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TITLE: 
AQUEOUS OXIDATION OF INCONEL ALLOY AND ITS INTERACTION WITH COBALT IONS

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ABSTRACT

The transport of radioactivity in the primary circuits of water-cooled reactors is an important problem in the nuclear power industry. It is generally believed that active species (particularly Co-60 and Co-58) are transported via particulates or in solution and may be incorporated into the oxide films on Inconel, which accounts for 75% of the total surface area exposed to the primary coolant in modern PWRs. This thesis describes investigation of the oxidation of the Inconel alloy in aqueous media at 473 K and 573 K, and its interaction with cobalt ion. The X-ray photoelectron spectroscopy in conjunction with argon-ion etching has been utilised in achieving this objective. By this technique the compositional depth distribution and the chemical state information of the elements in the oxide film on Inconel can be obtained.

Being aware of the damage that may be induced by the ion beam, an alternative has been sought in order to have more information on the way the elements are orderly distributed in the film. Cr 2p spectra have been analysed thoroughly by the method of 'peak fitting' with the use of constant intensity energy loss backgrounds. It has been shown that this method is useful in determining the chemical states of the elements in the oxide film and the presence of cobalt on top of the chromium oxide at the base of the film.
The proportion of cobalt incorporated was observed to be dependent on the concentration of cobalt in the solution but apparently unchanged when the water chemistry was modified to simulate reactor coolant. Cobalt was shown to be incorporated in the divalent state; at a higher proportion in the oxide/solution interface and decreases towards deeper depth in the oxide film.
ACKNOWLEDGEMENTS

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<tr>
<td>AERE</td>
<td>Atomic Energy Research Establishment</td>
</tr>
<tr>
<td>AES</td>
<td>Auger Electron Spectroscopy</td>
</tr>
<tr>
<td>AISI</td>
<td>American Iron and Steel Institute</td>
</tr>
<tr>
<td>AP</td>
<td>Alkaline Permanganate</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for the Testing of Materials</td>
</tr>
<tr>
<td>BWR</td>
<td>Boiling Water Reactor</td>
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<tr>
<td>CANDU</td>
<td>Canadian Water Reactor</td>
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<tr>
<td>DF</td>
<td>Decontamination Factor</td>
</tr>
<tr>
<td>EFPY</td>
<td>Effective Full Power Year</td>
</tr>
<tr>
<td>ELTH</td>
<td>Energy Loss Tail Height</td>
</tr>
<tr>
<td>EMF</td>
<td>ElectroMagnetic Filter</td>
</tr>
<tr>
<td>ESCA</td>
<td>Electron Spectrometry for Chemical Analysis</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum peak height</td>
</tr>
<tr>
<td>HTF</td>
<td>High Temperature Filter</td>
</tr>
<tr>
<td>LOMI</td>
<td>Low Oxidation State Metal Ion</td>
</tr>
<tr>
<td>LWR</td>
<td>Light Water Reactor</td>
</tr>
<tr>
<td>NP</td>
<td>Nitric Permanganate</td>
</tr>
<tr>
<td>PTFE</td>
<td>Poly-Tetra-Fluoro-Ethylene</td>
</tr>
<tr>
<td>PWR</td>
<td>Pressurised Water Reactor</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SGHWR</td>
<td>Steam Generating Heavy Water Reactor</td>
</tr>
<tr>
<td>XPS</td>
<td>X-Ray Photoelectron Spectrometry</td>
</tr>
<tr>
<td>XRF</td>
<td>X-Ray Fluorescence</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra High Vacuum</td>
</tr>
<tr>
<td>UKAEA</td>
<td>United Kingdom Atomic Energy Authority</td>
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UPS  Ultraviolet Photoelectron Spectrometry
VDU  Visual Display Unit
CHAPTER 1

INTRODUCTION

Plant monitoring has established the isotopes of cobalt - Co-60 and Co-58 - as the major contributors to the BWR and PWR radiation fields that cause occupational doses of radiation [1]. These isotopes are produced by neutron activation, in the reactor core, of the natural species, i.e. Co-59 is transmuted to Co-60 and Ni-58 to Co-58, which are released, together with other corrosion products, through wear and corrosion of the materials making up the reactor circuit. The high-nickel alloy Inconel-600 (76% Ni, 16% Cr, 8% Fe), which is present as the steam generator tubing materials, accounts for 75% of the surface area exposed to coolant under thermal operating conditions in a modern PWR plant [2]. This is a considerable source of Co-59 and Ni-58.

