-ray line width. The k\( \alpha \) lines used are actually doublets containing the k\( \alpha \)-1 and the k\( \alpha \)-2. The natural line width of each component is about 0.5 eV, but the doublet width is effectively 1.0 eV for aluminium and 0.7 eV for magnesium.

The use of a low pass energy and slit width to obtain maximum spectrometer resolution is therefore not justified due to the practical limitation of the X-ray line width, furthermore the transmitted intensity decreases with the analyser voltage. The signal to noise ratio for different analyser energies has been determined by Seah\(^{113} \) (fig.14), and the value of 50 eV used in this
FIG 14. The signal to background ratio for the Ag 360eV Auger electron peak using a monochromatic Al kα x-ray source, as a function of pass energy.
work can be seen to be close to the optimum.

The datasystem used comprises a Digital Equipment Corporation (DEC) PDP8e computer with 12k words of memory. This is interfaced to the ESCA 3 via hardware provided by VG Dataystems Ltd., who also provided the software for data handling. Data acquired from the ESCA is stored on magnetic tapes, and can subsequently be manipulated at a VDU as described in section 3.5. The datasystem has now been linked to the Prime 550 computer provided by the SERC, and developments in this area have considerably improved the data handling facilities available (see Chapter 8.).

When acquiring data the PDP8e steps the retarding voltage between values set by the user. The time spent at each voltage (on each 'channel') is also set by the user. The number of counts from the channeltron are summed then the voltage is stepped to the next channel, and so on. The maximum number of counts per channel is 8 million. Many different regions of the photoelectron spectrum can be scanned, usually several times. If required the computer could acquire data unattended all day, and turn off the X-rays when analysis is complete.

3.4 XPS SPECTRA

A typical XPS spectrum is shown in figure 15. This is a scan of photoelectrons coming from a stainless steel surface from orbitals of binding energy 0 to 1000 eV. The 'widescan' in fig.15 has been labelled by the Prime/ESCA datasystem (see Chapter 8.). The only peaks unaccounted for are the peaks due to the x-ray satellite present with Mg k\(\alpha\) radiation. Satellites are found at 8.5 eV below
XPS Analysis using magnesium radiation

OXIDISED STAINLESS STEEL

C = c  XPS PEAKS
O = o  AUGER PEAKS
CR = y
FE = x
NI = z
the main peak with a relative intensity of 10% for Mg \( \alpha \), and 9.8 eV below the main peak with a relative intensity of 6.15% for Al \( \alpha \).

The wide scan is useful for finding which elements are present, but this is usually followed by analysing specific regions of the photoelectron spectrum using a smaller energy step between channels (typically 0.2 eV). These narrow scans are used to obtain information about the chemical state of the particular element, and to provide accurate peak areas from which atomic percentages can be determined (see Section 3.6). Fig. 16 shows a narrow scan for cobalt, and indicates the peak positions observed for different chemical states.

The time spent on the acquisition of data from each stage in the depth profile depends on the number of elements to be analysed, and the sensitivity of analysis required. In the study reported here it was usual to analyse for silicon, carbon, oxygen, chromium, iron, nickel, and cobalt. This large number of elements, plus the need for qualitative and quantitative analysis of whatever traces of cobalt may be present, typically meant analyses of 45 to 50 minutes duration. Thus it can be seen that the acquisition of a depth profile is quite a lengthy process, as this may be repeated 10 to 20 times, with intermediate etches using the ion gun.

3.5 DATA MANIPULATION ON THE PDP8e

3.5.1 INTRODUCTION

The layout of the PDP8e system is shown diagramatically in figure 17. It comprises the PDP8e computer with twin magnetic tape drives, a VT8e graphics terminal for the display and
FIG 16. COBALT NARROW SCAN

FIG 17. PDP8e COMPUTER AND PERIPHERALS
manipulation of spectra, and a dot matrix hardcopy terminal. There is a line for the acquisition of ESCA data which may be switched between the ESCA2 and the two ESCA3 spectrometers in the laboratory. This line is also used to drive two Bryans X-Y plotters, in order to obtain hardcopies of stored spectra. Another more recent addition is a line connecting the PDP8e to the main university Prime computer network (see Chapter 8).

For data manipulation the PDP8e runs software supplied by VG Datasystems Ltd., under the OS/8 operating system. Focal and Fortran IV languages are available, but there is rarely much free computer time for their use. It is not possible to simultaneously acquire and manipulate the data.

There are a variety of routines available for data manipulation, but the two things that are usually required from the data are a quantitative analysis and chemical state information.

3.5.2 QUANTITATIVE ANALYSIS

In order to quantify the elements present in an ESCA spectrum it is necessary to obtain the peak areas for one of the main peaks from each element. The acquisition of these areas is complicated by the fact that XPS peaks tend to sit on a rising background (fig.15). This rise in the background occurs because a proportion of the photoelectrons from a particular element will suffer inelastic collisions and interactions before escaping from the specimen. To enable the subtraction of this background the computer provides a routine whereby the user can place a straight line where he chooses on the spectrum whilst it is displayed on the graphics VDU. The area
beneath the straight line is subtracted from the spectrum, and the remaining area is output at the terminal.

Figs.18a and 18b show the use of the baseline subtraction routine. The fact that the straight line is placed by eye means that two different users may get different quantitative results from the same spectrum. Although this variation is usually minimal it is at its worst when considering transition metal peaks as these tend to sit on a rising background (fig.19), and may have complex peak shapes, with adjacent peaks from other elements.

The use of a straight line is also an approximation, and it would be expected that the rising background should increase fastest beneath the peak maximum.

3.5.3 CHEMICAL STATE INFORMATION

The other important way in which peaks are analysed is the extraction of chemical state information. To do this two programs are provided. The first takes a narrow scan and automatically carries out the baseline subtraction detailed above. The computer finds the highest count value in the multiplet peak, and the two lowest count values either side. The two minima are joined by a straight line, and only the area above this line is considered in the further analysis. After smoothing the remaining spectrum, the program attempts to fit singlets, all of a fixed width set by the operator, into the spectrum to get a best fit. Some idea of the expected singlet width is required here, as a number of different solutions are possible. This program gives an idea of the singlet positions to be used for the curve synthesis program (see below), and
FIG 18a. CHROMIUM 2p PEAK BEFORE BACKGROUND SUBTRACTION

FIG 18b. CHROMIUM 2p PEAK AFTER BACKGROUND SUBTRACTION
FIG 19. TRANSITION METAL PEAK ON RISING BACKGROUND
is only used as a guide.

The subtracted and smoothed multiplet peak can then be passed on to the next program. This attempts to synthesise the multiplet peak from a combination of up to 4 Gaussian singlets of the same width. Having given the program relative heights and absolute positions for the peaks it synthesises a multiplet and compares it with the multiplet required. It then goes on to try varying the singlet positions and heights small amounts, to find the best fit possible.

When considering transition elements the curve synthesis routine has certain shortcomings:

i) It relies on an automatic straight line baseline subtraction routine to obtain the multiplet peaks.

ii) Real peak widths vary between elements and chemical states, the program uses a fixed singlet width.

iii) Real peak shapes are not necessarily pure, symmetrical Gaussian$^{114}$.

3.6 SENSITIVITY FACTORS

To quantify the XPS spectra the area from one peak of each element (usually the main peak) is obtained from the spectrum. These peak areas are then divided by appropriate sensitivity factors in order to obtain the relative proportions of each element present as an atomic %.

The sensitivity factors used are experimentally determined by running standards. Over the years considerable energy has been
expended in acquiring these factors. Some early workers used peak heights\textsuperscript{116}, but the use of peak areas has now generally been adopted, as the width (FWHM) of some peaks varies according to the chemical state, and thus necessitates the use of different peak height sensitivity factors for each component of the peak. The use of peak area measurement overcomes this difficulty. A number of papers have been published listing the sensitivity factors obtained by peak areas\textsuperscript{113,115,117-126}. There are however certain difficulties in exchanging data between different types of ESCA machines, and recently Seah\textsuperscript{113} has addressed considerable effort into fitting the data from different research groups into a common framework in order to make this exchange of data possible.

The sensitivity factors used here (Table 3) are based on the height sensitivity factors obtained from the work of Jorgensen and Berthou\textsuperscript{116}, and from the analysis of standards in this research group some years ago\textsuperscript{58}. They have been modified to exclude the height factors for the charged states, and the metallic sensitivity factors have been adopted in these cases. They compare favourably with recent published factors obtained using peak areas, yet retain a degree of self consistency with earlier work carried out in this group\textsuperscript{57,58,60}. All quantitative analyses reported here are based on the measurement of peak areas rather than peak heights.
<table>
<thead>
<tr>
<th>Element</th>
<th>Level</th>
<th>Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>1s</td>
<td>0.27</td>
</tr>
<tr>
<td>Oxygen</td>
<td>1s</td>
<td>0.60</td>
</tr>
<tr>
<td>Chromium</td>
<td>2p</td>
<td>1.1</td>
</tr>
<tr>
<td>Iron</td>
<td>2p</td>
<td>1.8</td>
</tr>
<tr>
<td>Nickel</td>
<td>2p</td>
<td>1.7</td>
</tr>
<tr>
<td>Cobalt</td>
<td>2p</td>
<td>2.1</td>
</tr>
<tr>
<td>Silicon</td>
<td>2s</td>
<td>0.25</td>
</tr>
</tbody>
</table>
4. ION BEAM PROFILING

4.1 INTRODUCTION

When using an ESCA technique the top few nanometres of a surface are analysed. To know what lies slightly further beneath the surface it is necessary to remove a few atomic layers, without unduly disturbing those beneath. Ion bombardment provides a way of doing this, and is almost universally used where depth profiles are required using XPS or AES. For AES the spatial distribution of the ion beam is not too critical as the electron beam used to generate the Auger electrons may be placed in the centre of the etched area. XPS analysis places greater demands on the ion beam, as the exciting X-rays cover an area of several square millimetres. Ideally the beam should etch uniformly over this entire area.

Early use of ion beam etching to obtain depth profiles assumed that the beam literally removed atoms from the surface without any ill effect on those beneath. Over the years it has become evident that ion beam profiling is a complex technique, and at least 3 mechanisms have been proposed to explain how atoms are removed. It has also been shown that ion beam induced artefacts can lead the inexperienced to quite erroneous conclusions regarding the nature of the surface being analysed. It was not until 1978 that growing appreciation of the problems involved prompted the ASTM to set up a sub-committee (E42.08) to study ion beam profiling. The original areas outlined for study were:
i) The variation of the sputter yield with energy and atomic number (including preferential sputtering).

ii) Non-uniform flux of bombarding ions, including comparison of rastered and static ion beams.

iii) Topography changes in the crater etched surface.

iv) Ion beam induced motion of impurities and ion bombardment damage.

These topics will be discussed later in this chapter.

The ion gun fitted to the ESCA 3 (fig.20) has already been discussed briefly (Section 3.3). The energy of the ions generated can be varied between 0 and 10 keV and the beam can be focussed according to the voltage on the lense (also 0 to 10 kV). Argon ions are used because an inert gas is less likely to interact chemically with the surface, and argon is readily available. The argon contains a small trace of oxygen, so this is removed by passing the argon through a small furnace containing titanium powder, before bleeding it into the ESCA 3 analyser chamber at \(1.3 \times 10^{-4}\) Pa (\(10^{-6}\) Torr).

4.2 PREFERENTIAL SPUTTERING

Different elements sputter at different rates. It would therefore be expected that any surface on which more than one element is present will become depleted in the element having the highest sputtering rate. There are two situations in which this has relevance to the experimental work described herein. The first is the use of an ion beam to clean polished specimens prior to exposure, and the second is the use of the ion beam on the oxide formed in high
FIG 20. THE AG2 ION GUN
temperature water in order to obtain a chemical depth profile.

4.2.1 SPUTTERING OF ALLOYS

When specimens are cleaned using the ion beam the objective is to remove the modified metallic surface arising from polishing. If this process results in surface enrichment of nickel or chromium due to preferential sputtering then this may modify the films formed during subsequent corrosion (especially thin films). Coburn has proposed a model to relate the surface composition of an ion bombarded solid to the bulk composition. If the solid has two components 'a' and 'b', the sputtering rates $R_a$ and $R_b$ are given by:

$$R_a = I \cdot S_a \cdot F_a$$
$$R_b = I \cdot S_b \cdot F_b$$

where:

$I$ = Ion flux
$S_a, S_b$ = Sputtering yields (atoms per ion) of 'a' and 'b'
$F_a, F_b$ = Fractional coverages of the surface ($F_a + F_b = 1$)
$C_a, C_b$ = Bulk concentrations of 'a' and 'b'

Sputtering will tend towards the steady state where, regardless of the surface composition, the ratio of the two components sputtered away from the surface reflects the bulk ratio, i.e.

$$\frac{R_a}{R_b} = \frac{C_a}{C_b}$$

Hence we get:

$$\frac{F_a}{F_b} = \frac{C_a \cdot S_a}{C_b \cdot S_b}$$

Unfortunately the sputtering yields $S_a$ and $S_b$ are not those of
pure 'a' and 'b'. This is because the sputtering process appears to involve a series of binary collisions with neighbouring atoms in the lattice, and the relative mass of collision partners is a major factor in determining the final energies and trajectories of the atoms involved. Thus, a 'b' atom surrounded by 'a' atoms will behave differently to a 'b' atom in a 'b' lattice when impacted by a high energy ion.

Reidel et al\(^2\) have used SIMS to study the sputtering of Fe-Cr and Fe-Ni alloys. The following sputtering co-efficients were obtained for the pure metals.

\[
\text{Iron} = 2.5 \quad \text{Nickel} = 2.6 \quad \text{Chromium} = 1.7
\]

In the Fe-Cr alloys it was found that the presence of iron increases the sputtering rate of chromium whilst the reverse is true for chromium. So for an 80\% iron, 20\% chromium alloy the following sputtering rates were observed.

\[
\text{Iron} = 2.0 \quad \text{Chromium} = 2.3
\]

Remarkably the sputtering rate of chromium is now higher than that of iron. A similar study of Fe-Ni alloys showed little variation in sputtering yield, probably due to the similarity of the elemental sputtering yields. Fig.21 shows the variation of relative sputtering yields with alloy composition for Fe-Cr and Fe-Ni. If we take the relative sputtering yields for the 80\% iron, 20\% chromium alloy as a fair approximation for 18/8 stainless steel (assuming iron and nickel have virtually the same sputtering rates). Then
FIG 21. VARIATION OF RELATIVE SPUTTERING YIELDS WITH ALLOY COMPOSITION
substituting in Coburn's equation:

\[
\begin{align*}
F_a &= 0.82 \times 2.3 = 5.24 \\
F_b &= 0.18 \times 2.0
\end{align*}
\]

also \( F_a + F_b = 1 \)

so: \( F_a = 84\% \)

\( F_b = 16\% \)

Thus only a small depletion in chromium from 18\% to 16\% is expected, assuming no diffusion from the bulk to the surface. Should this occur the difference would be even less.

This shows that the use of argon ion bombardment to provide a clean surface for corrosion is not going to modify the surface composition of 18/8 stainless steel greatly. This is supported by the results of other workers in the field\(^{133-134}\). The same is not necessarily true for alloys of other compositions\(^{135}\).

### 4.2.2 SPUTTERING OF OXIDES

Elemental sputtering rates are not of much use when sputtering the mixed oxides formed by corrosion. McIntyre et al\(^{136}\) observed the sputtering rates of different oxides, viz:

- \( \text{Cr}_2\text{O}_3 \): 1.5 nm/min
- \( \text{NiO} \): 4.0 nm/min
- \( \text{Fe}_2\text{O}_4 \): 4.0 nm/min
He found that the pure metals have a sputtering rate several times faster than the oxides, and that the single oxides also sputter at varying rates. To look for preferential sputtering in mixed oxides he prepared an intimate mixture of Fe$_3$O$_4$ and Cr$_2$O$_3$ by co-precipitation. The Fe/Cr ratio remained constant under ion bombardment, indicating little or no preferential sputtering of these elements.

When sputtering oxides other problems tend to predominate, and these are discussed in the next section.

### 4.3 BEAM INDUCED REACTIONS

The three main types of beam induced reaction are shown below, and are discussed in the following sections. Although each is considered separately, they are all inter-related. They can influence the results of XPS analysis in a major way and must always be borne in mind when interpreting data acquired after ion beam etching.
4.3.1 REACTION WITH SPECIES FROM EXTERNAL SOURCES

Contaminants in the argon feed to the ion gun must be minimised otherwise they will be thrown down onto the specimen in a very reactive form. It takes only a small amount of oxygen contamination to make it impossible to etch chromium to the metallic state.

Another source of contamination is the analyser vacuum, this may contain traces of water vapour which could be picked up by the ion beam. Carbon is also found to deposit from the vacuum onto specimens under analysis. Under the action of the ion beam this may react with other species on the surface, such as chromium, to form a carbide\textsuperscript{137}.

4.3.2 BEAM INDUCED DECOMPOSITION OR REDUCTION

In 1974 Kim and Winograd\textsuperscript{138} reported that an ion beam is capable of reducing some oxides. They found an approximate relationship between the standard free energy of formation of the oxides and their reducibility by argon ion bombardment with 400 eV ions.

Later in 1977 Holm and Storp\textsuperscript{137} etching with 5 keV argon ions reported the partial reduction of MoO\textsubscript{2} to lower valency oxides, reduction of Bi\textsubscript{2}O\textsubscript{3} to Bi, and reduction of SiO\textsubscript{2} to Si, these oxides having appeared stable in Kim and Winograd's study. The silicon reduction was found to occur at a beam intensity of 10 \(\mu\text{A/cm}^2\) but not at 1 \(\mu\text{A/cm}^2\). These experiments were carried out on thin film oxides grown on unoxidised substrates, whereas Kim and Winograd had studied bulk oxides. Holm and Storp's observations on the sputtering process
provide a plausible explanation for the difference in results between bulk oxides and thin film oxides.

Between several hundred eV and several keV, they state that the penetration of noble gas ions into solids is of the order of 1-10 nm. Most of the energy of the ions is thus absorbed within a radius of less than 10 nm from the point of incidence. Their view is that the absorbed energy is generally sufficient to break some metal-oxygen bonds, the displaced oxygen atoms will then relax and restore themselves to the initial state, unless:

a) They are sputtered into the spectrometer vacuum.

b) A second ion impact takes place before relaxation.

c) The oxygen reacts with the unoxidised substrate and is thus no longer available.

The $\Delta G$ relationship of Kim and Winograd$^{138}$ is thought to be valid as it is a measure of the metal-oxygen affinity after the bond is broken.

These results point to the fact that we can make a good guess at which species may decompose, although this will depend on the ion beam energy and the beam current. Other factors such as the angle of incidence of the ion beam and the thermal capacity of the specimen may also be important. This probably explains the variation in results between different research groups. Considering only iron, chromium, nickel, and cobalt the following has been reported.

$\text{Cr}_2\text{O}_3$ is very stable and reduction of this compound has only been observed by a few workers$^{134}$. 
Fe$_2$O$_3$ has been reduced to lower oxides in a number of cases$^{134,139-40}$ possibly to FeO via magnetite, however work in this laboratory$^{141}$ has shown that even after extensive etching haematite has remained unchanged. This seems to suggest that our standard ion beam conditions are considerably less aggressive than those used by most research groups. Iron is not observed to reduce back to the metallic state.

Nickel oxide seems to be fairly stable, and this is supported by the work of Clayton within this laboratory$^{58}$, but a number of workers have reported the decomposition of nickel hydroxide to NiO$^{140,142-3}$. Similarly cobalt hydroxide, Co(OH)$_2$, will decompose to CoO even more readily$^{140}$.

Reports on the stability of mixed spinels to beam reduction are rare, but Chuang et al$^{140}$ have studied CoFe$_2$O$_4$ and found that both species could be reduced, but much more cobalt metal than iron metal was observed. The overall ratio of iron to cobalt did not change significantly.

Assuming the mechanism of Holm and Storp$^{137}$ to be valid then in a mixed oxide you would effectively have both species competing for the oxygen. Thus in a mixed Fe/Cr spinel reduction of iron species is more likely, whilst the chromium becomes more stable. If cobalt is present in the oxide then this will become the most likely species to be reduced.

The effects discussed above can obviously lead to misinterpretation of chemical state information in XPS spectra. The results in the literature can be used to give a rough idea of the relative stability of species, but test specimens must still be run
as results can vary widely according to the ion bombardment conditions.

4.3.3 RECOIL IMPLANTATION

This is the basis of Holm and Storp's\textsuperscript{137} argument why they observed reduction of thin oxides on substrates, whereas Kim and Winograd didn't observe reduction of bulk oxides. They speculated that the capture of oxygen atoms by the substrate - due either to diffusion or recoil implantation (knock-on) - reduces the chance of the molecule relaxing to its original state. They observed the formation of low valence or non-stoichiometric oxides as an interim stage in reduction.

Kelly and Saunders\textsuperscript{144} produced a paper on recoil implantation which covers the implantation of surface species into underlying material by being knocked on by the ion beam. This is also applicable to damage caused to oxide films. Their theory necessarily indicates that for any binary (or more complicated) system where the two components have a different mass the outer surface becomes significantly deficient in the lighter component. This effect becomes greater at higher ion doses. This is supported by all their examples except NaCl where theory would predict that the surface would become deficient in sodium, the reverse is in fact observed. Al\textsubscript{2}O\textsubscript{3} , SiO\textsubscript{2} , SnO\textsubscript{2} and Ta\textsubscript{2}O\textsubscript{5} showed no surface alteration at all. Their theory predicts the following :-

a) Major stoichiometry change to 3 nm.

b) Minor changes to perhaps 15 nm.
c) Injection of point defects (e.g. oxygen vacancies) characteristic of the surface alteration.