The activated cobalt species are deposited and incorporated on the out-of-core metal surfaces as they are transported through the primary circuit. In course of time they are expected to accumulate and result in high dose rates at those surfaces. The need to keep the level and the sources of these doses down for the safety of the personnel working in the radiation fields is self evident. Before this need could be fulfilled the mechanism whereby the corrosion products, especially cobalt species, are transported through the primary coolant and deposited on the metal surfaces making up the coolant system as well as the influence that the coolant chemistry
might have on the transportation and deposition should well be understood.

This thesis describes work at the University of Surrey using the technique of electron spectrometry for chemical analysis (ESCA, but better described as X-ray photoelectron spectroscopy, XPS) to study the process by which dissolved cobalt ions are incorporated into the oxide films on Inconel-600 in high temperature water, i.e. at 473 K and 573 K. The ability provided by XPS to obtain the chemical state information should help in understanding the species in the oxide film. When XPS is combined with ion etching the composition of the surface may be revealed layer by layer thus providing the distribution of the incorporated cobalt with the depth of the oxide film up to the substrate level. Such a distribution is usually known as the depth profile.

The need to analyse XPS spectra especially those of transition metals in order to have additional information on the chemical states and depth distribution of a given element in the corrosion products on Inconel has prompted a thorough analysis on the chromium 2p X-ray photoelectron spectra using a peak fitting program. The inclusion of the Shirley [3] and constant intensity energy loss backgrounds in the XPS spectra has helped, at least, to understand the distribution of the corrosion products in the layer-like oxide mixture on Inconel.
The results are examined with reference to models developed for the take-up of cobalt ions in the oxide formed on 18/8 stainless steels. The behaviour of the oxide films on Inconel at 473 K is in some respects similar to that for oxide films on stainless steel, in that the cobalt content of the film is proportional to the cobalt concentration in solution, and there is in general a slight decrease in concentration with increasing depth in the oxide film. However, in other respects there are notable differences: content is lower in the Inconel oxide, and there is no evidence for the depletion of chromium which was found to be associated with the incorporation of cobalt into films on stainless steel. There also appears to be no significant effect from dosing the water with boric acid and lithium hydroxide.
2.1 INTRODUCTION

In this chapter some existing models on the oxidation of steel, stainless steel and Inconel at high temperature, plants observations and activity transport studies will be reviewed. These lead to a definition of the objectives of this investigation which are presented in the last section of the chapter.

2.2 OXIDE FORMATION ON STEEL AND STAINLESS STEEL IN HIGH TEMPERATURE WATER

Before reviewing the oxide formation on Inconel-600 it is of interest to look briefly at the oxidation of iron and steels as it forms the basis for understanding any mechanism involved in the oxidation of Fe-Ni-Cr alloy in high temperature aqueous solutions.

In 1961 Potter and Mann [4] investigated the thick corrosion film formed on carbon steel specimens exposed in autoclaves at high temperature water. The films, which are known as Potter-Mann type, were observed to be a duplex structure consisting a compact, thick, adherent inner layer and a coarse outer layer. The outer layer was proposed to grow by the transport of iron ions which are not
oxidised at the metal/oxide interface but travel across the inner layer to deposit at the solution/oxide interface [4]. The inner layer was proposed to be continuous and to grow by inward diffusion of oxygen ions [5]. Although the movement of the oxygen ion in the spinel lattice is too slow to account for the observed corrosion rate [6], there remains possibility that diffusion would be enhanced in an aqueous environment as a result of the incorporation of the hydroxyl ions into the lattice [7]. Nevertheless such effect was shown to be small [8].

At about the same time, Bloom and Krulfeld [9, 10] reported a single-layer film, known as Bloom-type, to be formed on iron under a similar conditions, rather than the Potter-Mann duplex films. Marsh [11] arrived at the conclusion that, subject to some limitations, the type of film formed depends on the presence or absence of a suitable cathodic surface in contact with the corroding surface. In the absence of an external cathode, Bloom-type films are formed. In contact with cathodic surface the corrosion film had the Potter-Mann duplex structure.

In 1966 Castle and Mann [12] demonstrated that the form of oxidation of the specimens is in accord with that predicted from the solution transport properties of the experimental systems. The driving force for the transport process is the difference in solubility between the base corrosion-film material and magnetite. If the system is large, and can act as a sink for the original products, then the duplex structure will be formed because of the
lower concentrations in the inner layer due to the diffusion outward. In Bloom's experiment, the system surface-to-volume ratio is quite large, and the solution becomes saturated rapidly. The pores in the inner-layer then heal and a single thick-layer film is formed. Thus, the Bloom type film reverts to two-layer form when the oxide layer is damaged.

The possibility that the inner layer is porous was first discussed by Field et al [13] and was proved later with the observations made by Field and Holmes [14] and Harrison et al [15]. Castle and Masterson [16] then proposed that these pores must be interconnected.

Based on the assumption that solution transport through the inner layer is the controlling step, Castle and Masterson [16] have derived a parabolic equation for the reaction kinetics of the Potter-Mann film. Later, in 1969, Castle, Foster and Masterson [17] proposed a mechanism of the growth of the duplex film based on the assumption suggested earlier [16], and a competition between oxidation and dissolution at the metal/oxide interface. The reaction scheme which was proposed is shown in Figure 2.1. Oxidant, in the form of water or hydroxyl ions, diffuses down the pores to the iron surface to produce the inner layer crystallites whilst the soluble iron species $\text{FeO}_2^{2-}$, formed as $\text{Na}_2\text{FeO}_4$ from the surface $\text{Fe(OH)}_2$ layer, diffuses in the opposite direction. Experimental observation showed that the formation of the inner layer is accompanied by a zero volume change.
Figure 2.1 A representation of the overall corrosion process of steel in high temperature aqueous solutions [17].

\[
3 \text{FeO}_2^{2-} + 6\text{H}^+ \rightarrow \text{Fe}_3\text{O}_4 + 2\text{H}_2\text{O} + \text{H}_2
\]

\[
\text{Fe} + 2\text{H}_2\text{O} \rightarrow \text{Fe(OH)}_2 + 2\text{H}^+ + 2\text{e}^-
\]

\[
3\text{Fe} + 4\text{H}_2\text{O} \rightarrow \text{Fe}_3\text{O}_4 + 8\text{H}^+ + 8\text{e}^-
\]

\[
\text{Fe(OH)}_2 \rightarrow \text{FeO}_2^{2-} + 2\text{H}^+
\]
Moore and Jones [18] find that on carbon steel in pH 11 LiOH the base film reaches a limiting thickness and its upper surface takes on a pebble-like structure. They interpret this result to indicate that the base film is being simultaneously generated at the metal-oxide interface and being dissolved at the oxide-solution interface. Initially the metal-oxide interface reaction would be the rate-controlling, but ultimately the oxide-solution interface would become the rate controlling step.

For two-layer films to grow without precipitation in the pores of the inner layer, there must be a solubility difference across the layer. On carbon steel, this has been attributed to a hydrogen concentration gradient in the film [19] and to a stoichiometry gradient [20]. The latter theory fits well with the parabolic growth model suggested earlier [16].

So far we have considered only the formation of duplex layers on steel. Early observations of the oxide film on stainless steel made by Francis and Whitlow [21] and Warzee et al [22] showed that the same type of film was formed. Francis and Whitlow made an observation on the oxide formed on AISI 304 stainless steel specimens exposed to water at 573 K and 623 K, whilst Warzee et al. made observation on AISI 304 steels corroded in water with varying conditions between 473 K and 623 K. Both groups of workers observed that, initially, a relatively thin layer of amorphous or finely textured oxide, which is quite protective, is formed next to the metal. In low oxygen conditions, nuclei of magnetite develop on
this layer. Francis and Whitlow identified the base film as an pure magnetite by diffraction analysis, whereas Warzee et al., on the basis of chemical analysis, conclude that it is a spinel of the FeO-Cr₂O₃ type.

Almost ten years later, using XPS in conjunction with ion etching, Castle and Clayton [23] studied the formation of oxide layers formed at 393, 433 and 473 K on stainless steel. At 393 and 433 K an outer iron-rich hydrated structure overlying an inner chromium-rich corundum structure was observed. At 473 K, however, the outer layer is replaced by an extensive iron-rich layer, but the chromium-rich layer is maintained. They suggested this as due to the change in the mechanism of film formation on stainless steel at 473 K that cation diffusion was sufficient to sustain continued growth beyond the initial barrier film.

Thus the observations made on steel and stainless steel conform the formation of the Potter-Mann two-layer structure at high temperature aqueous solutions.

2.3 CORROSION OF INCONEL 600 IN AQUEOUS SOLUTIONS AT HIGH TEMPERATURE

Desire for a material less susceptible than austenitic stainless steel to stress corrosion cracking had led to a search for alternatives. A survey by White [24], showed that the most satisfactory alternative for heat exchanger construction to be
Inconel. The long term corrosion behaviour of Inconel was then studied [25,26] in which the comparison of the Inconel with stainless steel general corrosion rates in solutions simulating reactor coolant was made. They found that the corrosion rates of Inconel were similar to those of austenitic stainless steel.