This theory\textsuperscript{44} is useful because it links recoil implantation to the reduction of surface oxides without forgetting that effects such as preferential sputtering will be important in causing surface alteration and must be considered in any complete treatment of the problem.

Recoil implantation will tend to homogenise an initially sharp interface\textsuperscript{130}, and this effect could be most important in the current study when reaching the base of the oxide film. Oxygen being the lighter species will tend to be knocked into the unoxidised substrate, where it will almost certainly associate with chromium. The resulting effect on the depth profile is one that could also be caused by several other complicating factors, viz:-

i) Non-uniform oxide thickness

ii) The presence of an interfacial zone or internal oxidation

iii) An uneven etch distribution over the analysed area

iv) Grain boundary oxidation

Fig. 22 shows a representation of a non-ideal surface being etched.

4.4 BEAM UNIFORMITY AND ETCH RATE

For the acquisition of XPS depth profiles a uniform etch rate is required over the entire area analysed. This is difficult to
achieve in practice as both the area etched and the area irradiated by the exciting X-rays can be difficult to define.

If the etch rate of the ion beam is sufficiently high then the etched area can be observed by eye, and is detectable using stylus type roughness and flatness measuring instruments (e.g. Talysurf and Talylin). Fig.23 shows the etch pit formed after 105 minutes of etching a stainless steel surface with 5keV ions using 5keV focussing voltage on the AG2 ion gun. This is referred to as fully focussed. The etch pit is conical in shape and has a diameter of 5.5 mm, this is totally unsuitable for XPS depth profiling both in terms of uniformity and in terms of spot size. The etch rate measured is not of much use as we require the etch rate of Fe/Cr oxide, not metal, and these will differ considerably.

To get around these difficulties a new approach was adopted. Specimens of stainless steel were polished then oxidised in air at 920 K to produce thick interference films. These specimens were then etched under different beam conditions, and the beam uniformity and etch rate judged from the changes in the interference colours. This showed that a fairly even etch could be obtained using 3 keV beam energy and 1.5 kV focus. Fig.24 shows the resulting etched areas, the etch is fairly uniform and was estimated to be at a rate of 1.5 nm/min.

The area irradiated by the X-ray beam was obtained by irradiating double sided adhesive tape placed on a white background. The tape discolours due to the X-ray beam thus revealing the irradiated area (Fig.25).
FIG 24. UNIFORMITY OF 3KV ION ETCH ON STAINLESS STEEL SPECIMEN OXIDISED IN AIR AT 920 K

FIG 25. DISCOLOURATION OF DOUBLE-SIDED TAPE DUE TO EXPOSURE TO X-RAYS
4.5 PRESENTATION OF DATA

The most concise way to present the data from an etch profile is to plot atomic % of different species against etch time in a cumulative form. The data is obtained in such a way that the total is 100 atomic % (Section 3.6). The proportion of any species on the surface at time, t, is then given by the distance between adjacent lines on the graph (fig. 26a). Although this is a compact way of presenting the data it can be difficult to tell at a glance how the atomic % of species plotted in the middle of the graph varies with etch depth. This is best seen by plotting in a non-cumulative form (fig. 26b), though here there is the complication that the lines representing various species may overlap. Both forms are used within this report.

The surface of all specimens in the unetched condition carries carbon contamination. This comes from the laboratory atmosphere during specimen transfer, and may also come from traces of organic material in the water used for corrosion. A very light etching rapidly removes most of this, showing that it is only a lightly bound surface layer. Some carbon is observed throughout analysis but this is usually excluded from the results unless it is of specific interest, as it arises for the most part from the vacuum of the spectrometer.
FIG 26a, b: ETCH PROFILE FOR SPECIMEN EXPOSED TO WATER CONTAINING 1mg/l OF COBALT AS CoCO$_3$ AT 353K FOR 1 HOUR.
5. EXPERIMENTAL

In order to follow the uptake of cobalt from solution it is important to remove the possibility of other metallic species acting in a similar way, thereby making the results very difficult to interpret. Thus a totally non-metallic system was required. Other requirements are a close control of water chemistry together with fast heating, cooling, and specimen removal in order that the oxide films grown in short exposures are representative of the temperature under investigation.

In order to satisfy these requirements the use of a conventional autoclave was dropped in favour of a lightweight non-metallic corrosion cell within a gas pressurised enclosure. The use of this high pressure gas environment meant the corrosion cell and associated equipment placed within the pressure vessel did not have to be built to withstand the stresses of containing high pressure water, thus much simplifying the manufacture of a non-metallic water system.

5.1 THE PRESSURE VESSEL

The cylindrical pressure vessel was manufactured from mild steel by Lintott Engineering Ltd. (fig. 27). It is approximately 90cm long by 37cm diameter, and has a large door at one end so that apparatus can easily be set up inside. It is pressurised with 'white spot' nitrogen, and the corrosion system is used in this high pressure and relatively inert environment. The vessel has been internally inspected and hydraulically tested for a safe working pressure of 2.3 MPa (330 psi), giving a maximum water temperature of 488 K before boiling occurs. Five ports carry electrical feedthroughs, gas or liquid feedthroughs, controls for pinch valves
within the pressure vessel, and a glass observation window. The vessel can be connected to a vertical pressure vessel originally intended as a large reservoir for water to be used in the lower, horizontal pressure vessel. Pressure is measured with a Budenberg gauge or via an Intersonde Ltd PR-350 pressure transducer to one of two Kent MkIII multi-channel recorders. The vessel has been modified by the adoption of a graphite bursting disc so that it can now be pumped down to a rough vacuum by an attached Speedivac single stage rotary pump.

For experiments at 473 K a total loss flow system was arranged (fig.28a). A PTFE needle valve allows water to leave the pressure vessel (expelled by the internal pressure), and this results in a flow from the water reservoir, through the gas dosing equipment and through the corrosion cell. Several modifications were made to the cell to prevent the ingress of nitrogen, as this formed bubbles within the flow circuit which passed rapidly through the flow controlling needle valve thus causing a transient increase in the flow rate of the system, and a subsequent temperature drop in the corrosion cell. The cell was used in this form for the work detailed in the following sections. Further modifications were undertaken to permit a wider range of parameters to be investigated in future programmes. The most important of these is control of the oxygen potential, using the gas dosing system detailed below.

To control the levels of dissolved gas in the water whilst the vessel is pressurised the effectiveness of silicone rubber as a gas transfer medium was utilised. By passing water through silicone rubber tubing in a controlled gas environment the water could either be dosed with gas (such as hydrogen), or could be stripped of gas
Fig 28a Water Flow System

Fig 28b Gas Control System
(such as oxygen), according to the partial pressure difference between the 'dosing gas' and the water.

To allow gas dosing to be carried out without contaminating the nitrogen atmosphere of the pressure vessel a gas control system was designed and built onto the vessel (fig 28b). Using a regulator controlled by the main vessel pressure the system enabled the second gas to be fed into the gas dosing equipment (within the vessel) at a pressure approximately 14-20 kPa (2-3 psi) below the main vessel pressure, this pressure difference being important to prevent the collapse of the silicone rubber tubing. The dosing equipment comprised a vessel through which the dosing gas passed, and through which water flowed in silicone rubber tubing. The dosing gas was bled out of the main pressure vessel into the atmosphere via a needle valve, and the automatic pressure regulator maintained the pressure, so continual refreshment of the dosing gas was achieved.

To measure the gas content of the water and thus control the gas dosing a system was devised to enable analysis of the gas mixture that bubbles out of the water as the pressure drops at the PTFE needle valve controlling the flow rate out of the pressure vessel. Analysis of the released gas mixture was to have been carried out using a purpose built gas chromatograph constructed by Pye-Unicam and currently at AERE Harwell.

5.2 CORROSION CELLS

Care must be taken in the choice of corrosion cell material, and the use of a pressure enclosure rather than an autoclave allows considerable flexibility in this respect. Mercer et al\textsuperscript{137} have reported that silicon pickup may occur in silica corrosion cells.
Previous work by Clayton\textsuperscript{57} has shown that silicon pickup is not significant at up to 353 K, however he used a PTFE cell at higher temperatures. In this study a borosilicate vessel was used at 413 K, and some silicon was incorporated into the film. Comparison with the results obtained by Clayton\textsuperscript{57} in this temperature range showed that the silicon did not appreciably influence the type of oxide film formed. All exposures at 473 K utilised a PTFE cell, thus preventing any contact between the high temperature water and glassware.

The glass corrosion cell used at 413 K had a capacity of 250ml. It was heated from the base by an electric mantle, the resulting convection currents gently stirring the solution. The temperature was controlled using a chromel/alumel thermocouple inserted into a pocket in the corrosion cell, this was in turn connected to a Eurotherm PID/SCR furnace controller.

The PTFE cell used for the higher temperature corrosion was a modified version of a design used previously by Clayton\textsuperscript{57} (fig.29). The PTFE had been heat treated at 653 K prior to manufacture as this was found to improve machinability and to alleviate the problem of fluorine contamination of the water. Within the cell the water only comes into contact with PTFE, the specimen, the thermocouple sheath, and the gold heater disc in the bottom. Beneath the gold disc heat is supplied by a Watlow Fire-rod, and is conducted to the cell by a copper disc. This heating arrangement had previously led to copper diffusing through the gold heater disc and contaminating the water within the cell\textsuperscript{58}. This problem was eventually overcome by careful pre-oxidation of the copper disc, so as to produce a thick adherent oxide. Using the copper disc in this condition together with a thicker gold disc removed any detectable copper contamination from
FIG 29. PTFE CORROSION CELL
The unsheathed chromel/alumel thermocouple used previously in the PTFE cell was found to release considerable nickel into the water at the maximum temperatures investigated. As changing to a platinum/rhodium thermocouple would mean sacrificing sensitivity, it was decided to use a fine chromel/alumel type sheathed with stainless steel. Specimens exposed in the cell with this thermocouple showed no sign of the nickel pickup previously experienced in Clayton's work. 

5.3 WATER PURITY

The water used for corrosion was obtained from an Ionmiser 6c de-ioniser and was then cyclically distilled under nitrogen until required (fig.30). The still was designed so that water only comes into contact with glass, PTFE, and a platinum conductivity cell. It is continuously purged with 'white spot' nitrogen and is collected in the reservoir containing the conductivity cell, before overflowing into the boiling vessel. When the conductivity is sufficiently low (typical conductivity of the water was 0.5 to 0.7 $\mu$S/cm), it is transferred by nitrogen pressure to one of the 2 litre transfer vessels. These can be pumped down to a vacuum or purged with nitrogen. They were designed so that they could be isolated, uncoupled, and transferred to the pressure vessel without exposure to the atmosphere. This posed considerable experimental difficulties when it came to adding traces of cobalt, etc. to the solutions. The pressure vessel was then modified to withstand a rough vacuum without damaging the bursting disc, and was connected to a rotary pump. Vacuum degassing tests on the high purity water showed that this was
FIG 30. CYCLIC WATER PURIFICATION APPARATUS
far superior to purging with nitrogen (fig. 31) so this was adopted as the standard technique. Oxygen levels were measured using an E.I.L. model 1520 dissolved oxygen meter and model 1521 oxygen electrode, and although this was reaching the limit of its sensitivity it can be seen from fig. 31 that approximate levels were 1mg/l after 23min pumping, and 0.2mg/l after 150min pumping.

The cobalt containing solutions were made by adding approximately 0.5mg of cobaltous carbonate to 1-1.5 litres of water from the still. In most cases, the correct solution concentration could then be obtained in a single dilution, though two dilutions were used for some of the lowest cobalt concentrations. Having achieved the required cobalt level, lithium hydroxide and boric acid were added if required.

5.4 SPECIMEN PREPARATION

The specimens of #304 stainless steel were cut from cold rolled sheet 1 mm thick. Analysis revealed the following composition:

<table>
<thead>
<tr>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
</tr>
<tr>
<td>0.20</td>
</tr>
</tbody>
</table>

Specimens were originally prepared prior to corrosion by dry abrasion with 600 grit emery paper. This was found to cause some surface enrichment of chromium, as has been reported by other workers. The surfaces of specimens prepared by dry abrasion were compared with those obtained after mechanical polishing followed by argon ion bombardment (fig. 32). It can be seen that chromium is enriched at the expense of iron and nickel in the specimen subject to
FIG 31. COMPARISON OF NITROGEN PURGING WITH VACUUM DEGASSING

RESULTS FOR 250 mL HIGH PURITY WATER
OXYGEN LEVEL MEASURED USING MACKARETH CELL

- PURGING WITH O.F.N. (Various conditions)
- VACUUM DEGASSING (Stirred)
METHOD OF PREPARATION

SOLID LINE: Polished and Argon Ion Cleaned
BROKEN LINE: Dry Abrasion with 600 Grit Emery

ETCH TIME (SECONDS)

FIG 32. COMPARISON OF SPECIMENS PREPARED BY MECHANICAL POLISHING FOLLOWED BY ARGON ION CLEANING, AND BY ABRASION, FOLLOWED BY 3 MINS EXPOSURE TO LAB AIR
coarse abrasion. All the specimens reported here were prepared by polishing to one micron finish in order to produce a flat surface and to reduce the effect of chromium enrichment, they were then ultrasonically cleaned in acetone. This was followed by transferring them to the ESCA where they were cleaned using a 3keV argon ion beam (this more fully discussed in section 4.2.1), in order to remove any modified surface resulting from the polishing process.

After ion cleaning they were again ultrasonically cleaned, this time in acetone followed by high purity water. This was to remove any trace of adhesive from mounting on the ESCA 3 specimen holder. The specimens were then stored immersed in high purity water in sealed containers until required (not more than a few days).

5.5 TYPICAL EXPOSURES

For exposures at 413 K specimens prepared as detailed above were suspended in a PTFE cradle hung on a glass hook within the glass corrosion cell containing 250ml of water. The cell was then placed in the pressure vessel which was pumped down to a rough vacuum to remove any dissolved gases from the water. The period of vacuum pumping was varied between specimens exposed under identical conditions and no appreciable difference was found in the cobalt uptake or depth profiles of specimens. It was assumed that oxygen levels between 1 mg/l and 0.2 mg/l have little effect on the thin oxide formed at 413 K. After vacuum pumping the vessel was then pressurised with nitrogen and the cell brought to 413 K as quickly as possible. After the exposure period the heater was turned off, and the vessel pressure was released, so that the corroded specimen could be removed from solution as soon as possible after reaching 373 K.
Corrosion at 473 K using the PTFE cell followed a different sequence. A 3 litre glass reservoir containing the water was placed in the pressure vessel, followed by the PTFE cell with the specimen inside. The flow system was connected up and the vessel pumped down to vacuum. This was maintained for about one hour. During this period gas could be seen to be bubbling from the water in the reservoir. The vessel was then pressurised with nitrogen to a low pressure of approximately 350 kPa (50 psi), to check the water flow system. This filled the cell with water, though it was still at room temperature. The vessel was then fully pressurised, and the water flow around the system set to approximately 2 ml/min. At this point the heater in the base of the PTFE cell was turned on. It took 25 min for the water temperature to reach 473 K. This time could be reduced, but only at the risk of boiling the water in contact with the gold heater disc, with consequent disruption of the flow system due to nitrogen bubbles forming downstream from the cell. These passed quickly through the PTFE needle valve, and were found to drop the cell temperature due to the sudden ingress of cold water from the reservoir. After the exposure period the cell was cooled rapidly by turning off the heater, but maintaining the water flow. The pressure was released gradually so as to prevent boiling, and the specimen was removed from the cell as soon as possible after the temperature had dropped below 373 K. Total cooling time was of the order of 10 min.

Specimens were mounted for XPS analysis then stored in tube desiccators (fig.33) before being transferred to the ESCA 3 for analysis. The oxide films formed have proved to be exceptionally stable in the UHV of the ESCA, so little change was anticipated by keeping them in a desiccator. The storage times for specimens were however kept to a minimum.
FIG 33. TUBE DESICCATOR
6. RESULTS AT 413 K

6.1 INTRODUCTION

The experiments carried out at 413 K were designed to give information on the chemical and compositional structure of the film and, in particular, of cobalt in the film. Exposure periods were varied in order to ascertain the rate of film growth, and an optimum exposure period for subsequent XPS analysis was selected. Film thickness and composition with and without cobalt were then compared to see if the presence of soluble cobalt had any effect on oxide growth. The relationship between cobalt levels in the film and the amount of dissolved cobalt in solution was determined within the limits determined by the sensitivity of the ESCA technique, and the solubility of cobalt. Finally a two stage exposure, first in pure water then in water containing 0.5 mg/l cobalt, was carried out to shed light on the mechanism of cobalt incorporation.

6.2 VARYING EXPOSURE PERIODS

Specimens were exposed for periods of 2, 6 and 24 hours in water containing 0.5 mg/l of cobalt as CoCO\(_3\), see figs.34-37. Although the position of the oxide/metal interface was difficult to place, comparison of the profiles shows that the films formed after 6 and 24 hours were quite similar, whereas that formed after 2 hours was considerably thinner. The 2 hour film also contained much less cobalt, which suggests a link between cobalt incorporation and film growth. From these profiles the 6 hour exposure period was adopted for all further tests at 413 K.
FIG 34. ETCH PROFILES OBTAINED AFTER 2 HOURS AT 413 K IN WATER DOSED WITH 0.5 mg/l OF COBALT AS CoCO₃.
FIG 35. NON-CUMULATIVE ETCH PROFILE FOR 6 HOURS AT 413 K IN WATER DOSED WITH 0.5 mg/l COBALT AS CoCO₃.
FIG 36. CUMULATIVE ETCH PROFILE FOR 6 HOURS AT 413 K IN WATER CONTAINING 0.5 mg/l OF COBALT
FIG 37. ETCH PROFILE FOR SPECIMEN EXPOSED FOR 24 HOURS AT 413 K TO WATER CONTAINING 0.5 mg/l COBALT.
The chemical state of the elements was examined for the 6 hour and 24 hour films, and was very similar. Nickel was not present in the outer portion of the films, and deeper in the film the nickel peak position indicated the metallic state (fig.38). It seems likely that nickel does not take part in the oxide film formed at this temperature. Chromium was observed in the trivalent state, and during etching was only observed to change to the metallic state (fig.39) when the iron signal had become entirely metallic (fig.40). Prior to etching iron was observed to be trivalent, and only a small amount was present. This changed to a mixture of divalent and trivalent states as soon as etching began. As etching proceeded a gradual increase in the ferrous iron component in the peak was observed. This is shown in fig.41 where all the iron peaks from the specimen exposed for 24 hours are presented in a montage. If we take one of the first peaks (which is almost entirely ferric), eg. the one minute scan; and subtract it from subsequent peaks it is possible to see the increase in the ferrous and metallic components which results after the residual ferric component is removed (fig.42). Repeating this procedure for a later peak, eg. the four minute scan, removes the ferric and a large part of the ferrous components. The resultant (fig.43) emphasises the increase in the metallic component as the metal/oxide interface is reached.

The main element of interest, cobalt, was seen in the divalent state in the unetched condition, as identified by the presence of a small satellite peak at higher binding energy than the main peak in figure 44a. This changed to the metallic state as etching proceeded. This is indicated by the main cobalt 2p peak moving to a lower
FIG 38. NICKEL 2p PEAK

Area 14992  0.8 atomic %

Nickel peak is first seen after 4 minutes of etching (~6nm), and indicates metallic state.
FIG 39. CHROMIUM 2p PEAK
Area 142516  15.1 atomic %
Considerable metallic chromium present.
FIG 40. IRON 2p PEAK
Area 587384 37.0 atomic %
Iron almost completely in metallic state

BINDING ENERGY (eV)

ETCH TIME 9 MIN.
706.8 eV

% INT.
100 80 60 40 20 0

Fe⁰ Fe⁺⁺
Fig 41, Iron Peaks for Etch Profile shown in Fig 37.
Fig 42. Result of Peak Subtraction on Fig 41.

Etch Time (mins)

Iron Peak Shape after 1 minute etch
Fig 43. Result of Peak Subtraction on Fig 41.

Iron Peak Shape after 4 minutes etch
FIG 44a. DIVALENT COBALT $2p^{3/2}$ PEAK

FIG 44b. TRIVALENT COBALT $2p^{3/2}$ PEAK
binding energy, and the disappearance of the satellite peak. The distribution of cobalt through the film was fairly constant, and only appeared to tail off as the metal/oxide interface was approached.

Oxygen was observed at a binding energy of 530.2 eV relative to carbon 1s at 285.0 eV. This is a position typical of the oxides of many transition elements. The peak was slightly asymmetric (fig. 45) and may contain a small hydroxide component (531.4 eV).

6.3 EFFECT OF SLOW COOLING

The first specimen exposed for 6 hours (not discussed above) served to highlight the importance of removing the specimen from the aqueous environment as soon as possible after the test was completed. This specimen was allowed to cool overnight in the dosed water, and this resulted in the deposition of a relatively thick cobalt rich layer on the surface. This could be seen by eye as an irregular brown stain. The etch profile (fig. 46) shows this with the level of cobalt approaching 20 at% after 4 to 8 minutes of etching. The cobalt peak shows the unetched surface to contain trivalent cobalt (fig. 44b), though after etching a mixture of divalent and metallic states was observed.

6.4 EFFECT OF COBALT ON OXIDE

For comparison with the specimen exposed in water containing 0.5 mg/l cobalt, a specimen was exposed to pure water for 6 hours (figs. 47 and 48). This specimen was contaminated with a trace of cobalt, probably picked up from the walls of the glass corrosion cell. A repeat run was carried out after a thorough washing of the
FIG 45. OXYGEN 1s PEAK

Area 412271 55.0 atomic %

Asymmetry indicates small hydroxide component

ETCH TIME 4 MIN.
FIG 40. ETCH PROFILE AFTER 6 HOURS AT 413 K IN WATER DOSED WITH 0.5 mg/l COBALT, FOLLOWED BY OVERNIGHT COOLING.
FIG 47. NON-CUMULATIVE PROFILE FOR 6 HOURS AT 413 K IN WATER WITH A TRACE OF COBALT
cell, and this time no cobalt was observed (fig.49). A comparison of these two runs (fig.50) shows remarkable consistency, the trace of cobalt has had no detectable effect on the depth profile. If we compare the depth profiles of 0.5 mg/l cobalt and pure water, we find that the oxygen and iron profiles are close suggesting a similar film thickness (fig.51), the chromium profile is however much lower, but is balanced by the presence of cobalt in the film and the somewhat increased silicon level.

It appears that the cobalt in the water even at the very high level of 0.5 mg/l (by reactor standards) has no measurable effect on film thickness, but changes the composition by reducing the chromium level in the outer regions of the film.

6.5 DEPENDENCE OF COBALT IN THE OXIDE ON SOLUTION CONCENTRATION

1.0 mg/l cobalt was considered to be the maximum solubility for cobalt in these experiments, so all the tests for a dependence on solution concentration were carried out at 0.5 mg/l or lower. The lower limit was set by the sensitivity of the XPS equipment for cobalt (approximately 0.1 to 0.2 atomic %). This gave a lower limit of approximately 0.05 mg/l in solution, so specimens were tested in solutions from 0.5 mg/l to 0.1 mg/l cobalt. The results are presented in figure 52. Each block represents the range of cobalt concentration found in the oxide on a specimen between the first etch and the appearance of a nickel signal (taken to mean that some portion of the specimen had been etched back to the metal/oxide interface).
FIG 49. ETCH PROFILE FOR 6 HOURS AT 413 K IN PURE WATER
6 hours at 413 K in pure water

6 hours at 413 K in water with trace cobalt

Etch Time (mins)

FIG 50 Reproducibility of results
FIG 51 COMPARISON OF DEPTH PROFILES FOR PURE WATER AND WATER DOSED WITH 0.5 mg/l COBALT.
FIG 52 INCORPORATED COBALT v SOLUTION STRENGTH
6.6 TWO STAGE EXPOSURE

The earlier tests on the rate of film growth showed little change in thickness between 6 hr and 24 hr exposure. It was decided to oxidise a specimen in pure water for 6 hours to produce the thicker oxide as shown in fig.49. This specimen was then removed from the cell, and the pure water changed for a solution of 0.5 mg/l cobalt. A further 6 hour exposure period ensued. The depth profile of the resulting film shows some interesting features at the limit of XPS sensitivity (fig.53). Cobalt was found in the outer portion of the film, and at the base of the film where the nickel signal began to increase, and the silicon contamination signal falls to zero. No cobalt was detected in the middle of the film.

6.7 DISCUSSION

After 6 hours, cobalt incorporated from solution extends into the oxide film to a considerable depth (fig.35). The level is also seen to be fairly constant over the outer 50% of the film. It might have been expected that the cobalt level would increase in the outer portion of the film as the rate of film growth slowed down. This is not supported by the results shown here. The amount of cobalt incorporated in the film is not sufficient to cause appreciable reduction in the solution concentration, so this can be ruled out as a contributing factor. It seems therefore that the level of incorporated cobalt is controlled either by the cobalt activity in solution or by the chemical nature of the oxide film.

At 413 K there is little information on the structure of films formed on stainless steel, this temperature lying midway between the
6 HOURS IN PURE WATER FOLLOWED BY 6 HOURS IN WATER DOSED WITH 0.5 mg/l COBALT

FIG 53. CORROSION OF 18/8 STAINLESS STEEL AT 413 K
thin, amorphous films formed at temperatures up to 323 K\(^56\), and the well characterised spinels\(^147-149\) formed at the temperatures involved in nuclear power plant operation (558-573 K). Similar crystalline oxides have been identified on plain carbon steel in the temperature range 323-423 K\(^75\) and thermodynamic calculations have been used to show\(^146\) the stability of various stoichiometric mixed spinels under these conditions. However, one of the characteristics of spinels is that the substitution of one cation for another can occur over a wide range of composition, and thermodynamic data on non-stoichiometric mixed spinels is still very limited.

Rummery et al\(^147\) found both a mixed spinel and magnetite on carbon steel removed from the system in a CANDU-PHW reactor. They concluded that the mixed spinel was formed by the interaction of the normal corrosion product (Fe\(_2\)O\(_4\)) with corrosion products in the coolant, and that the solid solubility of spinels is such that a mixed cation spinel containing all the elements identified by energy dispersive x-ray spectrometric analysis (EDS) was formed, viz:

\[
\text{Si}^{4+}_{0.06} \text{Mn}^{2+}_{0.03} \text{Ni}^{2+}_{0.61} \text{Fe}^{2+}_{0.35} \text{Al}^{3+}_{0.25} \text{Cr}^{3+}_{0.015} \text{Fe}^{3+}_{0.735} \text{O}_4
\]

Traces of cobalt-60 (5 x 10\(^{-4}\) Wt\%) were also detected by \(\gamma\) spectroscopy.

It is interesting to note that even though stoichiometric Fe\(_2\)SiO\(_4\) forms only at high pressure\(^150\) it was thought reasonable to assume that small amounts of silicon could be substituted in the film to form a stable phase at low pressure. Similarly, in this work, small amounts of silicon are found incorporated into the oxide film. The effect that this may have on the solid solubility of other elements in the film could be important in controlling film
In all the results obtained at 413 K there is no evidence that nickel is oxidised. The oxygen spectra from the films shows only a small hydroxide component and no bound water (fig. 45). This favours consideration of the film as a thin form of the higher temperature spinel rather than in terms of the hydrated oxide that composes the passive film formed at lower temperatures.

In iron-chromium spinels of low chromium content Francombe has shown that the inverse spinel structure of magnetite is retained, with Cr\(^{3+}\) ions substituting on octahedral sites in the lattice. As the chromium content rises, the structure changes to a normal 2-3 spinel, thus making more octahedral sites available for substitution of Cr\(^{3+}\) for Fe\(^{3+}\).

Cobalt forms mixed spinels both with iron as an inverse ferrite Fe\(^{3+}\)(Co\(^{2+}\)Fe\(^{3+}\))\(_0^y\), and with chromium as a normal chromite Co\(^{2+}\)(Cr\(^{3+}\))\(_0^{2}\). In both of these spinels the cobalt is in the divalent state, and this is the state of the cobalt observed in the films grown at 413 K presented in this report. Thus cobalt should be able to substitute in the corrosion film forming at 413 K whether the Fe-Cr has the normal or inverse structure.

Comparison of peak shapes and positions with published data for cobalt ferrite\(^{153}\) shows good agreement for cobalt and oxygen peaks, though the iron peak differs. For cobalt ferrite the main iron 2p\(^{3/2}\) peak is seen at 710.6 to 710.9 eV, whereas in the work reported here the maximum of the peak envelope is at 709.9 eV, the position seen for ferrous iron. This is presumably due to the chromium occupying trivalent sites thus reducing the ferric contribution to the signal,
whilst a lower cobalt content than cobalt ferrite increases the amount of ferrous ions present.

It is of interest to note that the specimen exposed for 6 hours at 413 K in water containing 0.5 mg/l of cobalt, then cooled overnight, had an appreciable overlayer containing a large proportion of iron/cobalt, but very little chromium. It was observed that even with prompt (10 to 15 minutes) removal from solution the specimen exposed for 6 hours in water containing 0.5 mg/l cobalt had a much lower chromium level in the outer region of the film than similar specimens exposed to pure water (fig.54). It seems likely that the cobalt in solution encourages the deposition of a mixed film on cooling, which would otherwise seem unlikely due to the inverse solubility of magnetite.

Of all the results obtained at 413 K the last one is probably the most interesting (fig.55). The two stage exposure has revealed that cobalt is incorporated at the metal/oxide interface. The presence of cobalt in the outer region of the film is inconclusive. This may have arisen due to a small amount of solid state diffusion, or because the oxide has a more porous nature and thus retained some solution, or because some oxide was deposited from the solution during the exposure period or subsequent cooling (see above).

The cobalt at the metal/oxide interface is not open to such a variety of interpretations. If cobalt reached this interface during the second stage exposure then the oxide must be porous and growth is almost certainly occurring at the interface, resulting in cobalt being incorporated. The cobalt concentration profile from the specimen shows that the cobalt distributions seen in previous
specimens are not due to solid state diffusion (as assumed in some models$^{93}$).

The apparent similarity in growth mechanisms between corrosion at 413 K and inner layer growth under reactor conditions prompted a look at the various mathematical models proposed for the higher temperature to see what the predicted distribution of cobalt through the oxide would be. The model proposed by D.H.Lister$^{100}$ fits the observed mechanism nicely, with the formation of a duplex layer in the accepted manner (section 2.4), the outer layer by deposition from solution and the inner layer by oxidation at the metal/oxide interface as illustrated in fig.55. Listers mathematical model was designed to predict the rate at which active corrosion products are picked up by the oxide growing in this manner within a flowing system.

Let us first look at Listers model and how this can be simplified to treat the results obtained in this work at 413 K.

If coolant flows with an average velocity '$u$', in a pipe of diameter '$d$', then $C_w^*(x,t)$ - the surface radioactivity corrected for decay - as a function of time is given by:

$$\frac{\delta C_w^*(x,t)}{\delta t} = C_b \eta(t) \exp \left[ -\frac{4x}{ud} \eta(t) \right]$$
Outer layer growth by deposition from solution at the oxide/solution interface.

Inner layer growth by dissolution and precipitation at the oxide/substrate interface.
Where $C^o_b$ is the constant bulk concentration of activity at the pipe inlet and $x$ is the distance downstream from the inlet. $n(t)$ is the kinetic parameter that is equal to the depositon coefficient at zero time. This can be expressed in terms of the processes resulting in the incorporation of the active species into the oxide.

\[ n(t) = \frac{1}{\text{DIFF}_i + \text{CRYST}_i} - \frac{1}{\text{CRYST}_0} \]

$\text{DIFF}_i$ is the 'transport resistance' for the diffusion of active ions through the pores in the inner layer.

\[ \text{DIFF}_i = \frac{m(t)}{2\rho_i D_i \phi_i (1-\phi_i)} \]

Where
- $m(t) = \text{Mass of oxide on surface}$
- $\rho_i = \text{Density of inner layer}$
- $D_i = \text{Diffusion coefficient of active ions in the liquid}$
- $\phi_i = \text{Porosity of the inner layer}$

$\text{CRYST}_i$ and $\text{CRYST}_0$ are the terms for the kinetics of crystallisation at the base of the inner layer and on the top of the outer layer, respectively.

\[ \text{CRYST}_i = \frac{C_{si}}{0.35\rho_i (\frac{dm(t)}{dt})} \]
\[ \text{CRYST}_o = \frac{C_{so}}{0.35P_o(d\text{m}(t)/dt)} \]

\(C_{si}\) and \(C_{so}\) are the inner and outer layer oxide solubilities in the aqueous phase.

\(P_i\) and \(P_o\) are the partition co-efficients which define the ease with which the active species are incorporated in the inner and outer layer oxides. This is discussed in more detail later.

For the purpose of this study Listers model can be simplified. The decay of radioactive cobalt need not be considered, so the distance from the pipe inlet \((x)\) is no longer required, hence:

\[ \frac{\delta C^*_w(t)}{\delta t} = C^o_b \eta(t) \]

At 413 K the specimens were exposed in sufficient volume of water to prevent saturation with magnetite, so the films studied probably have little or no outer layer, hence:

\[ \eta(t) = \frac{1}{\text{DIFF}_i+\text{CRYST}_i} \]

The 'i' subscript is used hereon to refer to inner layer parameters.
$C^*_W(t)$ and $C^O_D$ were originally taken to represent cobalt activity levels in Ci/m$^2$, but can now be taken to represent atomic concentrations.

Before discussing the concentration profiles that can be obtained from this simplified expression it is useful to derive it from basics so that the assumptions on which it rests can be discussed.

The basic mechanism is growth of the outer layer by deposition from solution, and growth of the inner layer by the diffusion of aqueous species through pores in the inner layer to the oxide/metal interface. The inner layer grows at this interface with zero volume change. This is made possible by the outward diffusion of metal ions to the bulk solution where they may take part in outer layer formation. This mechanism is shown schematically in fig.55, and is discussed in some detail in chapter 2. It is almost universally accepted as the growth mechanism for duplex oxides in aqueous media.

Considering diffusion of solution down a pore in the inner layer to the metal/oxide interface, the flux of cobalt $j(t)$ can be expressed as:

$$j(t) = \frac{D_I [C^O_D(t) - C^O_O(t)]}{\delta(t)}$$
Where \( C_b \) and \( C_o \) represent the cobalt concentrations in the bulk solution and at the base of the pore, respectively. \( \delta \) is the oxide film thickness.

If each pore has a cross-sectional area 'a', and if there are 'n' pores per unit area, then the actual flux through the film is given by:

\[
J(t) = \frac{D_l [C_b(t) - C_o(t)] na}{\delta(t)}
\]

But 'na' is approximately equal to the interconnecting porosity \( \psi_1 \), so:

\[
J(t) = \frac{D_l \psi_1 [C_b(t) - C_o(t)]}{\delta(t)}
\]

The thickness, \( \delta(t) \), at time 't', is given by:

\[
\delta(t) = \frac{m_i(t)}{\rho_i (1 - \psi_1)}
\]

Where \( m_i(t) \) is the mass of the inner layer oxide per unit area, and \( \rho_i \) is its density. Substituting for \( \delta(t) \) in the previous equation we obtain:

\[
J(t) = \frac{\rho_i D_l \psi_1 (1 - \psi_1) [C_b(t) - C_o(t)]}{m_i(t)}
\]
Lister's model assumes that the crystallites composing the inner layer grow by a mechanism of dissolution and re-precipitation. The surface of each micro-crystal will have a concentration of metal ions at its surface equal to the saturation value, i.e. the solubility $C_{si}$. The proportion of cobalt in the precipitated oxide is then given by $C_0(t)/C_{si}$, multiplied by 0.7 (30% of the oxide is oxygen), and multiplied by a term $P_i$ - the partition co-efficient that describes the ease with which the cobalt is accommodated into the lattice. Most transition metals are readily incorporated into ferrite type structures so $P_i$ is expected to be close to unity.

From the assumptions above we obtain:

$$\frac{dC_{wi}(t)}{dt} = \frac{0.7 P_i C_0(t)}{C_{si}} \cdot \frac{dm_i(t)}{dt}$$

From this equation and the previous diffusion equation it is possible to eliminate $C_0(t)$, (the concentration of cobalt at the base of the pores). This gives us:

$$\frac{dC_{wi}(t)}{dt} = \frac{C_b(t)}{\frac{m_i(t)}{\rho_i D_i \phi_i (1-\phi_i)} + \frac{C_{si}}{0.7 P_i (dm_i(t)/dt)}}$$
This is the simplified version of Listers model that we aimed to derive. The only difference is that we have expressed it in terms of the amount of inner layer oxide \( (m_i) \), rather than the total amount of oxide assuming a full duplex layer \((m)\).

This equation can now be modified in order to predict the depth distribution of cobalt in the oxide. This can be done using the following relationship:

\[
\frac{dC_w(t)}{dm_i(t)} = \frac{dC_w(t)}{dt} \cdot \frac{dt}{dm_i(t)}
\]

We can then solve the equation by substituting the appropriate growth kinetics. If crystallisation controls the uptake then the proportion of cobalt (by weight) incorporated at time 't' is given by:

\[
\frac{dC_w(t)}{dm_i(t)} = 0.7 P_i \frac{C_b(t)}{C_{si}}
\]

However, if cobalt incorporation is controlled by diffusion down the pores then the uptake depends on the growth kinetics. For parabolic kinetics \(- m_i(t) = (k_p t)^{1/2}\)

\[
\frac{dC_w(t)}{dm_i(t)} = \frac{1}{k_p} C_b(t) \cdot 2 \rho_i D_i \phi_i(1-\phi_i)
\]
For logarithmic kinetics:

\[ m_1(t) = k_1 \ln(a_1 t + 1) \]

\[
\frac{dC_w(t)}{dm_1(t)} = \frac{\rho_1 D_1 \phi_1 (1-\phi_1) C_b(t) \exp[m_1(t)/k_1]}{k_1 a_1 m_1(t)}
\]

As would be expected from the initial model, if sufficient cobalt can diffuse down the pores to the metal oxide interface (crystallisation control), then the amount of cobalt incorporated is linearly dependent on the bulk solution concentration and is independent of the depth of oxide.

The same relationship is also predicted for parabolic kinetics where diffusion controls the pickup, assuming that the porosity \( \phi_1 \) of the oxide is constant with thickness. The corresponding prediction for logarithmic kinetics is still linearly dependent on the concentration of cobalt in the bulk solution, but has a more complex dependence on the thickness of oxide formed.

The use of a model developed for 573 K at 413 K is obviously rather tentative, however no mathematical models have been proposed for aqueous oxidation of stainless steel at this temperature, and the growth mechanism indicated by fig. 53 does suggest oxide growth at the metal oxide interface - as assumed in the high temperature mechanism. In accordance with Listers model we see a direct relationship between the cobalt level in the oxide and the dissolved cobalt level in solution, and we do not see a direct relationship with the kinetics of oxide growth. The cobalt distribution observed in the oxide is quite even (fig. 35), until the metal/oxide interface is reached, here
the cobalt level falls off gradually, as would be expected for a rough interface or a non-uniform oxide thickness.

6.8 CONCLUSIONS

The following conclusions were drawn from the work at 413 K:

i) Film growth slows appreciably after 6 hours exposure, at a thickness of 10-15 nm.

ii) The presence of cobalt has no apparent effect on film thickness except where specimens are allowed to cool in solution, in which case cobalt encourages the deposition of a mixed cobalt/iron overlayer.

iii) The oxide contains Cr$^{3+}$, Fe$^{2+}$, and Fe$^{3+}$ but no oxidised nickel.

iv) Incorporated cobalt is evenly distributed through the oxide.

v) Cobalt in the oxide is in a divalent state.

vi) Cobalt concentration in the oxide is directly related to solution concentration.

vii) Cobalt is incorporated at the metal/oxide interface during growth.

viii) Diffusion of cobalt within the film is small compared to the film thickness.
7. RESULTS AT 473 K

7.1 INTRODUCTION

The work of Castle and Clayton indicated that the rate of film growth on stainless steel increases markedly between 433 and 473 K. The experiments carried out at 473 K were designed to look for any differences in cobalt uptake, distribution, and chemical state which might be related to this change in growth rate.

All specimens were exposed using the PTFE cell and flow circuit described previously. Initial tests on the cell were troubled by problems maintaining a constant flow rate through the circuit. This was caused by the cell not being gas tight leading to nitrogen bubbles accumulating in the outlet tube. When these bubbles passed through the PTFE flow metering valve the flow rate suddenly increased leading to a temperature drop caused by the rush of unheated water into the cell. Re-sealing the cell cured the problem, and made it possible to get nearer to the maximum temperature of 488 K without boiling, whilst maintaining a flow rate between 1 and 1.5 ml/minute.

The exposure period was chosen in order to produce a film thickness sufficiently thin for XPS depth profiling, yet thick enough to contain useful information. The use of a double exposure, as at 413 K, to yield information on the mechanism of cobalt uptake was tried, as well as varying the amount of cobalt in solution.

Finally a few specimens were exposed to water containing approximately 1 g/l boron as boric acid and 2 mg/l lithium as lithium hydroxide, to see the effect of reactor water chemistry on film formation and cobalt uptake.
All etch profiles are plotted as atomic % against etch time, the etch rate assumed to be approximately 1.5 nm/min.

7.2 VARYING EXPOSURE PERIODS

Figure 56 shows the cumulative etch profiles for specimens exposed to pure water for periods of 7 and 4 hours. The 7 hour exposure showed a considerable increase in film growth over previous 6 hour exposures at 413 K (see fig.36), and the 60 minutes etching required to remove the oxide film was considered too great for routine analysis.

A four hour exposure period was found to give a more suitable oxide thickness, though still three times as thick as that produced during previous 6 hour exposures at 413 K.

Both profiles show a considerable reduction in the amount of silicon picked up from solution. This being due to the use of the PTFE cell thus avoiding contact between high temperature water and glassware.