Cheng [27] noted the initial instantaneous corrosion rate is lowest at around pH 10 on annealed Inconel exposed to a series of 600 F lithiated static waters, ranging from pH 7 to pH 12. All pH measurements were made at room temperature. Later, Whyte [28] observed that Inconel-600 appears to be sensitive to both pH and surface conditions in boric acid solution. It was also noted that there was a considerable effect of alkali additive in reducing the short term corrosion and apparent metal release rate of mechanically polished Inconel at 600 F.

Van Rooyan and co-workers [29] studied the effect of surface finish on the corrosion of Inconel-600 at 550 to 650 F in water of different pH. They found that bright annealed or pickled specimens exhibited much less metal attack than those that were ground.

Studies of thick corrosion films on Inconel in pure water with varying solution pH, dissolved oxygen concentrations, and refreshment rate at 285°C have been reported by McIntyre et al [30] in 1979. Samples of Inconel were exposed to aqueous attack in static and continuous autoclaves for periods ranging from 1 to 168 hours. The pH range of 7 to 14 was studied and the dissolved oxygen
concentration was varied from <0.005 mg oxygen/kg. water to 20 mg/kg. Using XPS and ion bombardment technique they found that a thin film (<10 nm) rich in chromium oxide was formed in hydrogen saturated water of pH 10. It was suggested that this resulted from solid state growth process. A similar film grew on Inconel in water of pH 10 containing higher concentrations of dissolved oxygen but rapidly overgrown by a non-passivating layer of metal hydroxides whose compositions and growth rate vary with the oxygen concentration in the solution. They also suggested that the stability of the alloy is likely determined by the solubility of the chromium oxide formed in the initial oxidation.

Elemental release studies have been made by Bird et al [2] on Inconel-600 and stainless steel under simulated PWR coolant chemistry conditions at 320 °C. A very thin oxide film of 0.5 μm thick was observed on the Inconel specimens after they had been exposed for 209 days and the authors showed by EDAX/SEM analysis that there is no major differences in elemental composition of oxide films and alloy substrate. They assumed NiO, Fe₂O₃ and Cr₃O₄ were the only oxides present on the surfaces of both irradiated specimens.

2.4 REACTOR PLANT OBSERVATIONS

The radiation exposures accumulated annually at light water cooled nuclear power plants in the United States were reported to increase [1]. Figure 2.2 shows the annual averages per plant for
Figure 2.2 Average U.S. LWR occupational radiation exposure [1].
United States plants. One of the factors which determines this radiation exposure is the magnitude of the radiation fields built up at the point of concern. For example, the radiation fields measured at or near the inlet and outlet heads of the Westinghouse U-tube steam generators (Figure 2.3) show a generally increasing trend with the average rate of increase around 4 R/h per effective full power year (EFPY) of operation [1]. Figure 2.4 shows another example of increasing activity level at the average of 150 mR/h per effective full power year monitored on the recirculation pump suction piping of American BWRs. Plant monitoring has also established cobalt radionuclides as the major contributor to the radiation fields for both BWRs and PWRs. A correlation between coolant conductivity and Co-60 activity deposition in the operating BWRs has been suggested by Dehollander [31] and in Figure 2.5 shows such a correlation with additional data observed at the Winfrith Steam Generating Heavy Water Reactor (SGHWR) by Comley and Bird [39]. Figure 2.6 shows the variation of the activity of the primary coolant water and suspension recorded during the shut down procedure of the KCD II, Belgium [32]. It is noted that at the decreasing power the activity increases with a factor of 5 to 10 for the Co-58 and Co-60. Another measurement on the Co-60 radioactivity as a function of EFPY which was made on the Inconel surface of the steam generator tubes has also shown the increase in the surface activity with EFPY (Figure 2.7) [33]. These observations lead to the examinations of the coolant surfaces and studies of the activity transport and decontamination which are all directed towards the controlling of the radiation fields build up on the out-of-core surfaces. The
Figure 2.3 Radiation fields at or near the inlet and outlet heads of Westinghouse U-tube steam generators [1].
Figure 2.4 Shutdown radiation levels on BWR recirculation pump suction piping [1].
Figure 2.5 Variation of Co-60 activity retained on coolant pipework and reactor coolant conductivity [39].
Figure 2.6 Variation of the activity of primary coolant during shutdown procedure [32].
Figure 2.7 PWR radiation fields at steam generator channel head center with plant energy generation [33].
presence of cobalt in the oxide film on the out-of-core material surfaces could well be related to the oxide structure on the surfaces. It is this relationship that will be reviewed in the following section.