Another interesting change from observations at 413 K is the presence of nickel in the film, although at a level only just detectable by ESCA analysis. The chemical state of this nickel is hard to determine due to the small quantity present, but is in an oxidised rather than metallic state. As the film is etched away the amount of nickel is initially constant, then metallic nickel predominates as the nickel signal increases in the region of the metal/oxide boundary (fig.57). The presence of nickel within the film prevents the use of the nickel signal to indicate the approach of the metal/oxide interface, as was done at 413 K.
Fig 56. Comparison of 4 hour and 7 hour exposures of #304 stainless steel in pure water at 473 K.
FIG 57. NICKEL 2p PEAK OBSERVED WHILE ETCHING SPECIMEN EXPOSED TO PURE WATER FOR 4 HOURS AT 473 K (FIG. 56)
In the outer part of both films the iron/chromium ratio lay between 1.5 and 2.0, close to that observed at 413 K. Deeper into the film the proportion of chromium increased slightly to give a minimum ratio of approximately 1.2.

Chemical state information from the iron, chromium and oxygen signals revealed the same pattern as observed at the lower temperature. The unetched surface of the oxide contained a small amount of trivalent iron and very little chromium. The oxygen peak shows a 50:50 oxide/hydroxide mixture (fig 58).

The first brief etch removed loosely bound surface species and resulted in an increase in both chromium and iron signals. The iron peak showed a shift to a mixed ferrous/ferric state (fig 59), and the oxygen peak became predominantly oxide-like with a trace of asymmetry in the hydroxide direction. As etching continued the chemical state of the iron peak followed the same general trend as had previously been observed at 413 K (figs.41-43). An increase in the ferrous component was followed by the appearance of a metallic component. This eventually dominates as the oxide is removed by the action of the ion beam. The chromium peak does not begin to show metallic character until the iron peak has become predominantly metallic.
OXYGEN 1s PEAK IN UNETCHED CONDITION

FIG 58. OXYGEN PEAK FROM SPECIMEN EXPOSED FOR 4 HOURS AT 473 K (FIG. 56)

FIG 59. IRON 2p PEAKS AFTER 30 SECONDS ETCH

FIG 59. IRON PEAK FROM SPECIMEN EXPOSED TO PURE WATER FOR 4 HOURS AT 473 K (FIG. 56)
7.3 THE EFFECT OF COBALT ON OXIDE FORMATION

The first specimen to be exposed to cobalt containing solution at 473 K was marred by the failure of tubing in the water circuit after 20 minutes at temperature. This necessitated closing the flow controlling valve, thus stopping the flow of water. Considering the small cell volume, and cobalt concentration of 0.4 mg/l, it is quite likely that the solution in the cell was considerably depleted of cobalt by the end of the four hour exposure period. The depth profile for this specimen is shown in fig. 60. Cobalt and chromium have been plotted adjacent to each other, and the complementary concentrations of these elements is clear. The amount of incorporated cobalt is at a maximum of 10.5 at% in the outer surface of the film, and decreases steadily as the film is etched away. Chemical state information from the cobalt peak reveals a divalent state, furthermore no change is observed in the peak position as etching proceeds (fig 62), unlike previous specimens exposed at 415 K where cobalt was observed to change to the metallic state as the film was etched away.

The presence of cobalt in solution seems to be associated with an increase in the silicon content of the film, as has been observed at 413 K. The silicon is distributed through the outer portion of the film at a fairly level concentration of 2.7 at%, and does not seem to be closely related to the cobalt distribution.

The nickel distribution is similar to that observed in pure water, though a slightly greater proportion of nickel is seen on the extreme outer surface of the film.

After rectifying the problem with the flow circuit tubing a
Comparative profiles for films formed in cobalt-dosed water.

**TOP:** Water flow interrupted at start of run

**BOTTOM:** Flow circuit behaving normally
second specimen was exposed for 4 hours to water containing 0.5 mg/l cobalt (fig 61). As might be expected the amount of cobalt in the film was greater than for the previous specimen, reaching a maximum value of 13.3 at% after 2.5 minutes etching. Again cobalt and chromium appear to be complementary.

When compared with the previous specimen it seems that cobalt extends deeper into the film, the difference probably being due to the interruption of flow during corrosion of the first specimen.

The cobalt appears initially in a divalent state (fig.63) but, unlike the previous specimen, it shows the change to the metallic state observed previously during ion beam etching of films formed at 413 K. Associated with the cobalt is a slight increase in the proportion of silicon in the film, this having a depth distribution very similar to the previous specimen (fig.60).

Further specimens were exposed to lower levels of cobalt dosing in order to relate cobalt uptake to the concentration in solution. At 0.25 mg/l cobalt the same general trends as the previous specimens were observed (fig.64). A thick (~90 nm) film was formed containing traces of nickel, and the chromium content appeared to be dictated by the amount of incorporated cobalt. The chemical state of the cobalt was again divalent and remained divalent throughout the etch sequence. Neither iron nor chromium showed any metallic character by the end of the etch sequence, thus indicating that the metal/oxide interface had not been reached.
FIG 63. COBALT MONTAGE FOR SPECIMEN EXPOSED FOR 4 HOURS AT 473 K TO WATER CONTAINING 0.5 mg/l COBALT
At 0.125 mg/l cobalt a thinner film was formed (fig.65), together with a considerably lower proportion of cobalt than expected. It was suspected that the low cobalt level was due to the glass reservoir adsorbing cobalt from solution during a short storage period, so the experiment was repeated using freshly prepared solution. Analysis of this specimen revealed a greater proportion of cobalt (fig.66), confirming that adsorption had occurred. The oxide film on this specimen was, however, the thinnest so far encountered at this temperature. The nickel signal is seen to increase from the start of etching, and the iron/chromium ratio in the outer region of the film was approximately 1:1, considerably higher than that for films formed in pure water. Although the nickel and oxygen profiles of both specimens exposed to 0.125 mg/l cobalt indicate a thinner film than previously observed at 473 K, both show that the cobalt picked up from solution penetrates to great depth.

Apart from any difficulties in deciding where the metal/oxide interface was located, there was obviously a large variation in the film thickness between different specimens. Some factor other than cobalt concentration must be controlling film thickness (this is discussed further in section 7.7). This obscures any effect the cobalt might have on the rate of film growth. However, the film composition is significantly influenced by the cobalt concentration in solution. When thick films have been formed cobalt is present at the expense of chromium, although the proportion of iron seems unaffected. The presence of cobalt also appears to be linked to a small increase in the silicon content of the film. The two specimens that formed thin films had a chromium level higher than that of
Comparison of cobalt uptake from freshly made solution and solution allowed to stand for 3 weeks in glass container. Cobalt is depleted from solution with time.
thicker films formed in pure water at 473 K, and a chromium rich protective oxide may have formed. The effect of cobalt on the thin film is not known as no films of this type were produced in pure, cobalt free water at 473 K.

7.4 SIMULATED PWR WATER CHEMISTRY

In line with current PWR practice a few specimens were run in water modified by the addition of 0.5-1.0 g/l boron, as boric acid, and 1-2 mg/l lithium as lithium hydroxide.

For the first specimen 0.53 g/l boron and 1 mg/l lithium were added to water dosed with 0.18 mg/l cobalt. The etch profile for this specimen (fig.67) reveals a thick oxide containing considerable cobalt and an increased proportion of silicon, both of which are distributed evenly through the film. Chromium is also evenly distributed through the film, thus any complementarity of cobalt and chromium is not clearly evident.

The chemical state of the cobalt, though divalent initially, rapidly develops a shoulder indicating the metallic state (fig.68), and it appears likely that this accounts for the reduced proportion of oxygen in the film when compared with previous specimens.

No boron was detected in the film, and analysis for lithium is not possible (using XPS) when there is an appreciable iron signal due to a peak clash.

The next specimen was exposed to 1 g/l boron and 2 mg/l lithium, with 0.15 mg/l cobalt. The oxide formed was considerably thinner than the previous specimen (fig.69), with oxygen, nickel and silicon profiles similar to the specimen previously exposed to pure
Fig 67. 4 hours at 473 K in simulated PWR water (528 mg/l boron, 1 mg/l lithium), dosed with 0.182 mg/l cobalt.
FIG 68. COBALT MONTAGE FOR SPECIMEN EXPOSED FOR 4 HOURS AT 473 K TO WATER CONTAINING 528 mg/l BORON, 1 mg/l LITHIUM AND 0.18 mg/l OF COBALT AS CoCO₃.
FIG 69. "PWR" WATER CHEMISTRY, 0.148 mg/l COBALT

FIG 70. "PWR" WATER CHEMISTRY WITH A TRACE OF COBALT

COMPARISON OF ETCH PROFILES FOR SPECIMENS EXPOSED FOR 4 HRS AT 473 K TO WATER CONTAINING 1 g/l BORON AS BORIC ACID AND 2 mg/l LITHIUM AS LIOH, WITH DIFFERING LEVELS OF COBALT.
water dosed with 0.125 mg/l cobalt (fig.66). However, fig.69 clearly shows the increased uptake of cobalt, with cobalt seemingly extending past the metal/oxide interface.

Finally two specimens were exposed to 1 g/l boron and 2 mg/l lithium without any cobalt dosing. One specimen was subsequently exposed to cobalt dosed solution (see next section), whilst the other was analysed (fig.70). As can be seen from figure 70 a small amount of cobalt was picked up, this no doubt arising from a slight memory effect within the flow circuit.

The oxygen profile was very similar to that for the specimen exposed to the same solution dosed with cobalt (fig.69), though the silicon level had dropped until it was barely detectable. The much reduced cobalt level was countered by a corresponding increase in the chromium level, again reinforcing the complementarity of these two elements.

7.5 DOUBLE EXPOSURE SPECIMENS

Two double exposures were tried, one in pure water and one in water containing 1 g/l boron and 2 mg/l lithium. In both cases the first exposure was for 4 hours to water free of cobalt, and the second exposure was to cobalt dosed water. Neither specimen produced the sort of profile obtained using a similar double exposure at 413 K (fig.53).

The specimen exposed to water containing no boric acid or lithium hydroxide produced a thick film (fig.71) which only began to show signs of being etched back to the substrate after 51 minutes (∼75 nm) of etching, by which stage no more time was available on the
FIG 71. DOUBLE EXPOSURE SPECIMEN IN PURE WATER AT 473 K.

FIG 72. DOUBLE EXPOSURE SPECIMEN IN "PWR" WATER AT 473 K.

Pure water exposure: 4 hrs no Co, then 4 hrs + 0.25 mg/l Co.

"PWR" water exposure: 4 hrs no Co, then 4 hrs + 0.148 mg/l Co.

"PWR" water = 1 g/l Boron, 2 mg/l Lithium.
ESCA instrument, so analysis had to be stopped.

The resulting profile shows a maximum of 2.6 at% cobalt at the oxide/water interface, and this drops to approximately 0.5 at% after 12 minutes etching. Thereafter cobalt is still present in trace quantities, with no sign of an increase towards the base of the film. Silicon is also found predominantly in the outer region of the film, whilst nickel is largely restricted to the inner region. The other main difference between the outer, cobalt containing, region of the film and the inner region is the level of chromium - approximately 10-12 at% in the outer region, increasing to 16-17 at% from the point where the cobalt and silicon levels drop.

A second specimen subject to a similar exposure sequence in water containing 1 g/l boron and 2 mg/l lithium produced a film morphology (fig.72) rather similar to that found previously for a single exposure to cobalt dosed water with the same chemistry (fig.69). Although the cobalt level is reduced the general profiles for all the elements are very similar. Chemical state information from the two films again shows cobalt reduction, in line with the decrease in oxygen content of the film.

Unfortunately there seems to be no features in this depth profile which can be attributed exclusively to the double exposure, except that the pre-filming in the first stage approximately halved the amount of cobalt taken up by the film, compared with another specimen subject only to the second stage exposure (fig.69).
7.6 COBALT UPTAKE RELATIVE TO COBALT IN SOLUTION

The dependence of cobalt uptake on solution concentration observed at 413 K (fig. 52) was also seen at 473 K, however a considerable increase in the amount incorporated at a given solution concentration was observed, and a further increase was observed for the specimens exposed to water containing boric acid and lithium hydroxide.

As the oxide film formed at 473 K contained small quantities of nickel it was impossible to estimate the position of the metal/oxide interface on the basis of the appearance of the nickel signal as had been done at 413 K. Thus, instead of the range of cobalt uptake across the film thickness, the results for 473 K, together with those for 413 K, are re-plotted in fig. 73 on the basis of the maximum cobalt content observed whilst depth-profiling through the oxide film.

7.7 DISCUSSION

The film thicknesses and cobalt uptakes for specimens exposed both at 413 K and at 473 K are summarised in table 4.

It is clear from the results at 473 K that two different types of film were formed. The major difference being the film thickness. Thick films were formed on all but two of the specimens exposed to pure water (with and without cobalt dosing), whereas thin films were formed on three of the four specimens exposed to water containing boric acid and lithium hydroxide. The oxygen profiles for both thick and thin films are shown in fig. 74.

The thick films vary from an estimated 55-60 nm after 4 hours
FIG 73. EFFECT OF TEMPERATURE AND WATER CHEMISTRY ON COBALT UPTAKE
<table>
<thead>
<tr>
<th>Temperature K</th>
<th>Time h</th>
<th>Water Chemistry</th>
<th>Cobalt conc. mg.l⁻¹</th>
<th>Thickness nm</th>
<th>Max. cobalt conc. in oxide at.%</th>
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<tbody>
<tr>
<td>413</td>
<td>24</td>
<td>Pure</td>
<td>350</td>
<td>-</td>
<td>3.8</td>
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<tr>
<td>24</td>
<td>500</td>
<td></td>
<td></td>
<td>12</td>
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<tr>
<td>6</td>
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</tr>
<tr>
<td>6</td>
<td>500</td>
<td></td>
<td>13</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Trace</td>
<td></td>
<td>16</td>
<td>1</td>
<td></td>
</tr>
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</tr>
<tr>
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<td>0 + 500*</td>
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<td>3.4</td>
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<td>100</td>
<td></td>
<td>&gt;21</td>
<td>1.1</td>
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</tr>
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<td>7</td>
<td>Pure</td>
<td>0</td>
<td>100</td>
<td>0</td>
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<td>&gt;55</td>
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<tr>
<td>4+4±</td>
<td>0 + 250*</td>
<td></td>
<td>&gt;81</td>
<td>2.6</td>
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</tr>
<tr>
<td>4</td>
<td>250</td>
<td></td>
<td>81</td>
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<tr>
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<td></td>
<td>31</td>
<td>4.6</td>
<td></td>
</tr>
<tr>
<td>473</td>
<td>4±</td>
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<tr>
<td>4+4±</td>
<td>(1000 ppm B)</td>
<td>Trace + 148*</td>
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<td>27</td>
<td>4.5</td>
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<td>Trace</td>
<td></td>
<td>30</td>
<td>2.0</td>
<td></td>
</tr>
</tbody>
</table>

* Double exposure samples
† Water chemistry: 500 mg.l⁻¹ B, 1 mg.l⁻¹ Li
♯ Cobalt deposited during overnight cooling
FIG 74. OXYGEN PROFILES FOR FILMS FORMED AT 473 K.

THIN FILMS (above) AND THICK FILMS (below).
exposure (based on the time taken to etch back to 40 at\% oxygen), to
greater than 90 nm after 7 hours exposure (fig.56). This shows that
these films continued to grow throughout the exposure period, and is
in good agreement with the work of Clayton\textsuperscript{58}, which indicated a
change to linear growth kinetics at 473 K (figs.1 and 2).

The thin films formed had remarkably similar oxygen depth
profiles, the estimated film thickness being 23-30 nm. Even the thin
film double exposure specimen showed the same film thickness, thus it
seems a protective film had formed and film growth had effectively
ceased after 4 hours. This appears to be the same sort of film
growth mechanism as was observed at 413 K, although the film
thickness at this lower temperature was only 10-15 nm. Similar film
growth was also observed by Clayton\textsuperscript{58} at 433 K, and he was thus able
to place the change in mechanism somewhere between 433 K and 473 K.
The results from this work indicate that this transformation is very
close to 473 K, thus small changes in flow rate, oxygen level or
specimen position within the flow cell were sufficient to promote
either type of film.

7.7.1 THIN FILMS

The top of fig.74 shows that the oxygen profiles of the thin
films are very consistent, including the double exposure specimen in
PWR water. This consistency is very useful in the interpretation of
all the etch profiles presented here. It shows that the etch rate of
the ion gun does not vary greatly between specimens, and that surface
effects due to adsorbed species are small.

Within these films there is a trace of nickel (< 1 at\%) at the
oxide/water interace (fig.75). After the removal of approximately
3 nm the proportion of nickel increases reaching a plateau of between
2 and 4 at% after 6 minutes etch (approx. 9 nm). Nickel stays at this
level for the next 15 nm, then increases again as the metal/oxide
interface is reached. It appears that the majority of the film
contains a constant level of 2-4 at% nickel, and there is a thin
outer layer containing < 1 at. % nickel.

The iron profiles (fig.76) are very similar, and appear to be
unaffected by the presence of cobalt within the film. Again the
double exposure specimen fits in well with the other results
indicating little change in the film thickness.

The chromium profiles vary greatly according to the amount of
incorporated cobalt. The profiles for the thin film containing least
cobalt, and the two cobalt free thick films are plotted in fig.77.
The thin film is far more chromium rich, containing almost 20 at% in
the outer region of the film.

Also plotted on this figure is the chromium profile for the
specimen exposed to pure water for 6 hours at 413 K. The shape is
quite similar to the thin film formed at 473 K, except that the film
is thinner and the outer region of the film contains slightly less
chromium.

In the paragraphs above it has been shown that neither the iron
nor the oxygen profiles are affected by the presence of cobalt within
the film. The amount of nickel also seems largely unaffected, and
this means that any cobalt or silicon entering the film is
accommodated by a reduction in the chromium content. The chromium
profiles for cobalt containing films are therefore dominated by the
FIG 75. NICKEL PROFILES FOR THIN FILMS
Fig 76. Iron profiles for thin films

Fig 77. Chromium profiles
distribution of cobalt.

Cobalt profiles for the thin films are shown in fig.78. The main feature is that cobalt reaches a maximum after 6 to 15 minutes etching, corresponding to 40 to 50 at.% oxygen. This is below the chromium rich outer region of the film (illustrated in fig.77). Most of the profiles also show a slight increase in the cobalt content at the oxide/water interface, possibly corresponding to the outer layer seen in the thick films.

Examination of cobalt uptake versus solution concentration (fig.73) shows that the amount of cobalt incorporated at 473 K is some 2.5 times greater than was observed at 413 K, and that addition of boric acid and lithium hydroxide to the water results in another large increase in the affinity of the oxide for soluble cobalt species.

There is no clear distinction between the amount of cobalt incorporated in thin and thick films. For example the two points in fig.73 indicating cobalt uptake by specimens exposed to PWR water chemistry represent the two different types of film. The specimen exposed to 0.5 g/l boron, 1 mg/l lithium, and 0.18 mg/l cobalt had a film thickness of 63 nm; whereas the specimen exposed to 1 g/l boron, 2 mg/l lithium, and 0.15 mg/l cobalt had a film only 25 nm thick (based on the time taken to etch back to 40 at.% oxygen). This might be interpreted in a number of ways. It could be that the amount of cobalt incorporated from solution is governed by fundamental thermodynamic constraints which pay no heed to the growth mechanism. However, it seems likely that in order to form the thicker type of film it is necessary to pass through the thin film
FIG 78. COBALT PROFILES FOR THIN FILMS.
stage. If we assume that this is so and that the thicker films result from thin films that have lost their protective nature due to reaching some critical value of, for example, cation transport; and if the thin film incorporates more cobalt due to its slow growth rate or its composition - then the maximum cobalt level in the thick films would depend on the thin films from which they grew. The difference between thick and thin films would be in terms of the cobalt distribution and not the maximum cobalt content observed during etching.

The chemical state of cobalt in all cases at 473 K was initially divalent. The trivalent state was only seen once, and this was at 413 K at the oxide/water interface on a specimen allowed to cool overnight (see Section 6.3). As etching proceeded the divalent state sometimes changed to the metallic state. Unfortunately it is not possible to discern whether this is a true chemical state change within the film or whether it is a beam induced effect.

7.7.2 THICK FILMS

The thick films shown in the bottom of fig.74 show a greater variation in their oxygen contents. With 50 at% oxygen in FeO and 60 at% in Cr$_2$O$_3$, it was hard to see how our analyses could give oxygen levels reaching 72 at%, and why there should be this variation between specimens. At first it was thought that this might be due to a change in the hydroxyl content of the films. To investigate this the oxygen $^{18}$ spectra from specimens showing low and high oxygen contents were analysed (fig.79) using the peak fitting routine described in Chapter 8. There was no significant difference between
FIG 79. A COMPARISON OF THE OXYGEN 1s SPECTRA FROM HIGH OXYGEN FILMS (ABOVE), AND LOW OXYGEN FILMS (BELOW).
specimens. However a similar examination of the carbon spectra (fig.80) showed that the component of the carbon peak attributed to carbonate became significant in the high oxygen films. Carbon is not normally included in the analysis unless it is of specific importance (see Section 4.5). Although cobalt was dosed into solution as cobaltous carbonate, the amount of carbonate did not seem to be related to the level of incorporated cobalt. There is in fact a trend towards reduced oxygen content with increased cobalt uptake (fig.81).

A further possible cause of the high oxygen content in some thick films could be silicon. It was obvious that the silicon was not present as silica due to the absence of the appropriate component in the oxygen 1s spectra (just to the high binding energy side of the position for hydroxyl species). Examination of the interrelation of silicon and oxygen within the films (fig.82) showed a trend towards a lower oxygen level in the high silicon films. Silicon could not thus be used to account for higher than expected oxygen levels.

Considering that an increased proportion of cobalt and silicon both seem related to a reduced oxygen content in the film, and previous observations that increased cobalt uptake seems associated with the presence of more silicon, the relationship shown in fig.83 is hardly surprising. Increasing cobalt concentration in solution increased the amounts of cobalt and silicon found in the film, and the proportion of oxygen in the film was reduced. This interaction between cobalt and silicon was also observed at 413 K, but the thin films formed didn't offer themselves to any useful measurement of the change in oxygen content. The silicon may be present because the
FIG 80. A COMPARISON OF THE CARBON 1s SPECTRA FROM HIGH OXYGEN FILMS (ABOVE), AND LOW OXYGEN FILMS (BELOW)
ETCH TIME 2.5 - 15 MINUTES

FIG 81. OXYGEN/COBALT CORRELATION

ETCH TIME 2.5 - 15 MINUTES

FIG 82. OXYGEN/SILICON CORRELATION
ETCH TIME 2.5 - 15 MINUTES

FIG 83. SILICON/COBALT CORRELATION
concentration is increased in solution, or because the incorporation of cobalt favours the presence of silicon within the film, this is discussed later in this section.

The nickel profiles for the thick films (fig.84) are completely different from those for thin films (fig.75). The outer surface of the film contains up to 1.5 at.% nickel, but as etching continues this level falls to 0.3 to 0.8 at.%. After some 15-30 nm have been removed, the nickel level begins to climb, and most of the thick films show a second plateau at 2 to 4 at.%. So it seems from the nickel profiles that the thick films have a two layered structure. The inner region seems similar to the thin films and contains more nickel than the outer region.

The increase in nickel content of the outer layer at the oxide/water interface was also noted by Clayton\textsuperscript{58}, who observed from 5 to 20 at.% depending on the flow rate and time of exposure. This was interpreted as solution transport from a chromel/alumel thermocouple. The lower level observed here reflects the replacement of this type of thermocouple by a stainless steel sheathed thermocouple, thus any nickel in solution must have arisen from a corroding stainless steel surface.

The iron profiles (fig.85) show some consistency in that, regardless of cobalt content or water chemistry, they all contain between 17 and 20 at% iron after 8 minutes etching (approx.12 nm), this being the middle of the outer layer. Deeper in the film there is a considerable difference between specimens, presumably due to variations in the film thickness. There is no obvious effect of cobalt on the iron content of the films.
FIG 84. NICKEL PROFILES FOR THICK FILMS

FIG 85. IRON PROFILES FOR THICK FILMS
Fig. 77 shows that the thick films contain less chromium than the thin films. The chromium content is 10-12 at% in the outer layer, increasing to a peak of 16 at% in the inner layer before falling back to 14 at%. This is for cobalt free films, when cobalt is present the amount of chromium is reduced.

As with the thin films chromium and cobalt seem complementary, however the cobalt distribution is rather different (fig. 86). The cobalt profiles vary greatly between specimens, and only in the thick film grown in 'PWR' water chemistry is the inner region of the film as rich in cobalt as the outer. Cobalt is again observed to be in a divalent state initially with varying proportions of the metallic state appearing as etching proceeds.

7.7.3 MECHANISMS

If we consider the thin films formed at 413 K and 473 K it appears we have the formation of a protective oxide which acts as a barrier between oxidising species in solution and the unoxidised substrate. This coherent oxide film could form by outward diffusion of cationic species to the oxide/water interface, or by inward diffusion of oxidising species to the oxide/metal interface. The double exposure specimen at 413 K (fig. 53) suggests the latter mechanism, as cobalt has reached the metal/oxide interface during the second stage of exposure. The presence of cobalt at this interface and not in the middle of the film suggests that there are short circuit diffusion paths in operation. The oxide that forms is depleted in iron with respect to the substrate metal, this occurs because a certain proportion of the iron at the metal/oxide interface
FIG 86. COBALT PROFILES FOR THICK FILMS
dissolves then diffuses outwards along the same short circuit paths proposed for the inward diffusion of cobalt and oxidising species. This dissolved iron does not contribute to film growth and is carried away by the constantly replenished solution before it reaches saturation.

It is also possible that there is an internal oxidation mechanism at work at the base of the film involving the reaction of the oxide already formed with unoxidised chromium in the substrate. The effect of this will depend on the diffusing species. If chromium can diffuse to the oxide/metal interface it may react to form a healing $\text{Cr}_2\text{O}_3$ film at the base of the oxide. Alternatively, if oxygen can diffuse through the oxide to the substrate, it may react selectively with chromium to produce an internal oxidation region of chromium oxide and metallic iron. Subsequent reaction of this iron leading to both oxidation and dissolution might easily support the sort of growth mechanism dependent upon solution transport through pores in the inner layer.

Although diffusion distances are likely to be small it is still possible that these processes could be crucial in determining the nature of the metal/oxide interface and thus governing the changeover from thin film to thick film growth kinetics. The thin films being stable when cation diffusion predominates and thicker films forming when anion diffusion takes over. Another possible reason for the changeover in mechanism is that the film reaches a critical temperature and/or thickness at 473 K that enables it to change from the amorphous or short-range ordered films formed at lower temperatures to the crystalline films known to form at 523 K.
Clayton\textsuperscript{58} reported that the growth kinetics of the thick films he formed at 473 K appeared to be linear, and this could well be true of the results reported here. The growth rate of the thick films is faster and does not appear to reach a limiting thickness within an 8 hour exposure. The most obvious conclusion is that the film growth mechanism has moved from that seen in room temperature passivity to that observed at 573 K. The thick films observed here are thus probably the initiation of duplex layer formation, and although the films are still very thin compared to those formed at 573 K it seems reasonable to describe their growth in terms of the mechanisms discussed in section 2.1.2 and Listers mechanism (Section 6.7).

The high temperature growth mechanism leading to the formation of duplex oxides involves two main processes. The inner layer grows by oxidation at or close to the oxide/metal interface, during this process iron and nickel species are dissolved and are transported into solution where they may take part in the formation of the outer layer. This grows by deposition from solution, and is composed largely of magnetite and nickel ferrite. Chromium is restricted to the inner layer in most cases, where it is part of a mixed iron/chromium/nickel spinel.

The chromium profiles shown in fig.77 indicate that chromium is present throughout the thick films formed in this work. These films therefore probably represent the nucleation of the inner layer of the classical duplex film structure, and the outer layer is not formed due to the continual solution replenishment.

From the mechanism proposed above it can be seen that the outer region of the thick films should be the remains of the thin film from
which it grew, and that the inner region should be the oxide formed since the film lost its protective nature. It is hard to find any trends to reinforce this within the results, probably because the films underwent extensive changes during and after the changeover from thin film to thick film growth regimes.

The mechanisms for cobalt incorporation must relate to the oxidation mechanisms discussed above and must fit in with the following trends:

i) The maximum proportion of cobalt within the films is directly related to the cobalt concentration in solution, but varies with changes in temperature and water chemistry.

ii) The maximum proportion of cobalt within the films appears to be independent of the film growth mechanism.

iii) The distribution of cobalt within thick and thin films is different.

iv) Cobalt is incorporated as a divalent ion, apparently reducing the proportion of trivalent chromium within the film.

v) Cobalt distributions within thick and thin film double exposure specimens at 473 K differ considerably.
To explain these results it is necessary to consider the driving force for cobalt incorporation. When considering corrosion product stability Rummery and MacDonald\textsuperscript{154} showed that cobalt ferrite is thermodynamically more stable than magnetite between 298 K and 573 K, both in reducing and oxidising water chemistries (fig.87). Conversely nickel ferrite was not stable below 473 K. Unfortunately they were not able to calculate the behaviour of non-stoichiometric spinels, and did not discuss the stability of chromium species.

The extra stability of the cobalt bearing spinel could modify the oxidation/dissolution reaction of iron at the base of the film so that cobalt containing spinel would be formed and the amount of iron entering solution would be reduced (fig.88). This would increase the Fe/Cr ratio in the film, thus apparently reducing the chromium level.

This mechanism explains the observed thin films if the iron/cobalt spinel behaves in the same way as the iron/chromium spinel in forming a protective oxide layer, so that the overall oxide thickness is the same. The valence difference between cobalt and chromium would be accommodated by an increased proportion of trivalent iron species.

From the double exposure specimen at 413 K (fig.53) we assume that during thin film formation soluble cobalt is incorporated at the metal/oxide interface. A thin film was produced in one of the double exposure tests at 473 K (fig.72). The cobalt distribution indicates either that diffusion processes within the film have greatly increased, or that the film itself is now more dynamic than passive in nature. This may well be a clue to why the thin films give way to thick films above 473 K.
FIG 87. Hydrogen equilibrium partial pressure versus temperature for the reduction of CoFe₂O₄, Fe₃O₄, NiFe₂O₄, CoO and NiO; and hydrogen partial pressure versus temperature corresponding to a hydrogen concentration of 0.446 mmol/kg.
FIG 88. MODIFICATION OF FILM GROWTH MECHANISM BY SOLUBLE COBALT
Although the amount of incorporated cobalt in thin films and in the outer region of thick films is much the same (as discussed in section 7.7.1) the distribution of cobalt in the thick films is much more variable (fig.86). The cobalt profile that falls off fastest as etching proceeds, is for the specimen which spent the majority of its exposure period with no flow through the cell due to a failure in the water circuit. Thus it appears that the depletion of cobalt from solution has decreased the amount of cobalt in the inner region of the film. It seems reasonable to assume from this that film growth is occurring at the metal/oxide interface.

The thick film double exposure specimen that might have indicated this mechanism (fig.71) shows a remarkably low level of cobalt uptake compared with control specimens. It seems that during heating or cooling periods it was able to form a more protective film, thus reducing film growth during the second stage of exposure. This result also tends to indicate that the distribution of cobalt through the thin film double exposure specimen at 473 K was due to the more dynamic nature of the film, rather than a substantial increase in the solid state diffusion of cobalt.

The cobalt distributions of the thicker films suggest that although growth is occurring at the metal/oxide interface, the soluble cobalt is not always able to reach this region of the film, possibly because it interacts with the existing film before it can reach the film base. The maximum amount of cobalt picked up by this interaction would be governed by the same principles as for the thin films, hence the observed similarity between the maximum cobalt level in thick films, and the cobalt level in thin films. Cobalt
incorporation would thus be expected to be mainly in the outer region of films initially, then to extend deeper into the film with time.

Only one specimen exposed to 'PWR' water produced a thick film, and this showed the most even distribution of cobalt (fig.67). It can be seen from this profile that the increased proportion of chromium near the metal/oxide interface in other specimens is not present when cobalt is incorporated in this region, thus the apparent complementarity of chromium and cobalt is again reinforced. The fact that cobalt is distributed right through the film suggests that the 'PWR' water has increased the permeability of the oxide. This specimen may well reflect cobalt uptake via crystallisation or diffusion control as predicted from Listers model (section 6.7), however this model cannot describe the cobalt distributions in the other thick films, although the same growth mechanisms seem to be in operation.

One possible criticism of Lister's model is the assumption of a constant amount of porosity through the film, and a sufficiently large pore size for cobalt species to diffuse through. The proximity to a critical pore size for the passage of dissolved cobalt species could explain the vast differences in cobalt distribution shown in fig.86, especially the very low cobalt uptake in the double exposure specimen. The present model may however be adequate in this respect for films formed in a reactor environment.

Listers model for incorporation fails to describe the results from this work, and would benefit from thermodynamic data on mixed Fe/Cr, Fe/Co and Fe/Cr/Co spinels. This would enable the solubilities of various species to be calculated. The incorporation
mechanism could then be modified if, as proposed above, the incorporation is controlled by the greater stability (hence lower solubility) of cobalt containing spinels causing a change in the oxidation/dissolution reaction at the base of the film.

### 7.7.4 CONCLUSIONS

The following conclusions were drawn from the results at 473 K:

1. Two types of film were observed, indicating that the change from low temperature to high temperature growth mechanisms occurs at or close to this temperature.

2. Nickel is a stable film constituent in small quantities.

3. Cobalt is incorporated in a divalent state.

4. The maximum cobalt concentration in the oxide is directly related to the solution concentration, and is approximately 2.5 times greater than at 413 K.

5. The maximum level of cobalt incorporated shows no dependence on the type of film formed.

6. The cobalt distributions through the film differ for the two different growth mechanisms.
vii) Incorporated cobalt depresses the amount of chromium in the film.

viii) The amount of silicon within the film increases with increasing cobalt uptake.

ix) The addition of lithium hydroxide and boric acid to the water increases uptake for both oxidation mechanisms.

x) A mechanism for cobalt uptake has been proposed to explain the observations from this work, based on the stability of cobalt containing spinel relative to the iron/chromium spinel formed in the absence of cobalt.
8. DATA HANDLING ON THE PRIME COMPUTER

8.1 INTRODUCTION

The work presented so far in this thesis has relied extensively on computerised data handling. Quantitative analysis, for example, requires the use of peak areas, rather than heights, because of differing peak widths from element to element and from one valence state to another. As is well known and has been pointed out earlier, photoelectron peaks contain much chemical state information. For the transition elements involved in any study of steels this information results in complex changes of peak shape rather than a simple shift in position. The satellite peak of Co(II) has been highlighted, but less pronounced satellites of several origins are included in the Fe(II) and Fe(III) envelopes. These, in pure standards of individual chemicals, can be related to bonding and structural considerations. The long term aim of understanding the incorporation of ions within a ferrite or magnetite structure would depend on the interpretation of these contributions to the peaks.

Consideration of such problems of detailed chemistry during the course of this project lead to the view that, on real samples, with mixed states and distributions, a microcomputer, used routinely to acquire data, could not in reasonable time undertake an adequate peak shape analysis for the full chemical state information to be available.

This chapter describes developments both in computer equipment (hardware) and programs (software) carried out with the aim of improving our data processing ability beyond the limitations of the
dedicated microcomputer and thereby increase our understanding of, and ability to interpret, the spectra of the transition metals. This project has been run in parallel with the work described in previous chapters, and much still remains to be done before the fitting of iron, chromium, nickel and cobalt becomes routine.

8.2 HARDWARE DEVELOPMENTS

In the summer of 1980 a Prime 550 multiple user mini-computer was acquired by the university from the SERC. This complemented the existing network of four Prime 750 computers, and was intended mainly for use by SERC backed groups within the university. The Prime 550 has 1.25 Mbyte of core memory and two 80 Mbyte disks, thus is quite a powerful computer (especially when compared to the PDP8e). As it is linked to the main Prime network at Surrey University it is possible to access a wide range of peripheral devices from plotters to an array processor. The Prime is also linked to the SERC computer network, and can thus access computers in universities and research laboratories throughout the U.K..

The possibility of using the Prime 550 (named SYPE) for data manipulation offered a real basis for peak analysis, so a terminal line was installed in the laboratory, and a graphics terminal was purchased. To provide an interface between the PDP8e and SYPE a serial input/output board was purchased for the PDP8e together with the Fortran language tapes required to drive it.

After obtaining the required level of expertise in Fortran usage on both the PDP8e and SYPE, two programs were written. One to interpret the encoded information on the PDP8e data tapes, re-format
it and send it through the interface board to the Prime and another on SYPE to read the incoming data and file it on disk. This interface was completed in August 1981, and has operated in much the same way since. The features offered by the Prime/ESCA datasystem have proved to be useful to all members of the surface analysis group and for this reason a second terminal line was installed early in 1983, together with another graphics terminal, in order to allow data transfer to SYPE from the Link 860 datasystem that runs the scanning Auger microprobe. This interface is now fully operational.

Currently an Apple based microcomputer network is being developed to control each of the spectrometers, and share a 10 Mbyte hard disk and a dot matrix printer (for graphical output). This network is also being interfaced to SYPE to take advantage of the facilities offered by the Prime/ESCA datasystem.

In order to provide high quality, colour graphical output a Hewlett-Packard multi-pen flatbed plotter has been purchased, and linked to one of the graphics terminals.

8.3 SOFTWARE DEVELOPMENTS

While the PDP8e was being linked to SYPE, a complex peak fitting program called GAMET (described in the next section) was acquired from Dr. P.M.A. Sherwood of Newcastle University. This large (5000 lines) Fortran program was transferred from Newcastle to Surrey using the SERC computer network. At Newcastle University the program is used on the Northumberland Universities Multiple Access Computer (NUMAC), an IBM 370/168. In order to compare program operation on SYPE with the NUMAC, and to facilitate the transfer of data to and
from Newcastle University, it was decided to adopt the same raw data format at Surrey.

Apart from peak fitting it was obvious that there were a considerable number of other features previously unavailable on the PDP8e which could be provided on SYPE. To provide these facilities and to present the users with an interface that required little or no knowledge of the Pr1me operating system the Pr1me/ESCA datasystem was written. This modular Fortran IV and later Fortran 77 program was designed to enable the addition of new facilities as they were developed, and to provide a simple user interface similar to that of the PDP8e datasystem.

8.3.1 THE GAMET PEAK FITTING ROUTINE

Garnet was developed by C.Lederer at the University of California Lawrence Berkely Laboratories. It was subsequently modified by R.Baird of Hawaii University, and by P.M.A. Sherwood of Newcastle University before being passed to Surrey University.

Starting with an initial guess of how many peaks are present and their positions, heights, widths, and any other parameters required; the program uses an iterative non-linear least squares fitting process in order to modify the peak parameters until the deviation between the synthesised peak envelope and the original ESCA spectrum is minimised. This is carried out via the Gauss or Gauss-Newton method. The key to the versatility of the program is the number of different parameters used to define each peak and the flexible manner in which constraints can be placed on the values of these parameters.
The peaks fitted by the program can be from 100% Gaussian to 100% Lorentzian in shape. Each of these peaks is further modified in shape by the addition of any subsidiary peaks induced by X-ray satellites in the exciting radiation (unless this feature is explicitly suppressed, e.g. for Auger peaks). Peaks may be further modified by the addition of exponential tails, constant tails, or any mixture of the two. Other peak fitting variables include position, height and width, plus there are two variables to describe the background slope and intercept (the background is always a straight line). The guessed peaks can be grouped and the Gaussian/Lorentzian mix, peak tails, and peak widths can be individually restrained to be either the same across all groups, the same within each group, or free to vary. Within each group it is possible to fix peak separations or height ratios. Any of the peak parameters (e.g. shape, height, width, position) can be individually fixed to a preset value, similarly each of the background parameters can also be fixed. One further variable sets a limit on the number of channels by which the program can move peaks during fitting.

For effective use of GAMET it is important to minimise the number of free variables. In most of the ESCA analyses carried out within the laboratory the same spectrometer analyser energy (50eV) is used in order to optimise the signal to noise ratio. This, in turn, governs the analyser broadening, which is sufficiently wide that most peaks can be fitted using 100% Gaussian peaks (the analyser broadening is Gaussian). This eliminates one variable per peak from the fitting process. Other variables can be constrained or fixed by running standards in order to determine peak widths and separations.
Input to GAMET is from a datafile which contains the raw data to be fitted plus the peak guesses with which the fitting starts, and a complex set of variables which control the way in which the program can modify the peak parameters during fitting. Other information includes X-ray satellite positions and intensities for the relevant X-ray source, and variables to control the type of output required. It is the complex form of this input datafile that made it necessary to write a program to produce it. This is an easy to use interactive routine which constructs the input datafile while conducting a dialogue with the user about peak guesses, constraints, etc. It is now built into the Prime/ESCA data system software.

Once the input file has been read in, GAMET carries out the fitting without any operator intervention, thus it can be run as a background job if required. In order to run the program on the Prime several modifications were initially required as the program included portions of non-standard Fortran code, and the IBM for which it was written had a greater degree of precision. The existing area calculation routine was removed as it was far too slow, and a faster routine was written. Finally the graphical output routine was removed and totally re-written using subroutines from the GINO graphics library. It is now possible to select a variety of different destinations for graphical output. The default is to plot the results directly onto one of the graphics terminals in the ESCA laboratory, then to write a plotfile suitable for subsequent plotting on the Hewlett Packard HP7221B flatbed plotter. Alternatively output may be directed to the Calcomp drum plotter in the university computing unit, or written in the form of device independent code to
8.3.2 THE PR1ME/ESCA DATASYSTEM

The datasystem software was written in order to provide members of the surface analysis group with a Prime based datasytem that is flexible, easy to use, and capable of continual development. It started as a Fortran IV program which simplified transferring data from the PDP8e and enabled the data to be viewed on the graphics terminal and plotted in the computing unit. It has since been converted to Fortran 77 and now includes routines for background subtraction, smoothing, automatic peak identification, spike removal, interfacing to the GAMET peak fitting program, and enhanced graphical output. The smoothing, spike removal, and background subtraction routines can all be used to pre-treat data before passing it to the GAMET peak fitting routine. The addition of the second SYPE line in the surface analysis laboratory together with another graphics terminal required further modification to convert the software for multiple user operation. Users are provided with a manual which describes how to use the datasytem and summarises the commands available. A copy of this is included in appendix A.

8.4 EXAMPLES

8.4.1 BACKGROUND SUBTRACTION

One of the restrictions of the PDP8e datasytem when applied to transition metals is the straight line background subtraction routine. Where there is a rise in background height across a peak
straight line subtraction allows more operator induced variation in the measured area than an 'S' shaped background. The latter also has more scientific significance. The datasystem software calculates an 'S' shape for a peak in such a way that the rise in background, due to an increase in the number of inelastically scattered electrons, is proportional to the number of electrons of higher energy within the peak that have not suffered an inelastic interaction. The two types of background subtraction are compared in fig. 89. The shaded area in each graph indicating the potential for operator induced variation in the area measurement.