2.4.1 OXIDE STRUCTURE AND COMPOSITION

As mentioned previously because of its known resistance to chloride cracking Inconel-600 was substituted for stainless steel in many steam generators. It is in 1964 that the first Inconel-600 steam generators were installed in commercial power plants. The first Inconel specimens taken from plants were only able to be examined and reported in the early 1970's.

In their attempts to investigate the response of BWR and PWR crud/oxide layers on out-of-core surfaces to the decontamination reagents Johnson et al [34] examined the composition and morphology of the oxide/crud layers on Inconel-600 specimens obtained from the steam generator tube of the Indian Point 2 PWR. An oxide film of 0.5 \( \mu \text{m} \) thick comprising two types of film was observed. On the outer layer a sparse population of large particles comprising Ni, Cr and Si was noted. The inner compact layer adjacent to the alloy surface tends to suggest a high chromium content film which they suggest to be that of high chromium spinel oxides, rather than nickel ferrite as found in fuel crud. However no observation was made on the cobalt distribution in the oxide.
Three years later a detailed examination by scanning electron microscopy together with X-ray analysis, gamma spectrometry and wet chemical analysis of the oxides on Inconel and stainless steel was reported [35]. The Inconel specimens were obtained from the steam generator tubings from various PWRs. Again two types of film were observed on the Inconel specimens. The fixed oxides on all specimens were observed to be rich in chromium and in general were similar in composition, although oxides on Inconel contained more nickel and less iron than oxides on stainless steel. The overlying particulate oxide was found to be very variable in composition but generally contained less chromium and more nickel and iron than the fixed oxides. It was noticed that over 75% of Co-60 resided in the fixed oxide on Inconel and in some specimens it was found to be more than 90%.

There is still a marked lack of detailed information on the chemical composition of oxide on PWR structural surfaces and in particular on Inconel surfaces. Nevertheless from the existing evidences mentioned earlier, it can be deduced in general that the oxide film on Inconel specimens taken from plants is of two-layer structure of particulate overlayer oxide and the growing oxide on the metal surfaces. The presence of cobalt on the out-of-core surfaces and the increasing radiation field build up trends have focused the attentions to reducing the cobalt activity level. This will be the subject that will be reviewed in the following section.
2.4.2 CONTROL OF RADIATION FIELDS STUDIES

A few solutions have been put forward, studied and applied in reducing cobalt activity level in the oxide film of the reactor system surfaces in contact with the coolant. Since the sources of these radioactive species are the construction materials of the system itself then the first solution to this problem would be reducing the cobalt content of the constructing materials. In BWRs, parts which are suspected to release cobalt into the coolant are the rollers and pins on the control blades. Since 1981, blades of cobalt free alloys, i.e. CFA (Nickel base alloy) rollers and Nitronic 60 (iron base alloy) pins, and, Inconel X750 rollers and PH 13-8 Mo pins have been installed in the Monticello and Millstone BWRs to replace conventional stellite (cobalt base alloy) rollers and Haynes 25 pins used in BWRs [1,36]. In PWRs the replacement of the steam generator tubes with low cobalt materials was proposed since it has been identified that Inconel steam generator tubing, which contributes up to 75% of the surface area exposed to the primary coolant, is the principal source of cobalt to PWR system [2]. It is now generally accepted worldwide that the direct reduction of Co-59 impurity level down to <0.015 for Inconel-600 for future steam generator tube material in future PWRs or in replacement steam generators [2] should be attempted. This approach may well be constrained by economic factors related to supply and demand for low cobalt Inconel.
Another alternative which is currently utilised and still undergoing studies in reducing radiation fields is the filtration at high temperature of the crud produced in the coolant. It has been noted that crud, suspended particles of corrosion product, is responsible for transporting the active species through the coolant system. Most of the filters use electromagnetic fields in a matrix of wire mesh stacks or steel balls. Performance of a large-ball type electromagnetic filter installed at KKI BWR in Germany has been reported [37]. Results from the studies of the EMF installed in the primary coolant circuit of the Winfrith SGHWR have also been reported [38, 39]. Preliminary efforts on the use of high temperature filter (HTF) in PWR were reported by Shaw et al [36].

Filteration of the crud together with the purification of the coolant water, e.g. by ion-exchange resins, would help in reducing the corrosion products in the coolant and hence hopefully would bring down the radiation field build-up on the out-of-core pipework in both BWR and PWR plants.