8.4.2 PEAK ANNOTATION

Automatic peak identification and annotation are also provided by the datasystem. This has proved very useful in indicating where clashes between the peaks of different elements occurs, thus preventing misinterpretation, for example it immediately brought to our attention the clash between the oxygen 1s photoelectron peak and an overlapping sodium Auger peak in a study of coating disbondment. Other researchers have unwittingly mistaken this sodium peak for a chemical state shift in the oxygen peak, and ascribed it to chemically bound water. An example of the labelling dialogue and the corresponding survey spectrum are shown in figs. 90 and 91 respectively. Currently 30 elements are available in the database, however like most of the datasystem the program is flexible and new elements can be included should they be required.
FIG 89. COMPARISON OF BACKGROUND SUBTRACTION ROUTINES
ABOVE: NEGligible difference between two 'S' shaped backgrounds

BELOW: significant difference between two straight line backgrounds
**FIG 90. EXAMPLE OF PEAK LABELLING DIALOGUE**

**COMMENTS ARE NOW SELF CENTERING!**

......SPECTRUM DETAILS.............

**FIG 91. EXAMPLE OF AUTOMATIC PEAK ANNOTATION**

......CUSTOMER DETAILS.............

**GINO-F MARK 2.6**

**PERCENT HEIGHT FOR LABELLING:** 1.1

**OPTION:** 3

- **C** - CHARGING ADJUSTMENT 0+3eV. 4 FITS
- **O** - CHARGING ADJUSTMENT 0+1eV. 4 FITS

**SILICON SEARCH MOVED UP TO 151eV DUE TO OXYGEN LEVEL**

- **CR** - CHARGING ADJUSTMENT 0+3eV. 4 FITS
- **FE** - CHARGING ADJUSTMENT 0+5eV. 4 FITS
- **NI** - CHARGING ADJUSTMENT 0+7eV. 0 FITS
- **SI** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **CO** - CHARGING ADJUSTMENT 0+7eV. 0 FITS
- **N** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **CU** - CHARGING ADJUSTMENT 0+5eV. 0 FITS
- **MO** - CHARGING ADJUSTMENT 0+5eV. 0 FITS
- **AG** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **SN** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **I** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **AU** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **PB** - CHARGING ADJUSTMENT 0+1eV. 0 FITS
- **NA** - OUTSIDE SPECTRUM BOUNDARY
- **AL** - CHARGING ADJUSTMENT 0+1eV. 0 FITS
- **AR** - CHARGING ADJUSTMENT 0+2eV. 3 FITS
- **S** - CHARGING ADJUSTMENT 0+1eV. 0 FITS
- **CL** - CHARGING ADJUSTMENT 0+1eV. 0 FITS
- **MO** - CHARGING ADJUSTMENT 0+3eV. 0 FITS
- **CA** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **MN** - CHARGING ADJUSTMENT 0+7eV. 0 FITS
- **E** - OUTSIDE SPECTRUM BOUNDARY
- **ZN** - OUTSIDE SPECTRUM BOUNDARY
- **NB** - CHARGING ADJUSTMENT 0+1eV. 0 FITS
- **U** - CHARGING ADJUSTMENT 0+5eV. 0 FITS
- **F** - CHARGING ADJUSTMENT 0+1eV. 0 FITS
- **F** - CHARGING ADJUSTMENT 0+7eV. 0 FITS
- **Ti** - CHARGING ADJUSTMENT 0+2eV. 0 FITS
- **IN** - CHARGING ADJUSTMENT 0+2eV. 0 FITS

**ELEMENTS FOUND:**

- C O CR FE AR

**ELEMENTS NOT FOUND:**

- NI SI CO N CU MO AG SN I AU PB NA AL
- S CL MO CA MN E ZN NB U F F TI IN

DO YOU WANT A RERUN? **N**

DO YOU WISH TO FORCE THE LABELLING OF ANY OF THE ELEMENTS NOT FOUND BY THE PROGRAM? **Y**

ENTER ELEMENT NAME AS TWO LETTERS, PUT A SPACE FIRST IF NECESSARY

**ELEMENT:** CO

DONE

**ELEMENT:**
FIG 91. EXAMPLE OF AUTOMATIC PEAK ANNOTATION

C = c  XPS PEAKS
O = o  AUGER PEAKS
CR = y
FE = x
AR = a
8.4.3 PEAK FITTING

Examples of output from the peak fitting routine can be found in figs. 79 and 80. The fitting of relatively simple peak shapes such as these is a routine matter, and takes only 1 or 2 minutes. As mentioned in the introduction to this chapter, similar quantification of the chemical state information in transition metal spectra is far less straightforward, e.g. when fitting chromium 2p peaks both the $2p^{3/2}$ and the $2p^{1/2}$ peaks must be fitted, as the $2p^{1/2}$ peak induced by the main X-ray satellite coincides with the main $2p^{3/2}$ peak (fig. 92). Furthermore the peak components due to core hole/conduction band interactions and other satellites could give supplementary chemical state information, but add greatly to the complexity of the peak fitting process. Considerable time has been spent developing routines for obtaining this information from the chromium 2p peaks, and work has been initiated on fitting the more complex iron 2p peaks.

Although it is possible to pre-treat data by prior subtraction of an 'S'-shaped background, it was realised that the contribution to the rise in background of each peak component would vary according to the depth distribution. This occurs because the escape depth of the scattered electrons is greater than that of the unscattered electrons$^{155}$. GAMET allows each fitted component to be given an energy loss tail of constant height. Just as the sum of the component peaks is fitted to the peak envelope, the sum of the individual loss tails is fitted to the background rise. To separate the constant tail from the peak to which it is appended each peak has its own 'S'-shaped background (fig. 92). Unfortunately the use of
**METALLIC CHROMIUM 2p PEAKS**

- Binding Energy: 574.1, 578.5, 583.3, 585.3
- Width: 2.40, 2.40, 2.40, 2.40
- Area (x1000): 1534.15, 21896, 643.65, 81.80
- % Area: 62.20, 8.76, 25.76, 3.27

\[
\chi^2 = 1285.
\]

**FIG 92. PEAK FIT TO METALLIC CHROMIUM STANDARD**

---

**OXIDISED CHROMIUM 2p PEAKS.**

- Binding Energy: 575.8, 585.7
- Width: 3.10, 3.10
- Area (x1000): 278.28, 132.04
- % Area: 67.82, 32.18

\[
\chi^2 = 232.
\]

**FIG 93. PEAK FIT TO Cr₂O₃ STANDARD**
individual constant tails increases the number of free parameters within the fitting program to a point where there can be more than one satisfactory fit to the same peak envelope. In order to reduce the number of free parameters and hence produce more rigorous results a large program of peak fitting was carried out to assess peak widths, and peak separations for the chromium 2p peaks (e.g. figs. 92 and 93). This has shown that it is possible to obtain previously unobtainable information about the depth distribution of different species from the height of the energy loss tails.

Although this has enabled the fitting of complex peak shapes (fig. 94) it is not yet possible to routinely fit large numbers of chromium peaks, as information is still required on how the separation of the $2p^{3/2}$ and $2p^{1/2}$ peaks varies with chemical state, and why the area ratios of these two components is usually nearer to 3:1 than to the 2:1 ratio predicted from the density of states.

8.5 SUMMARY

The need for sophisticated data handling techniques in order to extract chemical state information from the XPS spectra of transition metals has resulted in the provision of an ESCA software package on the Prime 550 multi-user computer. The software comprises some 9500 lines of source programs and 248 kbytes of runfiles, which provide users with a fully documented and easy to use interface, requiring little or no experience of the Prime.

The advanced peak fitting routine has been used to show that the quantification of chemical state information in transition metal peaks is practicable, and that the energy loss tail of each peak
component contains information not available from the unscattered electrons in the ESCA peaks.
9. CONCLUDING DISCUSSION

The broad objective of this work, to understand the mechanisms of cobalt incorporation in the oxide film formed on stainless steel in high temperature water, has been pursued by way of the experimental objectives outlined in section 2.4.

From the results obtained it is clear that the transition between low temperature and high temperature kinetics, previously observed to lie between 433 K and 473 K, occurs very close to 473 K. At this temperature both the thin films characteristic of low temperature passivation, and the thicker films characteristic of higher temperature oxidation, have been observed. Furthermore it has been shown that nickel becomes a stable film constituent somewhere between 413 K and 473 K.

The incorporation of cobalt into films formed at 413 K and 473 K has shown that there is no detectable effect on film thickness, except where specimens are allowed to cool overnight in which case cobalt encourages the deposition of a mixed Fe/Cr overlayer. Specimens removed promptly from solution show that cobalt is incorporated throughout the native film, predominantly in a divalent state, and in proportion to the concentration of cobalt in solution. This proportionality is a prediction of Lister's model for activity transport and can be analysed in terms of this model.

The most pronounced effect of cobalt incorporation on film composition is to reduce the proportion of chromium. It has been shown that this is not induced by the deposition of a mixed Fe/Cr overlayer because it has been observed to extend to the base of the oxide.
The apparent substitution of cobalt for chromium enables the models for cobalt uptake from solution to be defined more closely. It has been explained by postulating that the extra thermodynamic stability and hence lower solubility of cobalt ferrite promotes the incorporation in the film of iron (that would normally have gone into solution) perhaps as a mixed iron/cobalt oxide.

The amount of cobalt incorporated relative to that in solution has been shown to increase markedly between 413 K and 473 K for a given solution concentration, and to increase further at 473 K when additions of lithium as LiOH, and boron as $\text{H}_3\text{BO}_3$ are made to the solution to simulate reactor water chemistry. The change in chemistry also has a pronounced effect on the distribution of cobalt, increasing the amount incorporated close to the base of the film. This pickup of some cobalt at the base of the film is consistent with the observed performance of decontamination reagents.

The apparent substitution of divalent cobalt for trivalent chromium required that a careful examination of the chemical state of all the transition elements within the film be undertaken. As the available computing facilities were not sufficiently powerful to deconvolute the complex peak shapes involved, a datasystem was developed to investigate transition metal peaks, and this has layed the foundations for rigorous deconvolution and thus more direct evaluation of the chemical state of incorporated cobalt in any future studies.
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PRIME/ESCA DATASYSTEM
MANUAL
1. Introduction

Using the prime computer for data handling has several benefits:

i) It frees the PDP8e for acquisition.

ii) It allows the use of multi-pen plotters and line printers.

iii) Software can be written or adapted to suit the user.

A large (112K) software package has already been written to enable easy interactive data handling, and an extensive peak fitting routine is also available.
Software has been written which enables users to manipulate data in much the same way as the PDP8e datasystem. The source files are written in the Fortran 77 language, and use PRIMOS subroutines, as well as the Prime applications library (VAPPLB), and the Gino graphics library (VGINO).

The program allows for simultaneous use by several people, limited only by the number of lines to SYPE. In order to accommodate multiple users output files have a suffix indicating the line number of the user creating them. Thus the FPAGE command creates a file called FP.27 if created by a user on line 27, and FP.16 for a user on line 16 (in this document this is indicated by referring to the file as FP.lnum). Users are informed of their line number when they enter the datasystem software.

For those familiar with the Prime, data files are stored in user specific sub-ufd's within the sub-ufd .SPECTRA. Each data file is stored as a separate sequential access (SAM) file, and may contain several spectra. To obviate problems with files starting with a number each filename is prefixed with D$.

The data manipulation software is stored in another user file directory. It is run by typing 'ESCA' to the PRIMOS 'OK,' prompt. After several seconds the program is loaded into memory, and responds by telling the user which line the terminal is on, then with the message 'PRIME/ESCA DATASYSTEM'. It then asks the user to enter his/her user code.

Once the program has been supplied with a valid usercode it will only access data attributed to that code, unless the USER command is used (see section 4.20). After entering the user code the program returns to its own prompt 'ES.', indicating that it is waiting for a command.

When a command is typed the program calls the appropriate subroutine or subroutines, and when finished will return to ES. and await another instruction. By adding another subroutine to the program and getting the program to call it when the appropriate instruction is typed, new functions can be added. To this extent the program is modular and can easily be changed.

The data for a particular scan region is read in using the DATA command to ES., and it is then available to all subroutines by the use of Fortran common blocks. If a program operation is called which requires data and none has been read into program memory, then an appropriate error message is given. It is intended that all errors will eventually be trapped within the program and will result in an appropriate error message and a return to the ES. monitor. Any untrapped errors will return you to Primos command level, after a suitable error message.
3. RUNNING THE SOFTWARE

3.1 GETTING THE DATASYSTEM PROGRAM RUNNING

To use the Prime system it is first necessary to login as a registered user and give an appropriate password. To use the ESCA group software you will have to type:

LOGIN ETSYO3 xxxxxxx

Where xxxxxxx represents our password. The system will then give some output regarding the revision that is running, our allocation usage, and any messages of the day. It then responds with the 'OK,' prompt. When this is given the Prime operating system (PRIMOS) is awaiting an instruction, and you are logged in to the user file directory named ETSYO3. To run the ESCA software all that is necessary is to type ESCA. The terminal will then respond with:

PRIME/ESCA DATASYSTEM DATE

USER CODE:

A valid usercode should now be entered, new users should see me to be allocated a code. After the code is entered the program responds with 'ES.' The datasystem is now ready to accept one of the commands detailed in the following sections.

When you have finished type 'QUIT','Q','quit' to the ES. prompt and you will be returned to the PRIMOS 'OK,' prompt. Typing LO will then log you out and terminate the session.

3.2 USEFUL NOTES ON THE PRIMOS OPERATING SYSTEM

The PRIMOS operating system has some features with which you should be familiar.

Typing Ctrl H gives you a backspace should you make a typing error.

A '|' kills any previous input on the line concerned.

Ctrl P can be used to interrupt program execution at any stage without any ill effects. It will return you to the ES. prompt and in the process will close any open files.

Should an untrapped program error occur the operating system will eventually give you the ER! prompt (a substitute for OK,). This may result in files being left open, which can be closed by typing the following:

CLOSE ALL
For further details of commands accepted by PRIMOS, handouts are available from reception in the computing unit.
Details of each command are listed below. Modifications will be indicated at login time, and in periodic handouts. All commands are now accepted in both upper or lower case.

4.1 : COPY
4.2 : LIST (or L)
4.3 : QUIT (or Q)
4.4 : HELP
4.5 : DATA
4.6 : NEXT (or N)
4.7 : UR/L
4.8 : VIEW (or V)
4.9 : HARD
4.10 : HOFF
4.11 : PLOT and PL/A
4.12 : B, B/N, B/B
4.13 : KILL (or K)
4.14 : LABEL (formerly HP)
4.15 : FIT (or F)
4.16 : SPIK
4.17 : UD
4.18 : UC/A
4.19 : UR/R
4.20 : USER
4.21 : ARCHIVE COMMANDS
   4.21.1 : ARCHIVE (or AR)
   4.21.2 : AR/R
   4.21.3 : AR/U
   4.21.4 : AR/L
4.22 : PAGE
4.23 : KE and BE
4.24 : SCALE
4.25 : SHIFT
4.26 : FIX COUNT (or FC)
4.27 : SETUP and SEQ
4.28 : SEARCH
4.29 : Routines under development

The following internal Primos commands may also be issued to the ES prompt:

LISTF  : Lists files in top level of ETSY03 ufd.
CNAME  : Changes the name of a file in ETSY03.
STAT US : Lists all users on system.
STAT ME : Lists all users logged in as ETSY03
STAT UN : Lists all open files.
MESS user : Sends message to 'user' on SYPE.
CO     : Switches input from terminal to Cominput file.
4.1 COPY

Copy is the command to copy data from the PDP8e or the Link 860 onto the SYPE disk.

When you issue the COPY command you are presented with a number of different options, viz:

FROM PDP8e (KL:)  ?

This is the normal copy routine from the PDP8e

FROM PDP8e (KL8:)  ?

A backup copy routine for the PDP8e not normally used.

FROM LINK (XPS) :  ?

To transfer XPS spectra from the Link. This prompts for the exciting X-ray type, as this is not included in Link data files.

FROM LINK (AUGER) :  ?

To transfer Auger spectra from Link.

FROM LINK (EDAX) :  ?

To transfer EPMA or XRF spectra from the Link.

Answering Y,YE,YES or OK to any of these questions will enter the appropriate data transfer routine.

TRANSFER FROM PDP8e

To copy data across it is best to go to the PDP8e first. Type Ctrl C until you obtain the '.' monitor. Halt the computer and restart - there is no need to turn off the power switch. Write enable the system tape (LH side). To run the program type the following to the '.' monitor:

```
.R FRTS
*SYS:PRIME
*KL:3
*filename.E0/5
*filename.E0/6

*.
```

The '.EO' extender must be appended to each filename typed in, and the unit numbers appended (/5, /6, etc.) should increment by one each time, with a maximum value of 9, thus giving a maximum of 5 files transferred at any one time. All scan regions are transferred. When the above has been typed and the PDP8e is waiting with the * character,
go back to the Prime terminal and type COPY to the ES. monitor, then
YES to the question 'FROM THE PDP8?'. The Prime will then ask you to
switch the plugs over. The switch is on the wall to the left of the
terminal. Now go back to the PDP8e terminal and type the 'ESC' key -
transfer will then take place.

When the PDP8e has finished it types TRANSFER FINISHED, and you
should switch back to the Prime terminal and type your next instruction
as if the ES. prompt had been displayed.

TRANSFER FROM LINK 860

The Link 860 datasystem has a sophisticated interface to the
Prime, allowing the Link keyboard and monitor to be used in the same
way as a 'dumb' terminal connected to the Prime. This can be done at
any time, but is only necessary when you need to transfer data.

To enter 'dumb terminal' mode type RUN DPO:DECLINK to the LDOS
CLI. If this program is found on the system disk, then it will present
you with a screenfull of information on the monitor. Hit <RETURN> to
skip this, and the interface becomes active. Turn the switch on the
wall to connect the Prime to the Link rather than the Cifer terminal.

It is now possible to issue PRIME/ESCA DATASYSTEM commands
through the Link. Once the COPY command has been issued, and one of
the LINK options selected the program prompts for you to type CTRL-T
and select mode 4. Type <RETURN> once more and the program asks you
for the filename under which the transferred data is to be filed.
Several Link files can be stored in one Prime file, but they must all
be of the same type (XPS, Auger or X-RAY).

Once the filename has been entered (six characters maximum) the
Prime will prompt:

PRIME READY: TYPE CTRL-T TO PROCEED

Typing CTRL-T this time causes the Link to ask you for the name
of the file to be transferred. This must be on the default disk (ie on
DP1 if you issued the DIR DP1 command to the CLI).

When the filename has been entered, data transfer takes place.
During transfer there is a number on the bottom right of the Link
monitor which increments as each block of data is transferred. If for
any reason a block is not transferred successfully, a character will be
printed on the dot matrix printer, and the Link will re-try. This is
quite common and is solely to indicate that the Link to Prime
'handshake' is working OK. If characters continue to appear and the
block counter fails to increment, then the transfer can be interrupted
by typing CTRL-A.

Assuming data transfer is successful the Link asks if there are
any more files for transfer, and if affirmative it will prompt for the
name of the next Link datafile for transfer. This will then be
appended to the same Prime datafile as the previous transfer. NOTE to
do this successfully it is important that the second and successive
files should be of the same type as the first - do not mix Auger, X-ray,
ALUM XPS and MAGN XPS. If the Link receives a negative answer to its
question then it returns you to the ES. prompt.

Further files can now be transferred in the same way, alternatively the user can issue Prime/ESCA datasystem commands using
the Link as a 'dumb' terminal again. Typing CTRL-X will exit the
DECLINK program, and return the user to the LDOS CLI. Before doing
this either QUIT from the Prime datasystem and LOGOUT, or turn on the
Cifer and switch the connection to the Prime from the Link to the Cifer
in order to continue using the Prime/ESCA datasystem.
4.2 LIST

This command lists all the data files currently available in the sub-ufd indicated by the current user code. All files transferred on the same day as the LIST command is issued are marked with an asterisk. Do not expect the most recently transferred files to be on the end of the list, as it represents the order in which files are stored on the disc, and spaces are used as other users delete files.

Alongside each filename is the file size, the total size is given at the end of the list. If the total size exceeds a preset value users are reminded to delete or archive some of their data files. Failure to do so could result in ETSY03 exceeding its current disk space allocation. If this is noticed by the operating system it enforces a restricted command set on subsequent login's, thus preventing use of the data system until some files are deleted. Users are therefore asked not to exceed their allocation limit, and not to leave files on the disk for any longer than is absolutely necessary.
4.3 QUIT

The quit command leaves the datasystem and returns the user to Primos command level, it closes any open files in the process.

4.4 HELP

This gives a brief summary of each of the commands available to the Datasystem user. New commands may not be included until they have been debugged.

If a user wishes help with any commands at PRIMOS level, then typing HELP to the OK, prompt provides access to both the SERC and the PRIME help packages.
4.5 DATA

This command must be used to read data into the program memory before trying any data manipulation or plotting. The terminal will prompt for a filename, and this may be specified in two ways.

FILENAME : GOLDW

This reads region 0 of spectrum GOLDW into memory.