In parallel with the attempts to reduce coolant crud it was also recommended to control the boron-lithium level in the coolant [33, 40]. This is specially aimed to minimise core-crud and out-of-core radiation fields in PWRs. Coordinated lithium-boron control is currently being tested worldwide (see e.g. ref. 33, 40).

Another field of study involved in reducing cobalt activity is known as decontamination. In these techniques particular reagents are used periodically in the coolant to dissolve surface oxides
which are believed to hold the active corrosion products. The chemical considerations which must be addressed to achieve reagents which give efficient oxide dissolution, low corrosion, and also convenient waste disposal have been presented by Segal and Swan [41]. Decontamination tests performed on the stainless steel and Inconel-600 PWR specimens using nitric permanganate (NP) and alkaline permanganate (AP) based processes were reported by Pick [35]. He found that Inconel-600 and stainless steel oxides behave quite differently to these reagents, which he postulated as due to differences in structure and surface charge characteristics. The use of LOMI (Low Oxidation State Metal Ion) reagent seems to be favoured in this country (U.K.) and in the United States. For example it has been used extensively since 1980 in routine decontaminations of the reactor artefacts, fuel elements and the whole coolant circuits of the UKAEA pressure tube BWR at Winfrith [42-44]. LOMI reagents provide rapid dissolution of the corrosion product oxides rich in Fe(III) by a reductive dissolution mechanism with minimal corrosion of the underlying metal. Recently the use of LOMI, and LOMI in combination with NP processes [41,45] were applied in the laboratory [46] to coupons of stainless steel and Inconel which had been exposed at 570 K in DIDO Water Loop [44] during an irradiation experiment. It was found that most of the cobalt activity on stainless steel was in the chromium rich inner layer whereas on Inconel a different cobalt distribution was noted. Different responses shown by the oxides and the incorporated cobalt activity on several decontamination reagents tend to suggest different structure of oxide formation and cobalt incorporation on
the Inconel-600 and stainless steel specimens which needs further investigation.

2.5 ACTIVITY TRANSPORT STUDIES

The right choice of the water chemistry utilised as the primary coolant could well be the most important factor in controlling the radiation fields [33,40]. To achieve this goal the mechanisms and processes involved in LWR plants, in (a) in the generation of the corrosion products that have the tendency to be activated to active species, and, (b) the transportation and deposition of the active species, especially that of cobalt, should well be understood. To meet this requirement a few loops have been set up throughout the world to model the processes in LWR plants although the models put forward still remain semi-empirical. There are still too many aspects of corrosion product transport of which very little is known [1]. One of the aspects which is relevant to this work is the influence of the coolant chemistry on deposition and incorporation of the corrosion products, especially that of the active species, in the oxides on the out-of-core surfaces. Most of the models were applied to stainless steel surfaces. Nevertheless these models could throw some light on the processes involved on Inconel, thus they are worthwhile to be reviewed.

Anstine and Naughton [47] suggested two possible mechanisms for Co-60 deposition on out-of-core Type-304 stainless steel surface
More than 90% of the activated corrosion products are deposited in the inner layer through the second mechanism. The mechanisms by which Co-60 might be incorporated into the film were also suggested. These are:

(i) incorporation into the crystal structure as the particles are formed during the corrosion process,
(ii) chemical exchange of elemental cobalt and Co-60 for other elements in the oxide, and
(iii) isotopic exchange of Co-60 in the primary water for Co-59 in the oxide film.

Regarding the proportion of cobalt in the oxide film, they found that it is a function of the cobalt concentration in the water. They then concluded that chemical and isotopic exchange are probably the most important Co-60 incorporation mechanisms.

The influence of temperature and temperature gradient on the deposition of mainly particulate corrosion products on stainless steel surfaces has been studied in a high pressure loop called 'MAGGAN' in Sweden [48]. It is found that the deposition of cobalt
containing corrosion products is not influenced by these parameters but the deposition processes of the active species were not mentioned. Also in Sweden a computer code 'CRUD' has been developed to calculate the transport and activation of the corrosion products in BWR primary system [49].

Lin et al. [50] developed a mathematical model describing the corrosion product transport in BWR primary system. They placed the incorporation of cobalt during the oxide formation as the most important mechanism. Cobalt found in the 304 stainless steel surfaces was observed to be nearly proportional to the cobalt ion concentration in water.

Another computer code 'PACTOLE' was developed [51] to predict activation and transport of corrosion products in PWRs. In this model ion exchange (a) between the particles formed in the bulk of the liquid and the solution, and, (b) between the oxide layer and the solution, is taken into account.

Horvath et al [52] developed a computer code 'RADTRAN' to calculate activity transport by assuming, in the case of out-of-core surfaces, only soluble form of corrosion products take part in the contamination. This assumption was based on Lister model [53-55] which assumed the particle born activity is small in normal operation.
The Lister model [53-55] also suggests the incorporation of the soluble radionuclides into the growing oxide to form a stable spinel (CoFe$_2$O$_4$). The mechanism is postulated to be ion exchange between dissolved cobalt species and the growing oxide. Dehollander [31] then suggested that only a limited sites within the oxide layer can be occupied by cobalt ions, hence there is a Co-60/Co-59 specific activity dependence. For the outer layer, which crystallizes from the bulk liquid, the incorporation of the active ions was postulated by Lister model to take place by co-precipitation [53-54].

Elemental release studies on Inconel-600 and 304L stainless steel under PWR coolant chemistry conditions were reported by Bird et al [2]. Irradiated specimens were exposed at 578 K to PWR coolant chemistry and a thin film of 0.5 µm thick on Inconel and of 1 to 2.0 µm thick on stainless steel specimens were observed. EDAX/SEM analysis showed no major differences in the elemental composition of the oxide film and alloy substrates.

Recently investigations of the different processes involved in the cobalt incorporations into the oxide film on stainless steel specimens exposed in autoclaves at 473 K and 413 K to pure and simulated PWR water were reported [46, 56]. The maximum cobalt uptakes at both temperatures in pure water were observed to be proportional to the cobalt concentrations in the water but the cobalt uptake at 473 K was increased relative to uptake at 413 K. The change to simulated PWR water chemistry tends to increase the
uptake further for a given cobalt concentration in the solution, Figure 2.8. Cobalt distribution through the oxide film was shown to depend on the conditions of exposure and to be associated with the modification of the chromium content. The uptake was also shown to fit well with the modified Lister model [54-55].

2.6 OBJECTIVES OF THIS STUDY

All proposed models seem to be applicable to stainless steels and very little laboratory work is reported for Inconel-600 especially on the incorporation of cobalt into the oxide film. Furthermore, most of the techniques used for monitoring the activity level in and the structure of the oxide films are unable to show how cobalt is distributed through the oxide films. Only the work of Richardson and co-workers [46,56] has so far revealed the cobalt distribution layer by layer through the oxide film but only on stainless steel specimens. As a complement to Richardson's work and since there is an increasing tendency to employ more Inconel in the PWRs, this investigation is undertaken. The objectives of this work are to investigate :-

(i) the formation of the oxide film on Inconel-600 both in pure and simulated PWR water,
(ii) the uptake of cobalt ions from solution and its distribution into the oxide film,
(iii) the effect of cobalt concentration in the solution on the maximum cobalt uptake in the oxide,
Figure 2.8 Effect of temperature and water chemistry on cobalt uptake on stainless steel [56].
(iv) the effect of prefilming in pure water on the cobalt uptake, and
(v) the model which is suitable to describe the oxide formation and cobalt incorporation into the oxide on Inconel, all at 473 K.
(vi) the formation of oxide film at reactor temperature of 573 K in pure and reactor type water, and
(vii) the cobalt uptake into the oxide film in both pure and reactor type water at 573 K.

All 473 K exposures were carried out in the PTFE cell in the laboratory in this university while those at 573 K were run in the titanium autoclave at AERE, Harwell.

All of the investigations were carried out by using X-ray photoelectron spectrometer in combination with the argon ion bombardment technique.

To improve the understanding of the chemical states and distribution of the elements in the oxide film without recourse to destructive ion etching an investigation of the peak structure of the X-ray photoelectron peaks was undertaken. This study was made with special regard to the structure of Cr 2p, and its relation to the energy loss background. Details of the XPS theory and instrument, ion bombardment and data manipulation will be presented in the next chapter.
In this chapter the technique involved in characterizing the oxide film formed on Inconel 600 throughout this investigation will be discussed. It is divided into two main sections, namely photoelectron spectroscopy and ion sputter etching.