FILENAME : GOLDW .3

This reads region 3 of spectrum GOLDW into memory. Note that if an extension for the file region is specified (eg. .3), then the filename must be padded with trailing blanks to a length of 6 characters.

When the file has been read into memory, the spectrum name and region are echoed at the terminal. The binding energy range of the spectrum is also given so the user can immediately identify which region is currently in memory.

The next time the DATA command is issued, the previous data file is automatically closed and the new data file opened.

...... See also NEXT command.
4.6 NEXT

This reads the next sequential scan region into program memory from the data file specified in the last DATA command.

If the DataSystem finds there are no more regions left it gives the message:

END OF FILE - RETURNING TO BEGINNING.

If you started reading the data file at region .0 you will find this reloaded into memory, however if you specified a region when you issued the DATA command then you will return to this region.

As with the data command the spectrum name and region number are echoed at the terminal when the data has been read in, and the binding energy range of the scan region is given for easy identification of the spectrum.
4.7 UR/L

This is very similar to the PDP8e command of the same name. It gives a list of the various parameters that relate to the data currently in memory, such as acquisition parameters, and maximum and minimum counts.

4.8 VIEW

This displays the current region on the ESCA graphics terminal. Due to the nature of the terminal none of the single keystroke commands found on the PDP8e are currently implemented, and the program immediately returns to the ES. monitor. The graphical output on the TVI graphics terminal can be turned on and off using the GRAPH key, this does not affect the terminal interactions, and is merely to help when you find that the graph and the programs output clash.

The character output to the TVI terminal can be turned off using the ALPHA key, again this does not lose any terminal output, and it is still possible to type in responses to questions and commands even though the characters are not displayed.

The size and position of the display on the screen, together with the scaling of the counts are affected by the SCALE, SHIFT and FIX COUNTS commands respectively.
4.9 HARD

This option opens a file that keeps a record of all the terminal interactions, until the command HOFF is typed. The record is kept in a file called HARDCOPY. This can be printed at the departmental OMNI line printer by typing PRINT HARDCOPY to the PRIMOS 'OK,' prompt after quitting the datasystem. Alternatively the file may be printed in the computing unit using the SPOOL HARDCOPY command.

The departmental printer relies on Prime system A (SYSA), and will not work if this system is down.

4.10 HOFF

Terminates the keeping of a record of terminal interactions, see option 4.9 HARD.
4.11 PLOT

This command submits the data currently in memory to the spool queue for the CALCOMP drum plotter in the computing unit. It will not work if SYSA is down. Plots can be collected from the computing unit between 1 hour and 12 hours later, depending how efficiently they are working.

The PLOT routine prompts for a comment added by the user, and this is written across the top of each plot together with the PDP8e acquisition name. The size of the output can be influenced using the SCALE command and the scaling of the counts can be changed using the FIX COUNT command. If the B/N routine has been used both the data and the calculated background will be plotted.

Plots are now surrounded by an A4 border to help in cutting them down to report size.

PL/A

This command plots all the regions from a spectrum, (widescans are optional). There is no proviso for a comment line on each plot. Like PLOT the output is influenced by the SCALE and FIX COUNT commands.

Users are urged to spread the load on the spool queue by using their discretion when using PLOT or PL/A. Typing SPL to the OK, prompt shows the files in the spool queue, and should be used to keep the number of plotfiles due to ETSY03 below a maximum of approximately 30 at any one time.
4.12 B (Background subtraction)

The background subtraction routine uses an 'S' shaped background, and has 3 options (many more may be available soon).

- **B**: Subtracts background
- **B/B**: Displays background - no peak
- **B/N**: Displays background and peak - no subtraction

All that is necessary in this routine is to set the high binding energy and the low binding energy limits for the background calculation. This is done using the hardware graphics cursor (HGC). This appears on the screen after the B command, and should be moved to the appropriate binding energies using the keys on the bottom right of the keyboard. When in position it is necessary to type <space> then <return> to send the cursor position to the Prime. For the background subtraction routine it is only necessary to move the cursor to the appropriate binding energy, its position in the intensity direction (y direction) is ignored.

When the second cursor position is entered the background is automatically subtracted if the /B or /N options are not used. Type VIEW or V to display the modified spectra at the terminal. The area is calculated and should correspond roughly with that obtained on the PDP8e. The data stored in memory is modified by the background subtraction, and any subsequent operations will involve the modified data. Thus the results of background subtraction can be passed to the peak fitting routine.

The background is calculated on the assumption that the increase in background is proportional to the peak area due to unscattered electrons. This is carried out by an iterative process.
4.13 KILL

This restores the data in memory to its original condition, as read in from the data file, and saves the user from having to re-issue the DATA command. This is quicker.
This program has been written with our industrial users in mind, but it can prove very useful to internal users. Its function is to take a widescan, and find which elements are present, then label the peaks due to each element. Although you may know where to look to see if an element is present this helps stop you making mistakes in interpretation where the secondary peaks of an element interfere with the main peaks of other elements.

To use the program type LABEL or HP to the ES. prompt, after reading a widescan into memory (using the DATA or NEXT statement as appropriate). The program prompts:

<............SPECTRUM.DETAILS...............>

This is a line of the width indicated which is printed directly above the plot of the widescan in the final output. Having typed in this line the next prompt will be:

<............CUSTOMER DETAILS...............>

This is a line printed slightly higher on the output, and is useful for entering the name of an external customer, and the firm they belong to.

After this is input the program starts writing to a plotfile, this is indicated by 'GINO-F MARK 2.6'. The next input required by the user is the PERCENT HEIGHT FOR LABELLING : - this is the peak height necessary for labelling to occur, it is expressed as a proportion of the total height of the scan (ie maximum counts - minimum counts). With the sort of noise level typical in our widescans the value used should typically be between 1.5 and 2.0 (%). Too small a value will result in the noise in the spectrum being labelled, and too high a value might mean that some of the smaller peaks are considered too small for labelling.

The next prompt is for an OPTION. Values available are 0 to 3.

OPTION :

0 : Do not label peaks.

1 : Only label the peak for which the routine searches (not necessarily the main peak).

2 : Label the peak searched for, and any other XPS peaks due to that element.

3 : Label all XPS peaks for any elements found, and label any Auger peaks within the scan.
Having chosen the option required, the program lists a few details of the peak search routine, in the form of:

**CR - CHARGING ADJUSTMENT 0+3eV. 4 FITS**

This appears for each element searched for. 'CR' is the element (chromium). The 0+3 indicates the charging value, obtained by finding the difference between the position of the observed carbon peak and 285.0 eV. If a specimen has charged considerably (> 3eV) the labelling routine will probably be more effective if this is reduced by the UR/R routine available both on the PDP8e and the Prime. The second number (+3) is the amount the routine has searched beyond the expected value in order to find itself on a peak top. This is necessary to allow for chemical state shifts. A maximum of 10eV charging, and 6eV chemical shift is allowed. The last information in the line is the number of peak fits that have shown the peak to exceed the 'percentage height for labelling'. The program compares the peak with the background at four different distances from the peak centre. For a peak to be labelled the percentage height of the peak must exceed that specified earlier in the program in at least 3 out of 4 cases, ie:

- **3 FITS or 4 FITS** - Peak labelling
- **0,1 or 2 FITS** - Peak not labelled

Next the program lists the elements found, and then the elements not found. If you require the labelling of an element not in the program see me.

At this stage the program offers the user the option of a re-run. This will take the user back to the 'PERCENT HEIGHT FOR LABELLING :' prompt, thus allowing the sensitivity of the labelling to be changed without having to retype the specimen and user details.

Finally the program offers to force the labelling of any peak that was searched for but not found by the program. If you reply yes, you will be prompted for an element name. Only the peak position by which the program decides whether the element is present will be labelled (THIS IS NOT NECESSARILY THE MAIN PEAK FOR THE ELEMENT CONCERNED).

The width of the input data does not have to be 1000eV, in fact sodium and zinc will not be detected unless the wide scan extends above 1070eV due to peak clashes with other elements. Spectra narrower than 30eV are not peak labelled. This is not the recommended way of producing narrow scan plots due to the time taken in plotting out the result (> 5min.).

Output from the HP routine is in the form of a plotfile called
HP.lnum suitable for the Hewlett-Packard HP7221B plotter. Any successive peak labelling will overwrite the previous plotfile, to prevent this the filename can be changed without leaving the datasystem using the CN command to change the filename. The format is:

CN HP.lnum newfilename

To plot a plotfile at the Hewlett-Packard flatbed plotter type SEG #PLOT HP.lnum and follow the instructions. Pens for the plotter can be obtained from stores, and a couple of rough sets can be found in the ESCA desk.

To remove the plotfile from the ufd after plotting it, type:

ERASE xxxxxxxx
4.15 FIT

4.15.1 ABOUT GAMET

FIT is the datasystem command designed to interactively produce a datafile suitable for the GAMET peak fitting routine. The GAMET routine is a large Fortran IV program originally written at the University of California, since then it has been modified several times, notably by Dr. P. Sherwood of Newcastle University. The only input to the program is the above mentioned datafile and this contains all the instructions regarding the type of peak fitting, and the form of the subsequent output (graphical and numerical).

GAMET allows the fitting of peaks into a peak envelope. To do this it relies on a reasonable input guess. Fitting is by an iterative non-linear least squares process (Gauss or Gauss-Newton method). If a sufficiently good initial guess is provided the program will iterate until it achieves convergence (a good fit). Poor guesses can lead to a singular matrix, or may cause divergent iteration leading to a negative determinate. In either of these cases the iterative process is halted and the results from the best iteration are output.

In order to minimise the complexity of FIT many of the variables controlling fitting are set to default values, however the full potential of GAMET includes the fitting of peaks from 100% Gaussian to 100% Lorentzian in shape. Each of these peaks may be further modified in shape by the addition of satellite peaks (e.g., due to X-ray satellites), and by the addition of exponential peak tails, constant peak tails, or any mixture of the above. Other peak fitting variables include position, height and width, plus there are two variables to describe the background slope and intercept (the background is always straight line). The guessed peaks can be grouped and the Gaussian/Lorentzian mix, peak tails, and peak width can be individually restrained to be either the same across all groups, the same within each group, or free to vary. Within each group it is possible to fix peak separations or height ratios. Any of the individual peak parameters (e.g., shape, height, width, position) can be individually fixed, similarly each of the background parameters can also be fixed. One further variable sets a limit on the distance that the program can move peaks during fitting (in the binding energy sense).

For effective use of GAMET it is important to minimise the number of free variables. The FIT routine is intended to do this in a way that makes the use of GAMET simple for ESCA users. If you find you require to use GAMET for fitting outside the bounds dictated by the FIT routine there is further documentation to enable the experienced Prime user to do this.
4.15.2 Restrictions of FIT

FIT only allows Gaussian peak shapes to be used as these have been found to fit our ESCA data best.

FIT assumes that the contributions due to all the relevant x-ray satellites are present.

Constant and exponential tails are fixed to zero.

Tail mix is fixed to 0.5 (see above)

The height or area ratios of peaks can not be fixed via FIT.
4.15.3 The Use of FIT

Typing the FIT command to ES enters an interactive dialogue with the user. After prompting for a comment for inclusion on the graphical output the program asks:

DO YOU REQUIRE PEAK FITTING (YES OR NO)

If the user replies NO then the datafile written instructs GAMET not to try peak fitting, but to produce a plotfile for the HP7221B flat-bed plotter.

If the user gives any other reply the peak fitting dialogue is entered. I hope this is largely self-explanatory, but the following notes may prove useful.

The default output options tell GAMET to plot the resulting fitted peak at the TVI graphics terminal, and also to produce a plot-file for the flat-bed plotter. Other options include output to the Calcomp plotter, plotting on a kinetic energy scale, and choosing peaks for which the % area is calculated.

The restraining limit on peak positions is the limit in eV that GAMET can move the peaks during the fitting process.

Peaks may be put into separate groups. This is so that peak widths or peak separations can be fixed within a group, but allowed to vary between groups.

When you choose the binding energy limits for the fitted region the program calculates the slope and intercept of the straight line joining the two points specified on the spectrum. This background can be fixed thus reducing the number of free parameters for GAMET to consider, however it is not a good idea if you anticipate a significant X-ray satellite contribution at the low binding energy end of the fitted region.

When the program prompts for the actual peak guesses it asks for an estimate of the percentage height of the singlet. This is the height of the singlet as a percentage of the difference between maximum and minimum counts for the spectrum under consideration.

The dimensions of the output graph are controlled by the last use of the SCALE command to ES. If this has not been used the scaling factors are set to 1, resulting in A4 output.

After the last peak guess is made the program returns to ES., and the datafile is now ready for fitting by GAMET.
4.15.4 Running GAMET

In order to carry out peak fitting using the datafile produced by FIT, it is necessary to quit from the Pr1me/ESCA datasystem and return to OK.

The datafile produced by FIT will be named 'GAM$xxxxxx.x'. Where xxxxxx is the name of the spectrum and .x is the number of the particular scan region to be fitted. If the spectrum name was less than 6 characters long then the .x will not be appended, eg:

FIT file from spectrum EVAU03.3 is called GAM$EVAU03.3
FIT file from spectrum NIMG.4 is called GAM$NIMG

Once the GAM$ fit-files have been produced they can be run through GAMET using the FIT command to the OK, prompt.

To fit GAM$NIMG you should type FIT NIMG to the OK, prompt. If GAM$NIMG is not found then all the available GAM$ files are listed at the terminal and a new name is prompted for. Fitting times vary from about 30 seconds to several minutes according to the number of free variables, the accuracy of the initial peak guess, and the number of other users on the system.

The graphical output contains the original data, the fitted peak envelope, and the singlets used to make the envelope. At the top right hand side of the display is a number that indicates the mode of exit from the program, viz:

1 = converged fit
2 = converged fit with some peak parameters constrained
3 = maximum number of iterations (not converged)
6 = negative determinate (bad guess or unlucky)
7 = singular matrix (bad guess or unlucky)

When GAMET has finished and the command file has returned you to the OK prompt a plotfile exists called PLOT.lnum. If this is for the Calcomp it can be plotted by typing PLOT PLOT.lnum, or if it is for the HP7221B it can be plotted by typing SEG #PLOT PLOT.lnum. There is also a numerical record of the iterative process in a file called GOUT.lnum (lnum is the line number, eg GOUT.16). This can be printed in the department by typing:

PRINT GOUT.lnum

or in the computing unit by typing:

SPOOL GOUT.lnum

Familiarity with the Pr1me editor is useful here as it allows the user to skip through GAM.lnum should he suspect that convergence has
not occurred during fitting.
As any ESCA user will know spikes can occur due to external sources such as lightning, or Welsh nationalists blowing up the local sub-station. Other possible sources of spikes within the lab include the ventilation system, the nitrogen dispenser, and flashovers in the x-ray gun. Some of these may completely halt acquisition, or may just produce a few channels of very high counts in the acquired spectrum. These can be a nuisance as they mean the scaling is out when spectra are displayed, and they can interfere with peak area calculations.

To remove spikes on the Prime system read the appropriate data into memory, VIEW it, then type SPIK to the ES. prompt.

The routine uses the Hardware Graphics Cursor in a similar way to the routine for baseline subtraction. Move the HGC onto the plotted point to be moved, then type a space and 'return'. If you positioned the HGC incorrectly you will get a message 'MISSED, TRY AGAIN', otherwise the HGC should be moved to the required position on the screen. Then type 'space' 'return' again and the new point will appear, the old one will be replaced with an X. If the point moved was the highest point on the plot then the graph will be re-plotted. If it was the lowest point this will not happen, until I write the update.

This routine only modifies the data stored in program memory, so as of yet there is no way of removing spikes from the stored data. This is in the pipeline, so do not fret.

When the spike has been removed the program automatically returns to ES.
4.17 UD

This routine deletes spectra from the Prime. The routine will keep prompting for filenames until none is given. Specific file regions cannot be deleted.

4.18 UC/A

As on the PDP8e this routine lists the count values currently in memory at the terminal. If used in conjunction with the commands HARD and HOFF the user can obtain a hardcopy of his count values at any stage in data manipulation.

4.19 UR/R

As on the PDP8e. Used to recalibrate a spectrum to allow for charging, etc. Enter the desired offset in eV. Unlike the PDP8e the data on disc is not updated, if it is wished to permanently recalibrate a spectral region then it is currently better to use the UR/R command on the PDP8e before copying across to the prime.
When the USER command is typed the system prompts:

USER CODE

You should reply with your designated (4 figure) user code.

The USER command allows you access to the data attributed to a particular user. The username is also prompted for when you enter the datasystem. All users should have their own code, if not one can easily be allocated.

Using separate data storage for each user has several benefits, including monitoring individual usage of the system. Users who have an excessive amount of data stored on disc will be asked to archive these onto backup storage.
4.21 Archive Commands

Archiving is a method of storing data on magnetic tape, thus freeing disc space for new data. All archiving processes are run in the background because archiving relies on SYSA, which can be very slow during the normal working day.

The following important points should be noted:

Recall usually takes 24 hours so plan ahead.

Archive processes (except AR/L) work in the background then send a message to the ES. monitor when they have finished. Issuing a second command before the first has finished will probably cause the second command to fail.

The archive background process may occasionally fail because another user is archiving data. This cannot yet be detected by the datasystem, and this problem is still being worked on. To verify that an operation has been completed use AR/U to update the index and AR/L to list the files archived under your user code.

Logging out will not affect a background process, but the message notifying completion of the operation may be lost.

4.21.1 ARCHIVE (or AR)

This is the command to archive files. The datasystem prompts for filenames, and starts the archive process when <return> is typed without a filename being entered. Prepare a list of the files you wish to archive before starting.

When the operation is complete the datasystem will show a message indicating completion. If this is not seen within 15-20 minutes, update the archive index then look through it. Files just archived will be at the end of the list.

4.21.2 AR/R

This command is used to recall files from archive. To do this the command must be issued twice. The first call prompts the operators to load the appropriate magnetic tapes (done twice a day during term), the appropriate files are then copied of the tapes onto disc. This is indicated by a # character in the archive index.

When this has been done the AR/R command can be issued again, and the files should be copied from the archive disc into your filestore. The command again works in the background, sends a message to the ES. monitor to indicate its completion.
4.21.3 AR/U

This command updates the list of archived files. It is a background process and notifies the ES. monitor when complete. Thus the user can carry out other operations in the meantime. This can take some time as we have in excess of 700 files archived.

4.21.4 AR/L

This reads only the files belonging to the current user from the list of archived files stored in ETSY03. This is not a background process.
This program enables the use of the HP7221B plotter to write a front page in suitable format for our report covers. The dialogue is fairly self-explanatory. The format is designed for work carried out for outside customers, but is also adaptable for internal reports.

An example of the output format is given on the next page.

A plotfile called FP.lnum is created by the program, and can be sent to the flatbed plotter using the FUTIL command in the same way as plotted on the flatbed plotter by typing SEG #PLOT FP.lnum to the TVI terminal.
ADDRESS OF COMPANY FOR WHOM WORK WAS CARRIED OUT
(Self-centered)

XPS ANALYSIS.
MAY 1983

NAME OF VISITING USER

THREE LINES IN WHICH TO ENTER SPECIMEN DETAILS

ESCA member in charge

Sets of spectra grouped with annotated survey scans.

Radiation source as stated on each survey scan. Other details as below:

Widescans: Pass energy = 50eV
            Time/10 chan = 3 sec

Narrow scans: Pass energy = 50eV
              Time/10 chan = 5 sec
4.23 KE and BE

The 'KE' command changes the energy axis of any spectra plotted from increasing binding energy to increasing kinetic energy. The 'BE' command resets the default format, ie increasing binding energy.

4.24 SCALE

The physical dimensions of plots produced on the terminal and on the Calcomp can be varied using this routine. Both X and Y scaling can be varied independantly, thus the aspect ration can also be changed. The reset scale values stay in operation until they are either reset to 1, or until the user quits the datasystem.

This also affects the size of graphical output from the peak fitting routine.
4.25 SHIFT

This allows the user to move the origin of plots produced on the graphics terminal. It has no effect on the plots produced on the Calcomp plotter using the PLOT or PL/A routines. The amount of shift required should be entered in milimetres.

4.26 FIX COUNT (or FC)

There are occasions when it is useful to be able to plot files with a fixed scaling in the counts direction. Normally all spectra are plotted by the datasystem with automatic scaling of maximum and minimum counts to fill the plot entirely. When FIX COUNTS is used it tells the user the values of maximum and minimum counts for the spectrum currently in memory, and the difference between these two (the range). The user is then invited to select a new range, which is used in all subsequent plotting until reset.

To return to default scaling the FIX COUNT command is again used and a value of zero entered for the range.
4.27 SETUP and SEQ

The time spent using the FIT command when a large number of similar files have to be fitted has prompted the development of a way of recording the responses given to the interactive FIT section, so that they can be used again on another file.

The command SETUP initiates the process, it first tells you which, if any, of your five sequences exist and allows you to list them. It then prompts for which sequence you wish to update. The appropriate sequence will then be overwritten the next time the FIT command is used. The sequences are recorded on disc rather than in the program memory, thus will remain on the system until overwritten by a new sequence.

To run the sequence the command SEQ is issued. This asks the user for the sequence number to be run then asks you to hit return, and assumes that the data for fitting has already been read into program memory using the DATA or NEXT command. The FIT command sequence is then rushed through under program control. On completion the user is returned to ES.
4.28 SEARCH

The SEARCH command uses the peak labelling database to try and match a binding energy entered by the user, with possible peaks. It can thus be used to identify any strange peaks found on a spectrum (within the limitations of the database).

The user is first prompted to enter the appropriate exciting radiation, then to enter a binding energy value. The elemental codes of any peaks within a window spreading 5 eV each side of the entered binding energy are then displayed.

When zero binding energy is entered the datasystem returns to ES.

4.29 Routines under development

These include a Fourier transform based deconvolution program, peak addition/subtraction, smoothing and the use of 3-d graphics for presenting etch profiles.

Hardware developments in progress include moving the HP7221B plotter onto a separate line, and building a network of Apple machines, eventually also to be interfaced to the Prime via the COPY command.
Appendix B
Deposition processes on stainless steel surfaces

S. A. RICHARDSON, BSc, and J. E. CASTLE, BSc, PhD, CChem, FRSC, FIcorT, University of Surrey, and N. R. LARGE, MA, DPhil, and A. J. TENCH,* BSc, PhD, DSc, AERE, Harwell

The incorporation of radioactive cobalt into oxide films on the primary surfaces of a PWR leads to undesirable radiation fields. The techniques of XPS and argon ion etching have been applied to a study of the mechanism of the incorporation of soluble cobalt species into growing oxide films. Uptake is shown to be proportional to cobalt concentration in the solution and the cobalt is present as Co(II). Uptake is greater at 473K than at 13K, and is enhanced by the presence of lithium hydroxide and boric acid. The distribution through the oxide film depends on the conditions of exposure and is associated with modification of the chromium content. A model for incorporation is presented, and is consistent with observations of the distribution derived from decontamination tests on specimens from an in-reactor loop.

INTRODUCTION
1. The deposition of activated corrosion products on the surfaces of the primary circuit of a PWR leads to undesirable radiation doses being received by maintenance personnel. The most important nuclides giving rise to the radiation fields are Co-58 and Co-60, and the surfaces on which deposition occurs are of stainless steel and Inconel. Deposition may involve active species in solution or in particulate form.

2. The present study was planned to improve our understanding of the processes whereby soluble cobalt species are incorporated into oxide films growing on stainless steel and Inconel. The technique adopted involves the application of X-ray photoelectron spectroscopy (XPS), in association with argon ion etching, to determine the distribution and valence states of the incorporated cobalt species. Initial studies were carried out at 13K (140°C), and later studies at 473K (200°C). These temperatures span a range in which the mechanism of the oxide formation process appears to undergo a change (ref.1). The present report is concerned with deposition on stainless steel; the studies are being extended to Inconel and to temperatures around 573K (300°C).

3. Additional information on the location of deposited activity has been obtained during studies of decontamination processes in preparation for the decontamination of the DIDO Water Loop at Harwell. The various reagents attack different layers of the oxide film, so the location of residual activity can be deduced.

EXPERIMENTAL METHODS
Surface analysis
4. It has already been shown that the technique known as ESCA (Electron Spectroscopy for Chemical Analysis) or XPS (X-ray Photoelectron Spectroscopy), although a vacuum technique, is in many ways ideal for the analysis of films formed in aqueous environments. Its use has been fully described in other publications (refs.1,2), and the passive films formed on steel in water at 473K (200°C) have already been characterized (refs.3,4). The analytical depth is of the order of 2 nm and to provide a full analysis of the film XPS is usually combined with an etching technique such as argon ion bombardment (ref.5). In this way composition profiles as a function of depth are produced, and it is by this means that the distribution of cobalt in the film has been explored in the present work. The oxides of the steel-forming elements can all be distinguished from the metals; ions can also be distinguished (Fe(II) from Fe(III), and Co(II) from Co(III)) (ref.6).

5. The spectrometer used in this work was an ESCA 3 supplied by VG Scientific Ltd., and the data were collected and analysed by means of a DEC PDP8 datasytem. The ion gun used in depth profiling was designed to cover the area of analysis uniformly; its etch rate was estimated by etching through the range of interference colours on oxidised stainless steel and was 0.025 nm/s under the operating conditions used in this work. Each point on the composition profile was obtained by analysis for carbon, oxygen, silicon, chromium, iron, cobalt, and nickel, with Mg ka X-radiation as the exciting source. The background was removed from each spectrum peak by computational methods and the peak area was then normalised by means of an appropriate sensitivity factor (refs.4,7).

The pressure vessel
6. All high temperature exposures were carried out in test cells placed in a mild steel high pressure enclosure (Lintott Engineering Ltd.). It is pressurised with 'white spot' nitrogen to...
Corrosion cells
7. Care must be taken in the choice of corrosion cell material, and the use of a pressure enclosure rather than an autoclave allows considerable flexibility in this respect. Mercer et al. (ref.8) have reported that silicon pick-up may occur in silica corrosion cells. Work in this laboratory by C.R. Clayton (ref.9) has shown that this is not seen at temperatures up to 353K, but that a PTFE cell should be used at temperatures above 413K.

8. In this work specimens were corroded at 413K in a glass corrosion cell with a capacity of 250ml. The temperature was controlled using a chromel/alumel thermocouple inserted into a pocket in the corrosion cell, and connected to a Eurotherm PID/SCR furnace controller.

9. The PTFE cell used for corrosion studies at 473K (Fig.1) was based on a design used previously by C.R. Clayton (ref.9), modified to overcome the pick-up of copper and nickel previously experienced.

10. The volume of liquid within the cell is only 10ml; this ensures that the sample can be heated and cooled quite rapidly. The corroding water passes through the cell and leaves the pressure vessel via a PTFE needle valve.

Test medium
11. The water used for corrosion was obtained from an Ionmiser 6e de-ioniser and was then cyclically distilled under nitrogen until required. Typical conductivity of the water was 0.5 to 0.7 μS.cm⁻¹. Cobalt carbonate was added to the desired level and the solution reservoir transferred to the pressure vessel which was then vacuum degassed. Oxygen levels were measured using an E.I.L. model 1520 dissolved oxygen meter; approximate levels were 1ppm and 200ppb after 23min and 150min degassing time respectively.

Specimen preparation
12. The specimens of stainless steel (AISI type 304) were cut from cold rolled sheet 1mm thick. Analysis of the steel yielded the following composition (wt. %): Co 0.20, Si 0.006, P 0.015, S 0.71, Mn 1.26, Mo 0.06, Cr 10.23, Ni 8.75, C 0.050, Ti <0.03, Nb <0.03, Fe remainder.

13. The cobalt level was obtained by activation analysis. Although relatively high it is below the limit of sensitivity for the ESCA technique, and thus was not expected to significantly modify the analyses of the oxides formed. All the specimens reported here were prepared by polishing to a one micron diamond finish in order to produce a flat surface and to reduce the effect of chromium enrichment. They were then etched by a 3keV argon ion beam which should remove any modified surface resulting from the polishing process. After ion cleaning they were ultrasonically cleaned in acetone, followed by high purity water, to remove any trace of adhesive from mounting on the ion etching specimen holder. The specimens were then stored immersed in high purity water in sealed containers until required (not more than a few days).

Typical exposure
14. For corrosion at 413K specimens prepared as detailed above were suspended in a PTFE cradle hung on a glass hook within the glass corrosion cell containing 250ml of the corrodent. The period of vacuum degassing was varied between specimens exposed under otherwise identical conditions, but this variation did not significantly affect the cobalt uptake or depth profiles of specimens. It can be assumed that oxygen levels between 1ppm and 200ppb have little effect on the thin oxide formed at 413K. After vacuum pumping the vessel was then presurised with nitrogen and the cell brought to 413K as quickly as possible. After the exposure period the heater was turned off, and the vessel pressure was released, so that the corroded specimen could be removed from solution as soon as possible after reaching 373K.

15. Corrosion at 473K using the PTFE cell followed a different sequence. A 2 litre glass reservoir containing the corrodent was placed in the pressure vessel, followed by the PTFE cell with the specimen inside. The flow system was connected up and the vessel degassed. After one hour the vessel was pressurised with nitrogen to a low pressure, around 50 psi, to check the water flow system, and then, still at room temperature, fully pressurised, and the flow system set to approximately 2ml/min. At this point the heater in the base of the PTFE cell was turned on. It took 25 min for the water temperature to reach 473K. After the exposure period the cell was cooled rapidly by turning off the heater but maintaining the water flow. The pressure was released gradually so as to prevent boiling, and the specimen was removed from the cell as soon as possible after the temperature had dropped below 373K. Total cooling time was of the order of 10 min.

16. Specimens were mounted for XPS analysis then stored in desiccators before being transferred to the ESCA 3 for analysis. The oxide films formed have proved to be exceptionally stable in the UHV of the ESCA, so little change was anticipated by keeping them in a desiccator. The storage times for specimens were however kept to a minimum.

RESULTS
Experiments at 413K
17. Influence of cobalt on growth kinetics and composition of film. The experiments carried out at 413K were designed to give information on the chemical composition of the
Fig. 1. PTFE corrosion cell

Fig. 2. Reproducibility of results at 413K

Fig. 3. Comparison of depth profiles for pure water and water dosed with 0.5mg/l cobalt

Fig. 4. Effect of solution concentration on cobalt uptake
film and, in particular, on the influence of cobalt in the film. Two runs in undosed water acted as reference data (Fig.2). One of these was contaminated with cobalt from the cell wall (%0.05 mg/l) but this seemed not to affect the composition profiles which were in good agreement with each other.

18. Specimens were corroded for periods of 2, 6, and 24 hours in water containing 0.5mg/l (0.5 ppm) as CoCO₃. When the 6-hour exposure depth profiles for 0.5 mg/l cobalt solution are compared with those for pure water we find that the oxygen and iron profiles are close, suggesting a similar film thickness. The chromium concentration is however much lower (Fig.3); this is complemented by the presence of cobalt in the film and by a somewhat increased silicon level. Although the position of the oxide/metal interface is difficult to place, comparison of the profiles formed in cobalt solutions shows that after 6 and 24 hours the films formed are quite similar, whereas the film formed after 2 hours is considerably thinner (Table 1). The 2-hour film also contains much less cobalt, which suggests a link between cobalt incorporation and film growth. On the basis of these profiles the 6-hour exposure period was adopted for all further tests at 413K.

19. The chemical state of the elements was examined for the 6-hour and 24-hour films, and was very similar to that previously observed. Nickel does not normally appear in the outer portion of the films, and it seems likely that nickel does not take part in the oxide film formed at this temperature. Chromium is seen in the trivalent state, and during etching only reverts to the metallic state when the iron signal has become entirely metallic. Prior to etching iron is observed to be trivalent, and only a small amount is present. This changes to a mixture of divalent and trivalent states as soon as etching begins.

20. The main element of interest, cobalt, is observed to be in the divalent state in the unetched condition. This changes to the metallic state as etching proceeds, probably because of ion beam reduction. The contribution of cobalt through the film is fairly constant, and only appears to tail off as the metal/oxide interface is approached.

21. Oxygen is observed at a binding energy of 530.2eV relative to carbon 1s at 285.0eV. This is a position typical of the oxides of many transition elements. The peak is slightly asymmetric and may contain a small hydroxide component (531.4eV).

22. Dependence of cobalt in the oxide on solution concentration. Specimens were tested in solutions from 0.1 to 0.5 mg/l cobalt. The results are plotted in Fig.4, in which each block represents the range of cobalt concentration found in the oxide on a specimen between the first etch and the appearance of a nickel signal (taken to mean that some portion of the specimen had been etched back to the metal/oxide interface).

23. Two stage exposure. The earlier tests on the rate of film growth showed little change in

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* Double exposure samples
† Water chemistry: 500 mg.1⁻¹ B, 1 mg.1⁻¹ Li
‡ Cobalt deposited during overnight cooling
thickness between 6-hour and 24-hour exposure. In order to study uptake in pre-formed oxide a specimen was therefore exposed to cobalt-free water for 6 hours, and then subjected to a further 6-hour exposure period in a solution containing 0.5 mg/l cobalt. The depth profile of the resulting film shows some interesting features at the limit of XPS sensitivity (Fig.5). Cobalt was found in the outer portion of the film, and at the base of the film where the nickel signal begins to increase and the silicon contamination signal falls to zero. No cobalt was detected in the middle of the film.

24. Discussion of results at 413K. After 6 hours, cobalt incorporated from solution extends into the oxide film to a considerable depth. The level is also seen to be fairly constant over the outer 50% of the film. It might have been expected that the cobalt level would increase in the outer portion of the film as the rate of film growth slowed down. This is not supported by the results shown here. The amount of cobalt incorporated in the film is not sufficient to cause appreciable reduction in the solution concentration and it seems therefore that the level of incorporated cobalt is controlled either by equilibrium with the cobalt activity in solution or by an equilibrium within the oxide film.

25. Of all the results obtained at 413K the last one is probably the most interesting (Fig.5). The two stage exposure has revealed that cobalt is incorporated at the metal/oxide interface. The presence of cobalt in the outer region of the film is less significant since it may have arisen by a variety of mechanisms (e.g. exchange and solid state diffusion, retention of solution in porous oxide, or deposition from solution). The cobalt at the metal/oxide interface is not open to such a variety of interpretations. If cobalt reached this interface during the second stage of corrosion then the oxide must be porous and growth is almost certainly occurring at the interface, resulting in cobalt being incorporated. However the lack of cobalt in the central portion of the film shows that cobalt incorporation in continuously dosed situations does not arise from solid state diffusion (as assumed in some models (ref.10)).

26. Growth kinetics and composition. All specimens at 473K were exposed using the PTFE cell and flow circuit. Both pure water and water dosed with cobalt carbonate, giving cobalt concentrations ranging from 0.125 to 0.500 mg/l, were used. A 4-hour exposure period was chosen in order to provide an oxide suitable for ESCA analysis.

27. Two different types of film were formed at this temperature (Fig.6) — a thin protective film similar to that formed at 413K but of twice the thickness, and a thick non-protective film which continued to grow beyond the 4-hour exposure. The type of film that formed did not appear to depend on the presence of cobalt. It appears that 473K is a transition temperature between the low temperature and high temperature growth mechanisms reported by Clayton and Castle (ref.1).

28. Cobalt uptake at this temperature was still proportional to the solution concentration (Fig.7) but was increased relative to uptake at 413K. The maximum cobalt level found within the films was some 2.5 times greater than at 413K. There was however no indication that the maximum amount of cobalt within each film depended on the growth mechanism in operation.

29. As at 413K the cobalt was found to be in a divalent state, and examination of the profiles shows the same tendency for the chromate concentration to be depressed relative to that for pure water (Fig.8). The iron, nickel and oxygen profiles were seemingly unaffected by the incorporated cobalt.

30. A double exposure specimen was run in an attempt to identify the corrosion mechanisms in operation from the distribution of incorporated cobalt (as at 413K). This was exposed to pure water for 4 hours, then to cobalt-dosed water for the same period. It formed a thick film, but showed much less cobalt uptake than expected, and there was no evidence of cobalt deep in the film.

31. Influence of PWR water chemistry. Specimens were also exposed to water containing boric acid (1000ppm B) and lithium hydroxide (2ppm Li) and dosed with cobalt carbonate to give cobalt concentrations of up to 0.180 mg/l. Again two film types were formed, but the most noticeable effects were a further increase in the maximum amount of cobalt found within each film for a given solution concentration (Fig.7), and a much more even distribution of cobalt through the film.

32. A double exposure specimen in this water chemistry gave a thin film of identical thickness to thin film single exposure specimens and containing half the amount of cobalt expected, but evenly distributed through the film. This points to an increase in cobalt diffusion rate through the film, or a film more dynamic than passive in nature.

Decontamination studies
33. Two decontamination processes were applied in the laboratory to coupons of stainless steel which had been exposed at about 570K in the DlDO Water Loop (DWL) during an irradiation experiment. These processes, LOMI and NP/LOMI, and the decontamination of DWL itself are described elsewhere (ref.11). The LOMI reagent (essentially vanadous picolinate) dissolves nickel-iron spinel, and removes any active species associated with the outer spinel layer. The NP/LOMI process (nitric acid-permanganate followed by LOMI) attacks the chromium-rich inner oxide layer as well as any residual nickel-iron spinel.
SESSION 2: PWR COOLANTS

**Fig. 5.** Cobalt uptake at 413K on prefilmed stainless steel

**Fig. 6.** Two types of oxygen profile for exposure to water at 473K

**Fig. 7.** Effect of temperature and water chemistry on cobalt uptake

**Fig. 8.** Cumulative etch profiles for exposure at 473K to pure and cobalt-dosed water
and that the surface of each micro-crystal will have a concentration of metal ions equal to the saturation value. Our interpretation of this assumption is that ions in the solid state are in equilibrium with their concentration in solution. The proportion of cobalt in the precipitated oxide is then given by dividing the concentration of cobalt in solution at the metal/oxide interface by the effective solubility of the inner layer (Csi) and multiplying by 0.7 (30% of the oxide is oxygen), and then multiplying by a partition coefficient (P_i) that describes the ease with which the cobalt is accommodated into the lattice. Most transition metals are readily incorporated into ferrite-type structures so P_i is expected to be close to unity.

39. If cobalt uptake is controlled by crystallization the solution concentration at the metal/oxide interface is equal to the concentration in the bulk solution (C_b), and the fractional concentration at a depth m_i in the oxide film is given by:

$$\frac{dC_i}{dm_i} = 0.7P_i \frac{C_b}{C_{si}}$$

(1)

40. If cobalt uptake is controlled by diffusion down the pores, the concentration of cobalt in solution at the metal/oxide interface is related not only to the bulk concentration but also to the oxide thickness. The fractional concentration in the oxide film is then dependent on the growth kinetics. For parabolic kinetics ($m_i = (k_p t)^2$)

$$\frac{dC_v}{dm_i} = \frac{2D\phi(1-\phi)C_b}{k_p}$$

(2)

while for logarithmic kinetics ($m_i = k_p \ln(a_k t+1)$)

$$\frac{dC_v}{dm_i} = \frac{\rho D\phi(1-\phi)C_b \exp(m_i/k_p)}{k_p a_k, m_i}$$

(3)

where C_b = amount of cobalt in oxide (g.m^-2) 
 m_i = depth of inner layer oxide (g.m^-2) 
 dC_v/dm_i = fractional concentration of cobalt in oxide at depth m_i 
 C_b = concentration of cobalt in bulk solution (g.m^-3) 
 C_{si} = solubility of cobalt in inner layer type oxide (g.m^-3) 
 P_i = partition coefficient 
 \phi = porosity of inner oxide layer 
 \rho = density of inner oxide layer (g.m^-3) 
 D = diffusion coefficient of cobalt in the liquid (m^2.s^-1) 
 k_p = parabolic growth rate constant (g^2.m^-6.s^-1) 
 k^l = logarithmic growth rate constant (g.m^-2) 
 a_k = logarithmic corrosion kinetics constant (s^-1)

41. As would be expected from the initial model, if sufficient cobalt can diffuse down the pores to the metal oxide interface then the amount of cobalt incorporated is linearly dependent on the bulk solution concentration and
is independent of the depth of oxide.

42. The same relationship is also predicted for parabolic kinetics where diffusion controls the uptake. The corresponding prediction for logarithmic kinetics is still linearly dependent on the concentration of cobalt in the bulk solution, but has a more complex dependence on the thickness of oxide formed.

43. Although Lister's model is compatible with most of the observations from this work it is difficult within this model to explain the apparent substitution of divalent cobalt for trivalent chromium within the films (Fig.8). At the oxide/metal interface Lister's model implies that all the oxide formed is precipitated from solution, and cobalt is incorporated during this process.

44. Whatever mechanism operates at this interface it involves oxide formation by iron and chromium and the difference between Fe/Cr ratios in the film and the substrate indicates that a considerable amount of iron enters solution. Presumably this solution will contain iron at saturation level with respect to the iron/chromium spinel.

45. When considering corrosion product stability Rummery and MacDonald (ref.13) showed that cobalt ferrite is thermodynamically more stable than magnetite between 298K and 573K, both in reducing and oxidising water chemistries. Conversely nickel ferrite is less stable below 473K. Unfortunately they were not able to calculate the behaviour of non-stoichiometric spinels, and did not discuss the stability of chromium species. If we assume that Fe/Cr/Co or Fe/Co spinel is more stable than the Fe/Cr spinel present, then the cobalt-containing spinel will be less soluble, and cobalt ions will precipitate dissolved iron that would not normally have been involved in oxide formation. Thus chromium is apparently depressed by cobalt incorporation because cobalt reduces the amount of iron lost into solution, bringing the Fe/Cr ratio of the oxide nearer to that of the metal.

46. In the case of thin film formation the cobalt-containing oxide is just as effective as a protective film as the cobalt-free oxide; thus there is no increase in film thickness.

47. For the thicker oxides the availability of cobalt controls the distribution, with most of the cobalt found in the outer region of the film. The maximum level of cobalt in both thin and thick films is determined by the concentration of cobalt in solution, which in turn dictates the composition of the thermodynamically preferred oxide.

48. Care is needed in extrapolating the laboratory results, since even the 'thick' films are much thinner than those formed under reactor conditions, and the low cobalt levels in a primary circuit will not lead to significant depression of chromium levels in the oxide. Nevertheless the greater uniformity of cobalt distribution observed for PWR-type water chemistry (which indicates a lower resistance to cobalt penetration), and the differences in uptake pattern for preformed oxide under different conditions of water chemistry and temperature, suggest that a suitable choice of pre-filming technique could reduce the susceptibility to cobalt incorporation.

REFERENCES