3.1 PHOTOELECTRON SPECTROSCOPY

In analysing surfaces exposed at high temperature aqueous solution one usually needs to get information from the outermost atom layers. This is because in the formation of the oxide on the surface, some elements drawn from the underlying metal are often in different proportions from those in the alloy itself. Besides, some elements from the solution, for example oxygen and cobalt, may also be found in the oxide film. In addition to the proportions of the elements in the oxide one may also wish to have an indication of their valence states. The fact that the inelastic mean free path of electron in a solid is small, about $10^{-3}$ times that of an X-ray of equivalent energy, makes it easier to obtain surface composition information using characteristic energies in the secondary electron spectrum than by using characteristic X-ray emission. There are two available techniques which use characteristic electron energies for obtaining elemental compositions on the surface. They are photo- and Auger-electron spectroscopies. The advantage possessed by the
former over the latter technique in distinguishing chemical states of the elements present makes the X-ray photoelectron spectroscopy the most appropriate technique in analysing the surface oxides on all specimens in this work.

3.1.1 HISTORICAL BACKGROUND

The energy distribution of X-ray induced photoelectron was studied as early as 1914 by Robinson and Rawlinson [57]. In their work iron and lead were exposed to X-radiation from nickel anode and with the help of a homogeneous magnetic field the energy distribution of the emitted electrons was recorded photographically. The electron spectra obtained consisted of bands of 2 mm width, but the process involved was not really understood at that time.

After the initial studies of Robinson a few more measurements of the energies of emitted electrons, better known as beta-rays at the time, were made using the same technique in order to study the electronic structure of matter [58(a)-58(d),59]. However, the poor techniques available for particle detection, together with deficiencies of the magnetic spectrometers used, prevented them from achieving an accuracy that could compete favourably with the X-ray absorption and X-ray emission techniques which were developed earlier. This made X-ray photoelectron spectroscopy almost disappear.

The unique capabilities of the electron spectroscopy technique were only recognised in the early 1950s when Siegbahn and co-workers
studied these photoelectrons with high resolution energy spectrometers [60]. In their first paper, they discussed the importance of resolution and the need for controlling stray magnetic fields. They also reported the photo- and photo- induced Auger-electron peaks obtained from copper [61]. They then showed the possibility of distinguishing an oxide from its parent element from the photoelectron spectrum [62]. This is the cornerstone of the application of this technique to surface studies.

By 1967 the principles of surface analysis by X-ray photoelectron spectroscopy (XPS) were almost fully discovered [63] and since 1970 this technique has come to regular use in surface studies.

3.1.2 THEORY

3.1.2.1 ENERGY RELATIONSHIPS

A beam of either high-energy electrons or photons, incident on a material, will excite secondary emissions of both photons and electrons. In the case of photoelectron spectroscopy, the excitation source is a beam of photons of well-defined energy and the secondary emission are electrons which are generated by well-defined transitions within the atoms of the material.

Photon sources can be grouped into three categories depending, (a) and (b) on the energies of the orbital electrons in the atom of the material which are to be excited or (c) on the occasional
need for variable energy sources. Those falling into the first category, (a), are ones based on rare gas discharge lamps in the range of 10 to 50 eV. They are namely HeI and HeII and have a natural line width of 3.0 and 17.0 meV respectively. Due to the very low energy they possess, 21.22 eV for HeI and 40.82 eV for HeII, they make ideal sources for studying the valence orbitals of molecules and band structure of solids. Their use is referred to as ultra-violet photoelectron spectroscopy (UPS) for their energies fall into the range of ultra-voilet radiation. The second category, (b) includes the characteristic X-rays which have higher energies and broader linewidths, but can excite electrons from core orbitals. The production of characteristic X-rays is based on the principle that radiation is emitted when high energy electrons are suddenly stopped by a material. The stopping material, or the anode, determines the energy of the characteristic X-ray that will be obtained. The most commonly used are AlKα and MgKα X-radiations. However the use of other characteristic X-rays such as SiKα, ZrLα and AgKα radiations has also been reported for the special capabilities these radiations possess. Table 3.1 shows the excitation X-radiation sources available together with their energies. The ultra-violet sources are also included for comparison.
Table 3.1 Excitation radiation sources.

<table>
<thead>
<tr>
<th>Source</th>
<th>Energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HeI</td>
<td>21.22</td>
</tr>
<tr>
<td>HeII</td>
<td>40.82</td>
</tr>
<tr>
<td>MgKα</td>
<td>1253.6</td>
</tr>
<tr>
<td>AlKα</td>
<td>1486.6</td>
</tr>
<tr>
<td>SiKα</td>
<td>1739.5</td>
</tr>
<tr>
<td>ZrLα</td>
<td>2042.0</td>
</tr>
<tr>
<td>AgKα</td>
<td>2984.3</td>
</tr>
</tbody>
</table>

The third category, (c) of photons sources is the synchrotron radiation. It is based on the principle that when an electron beam is accelerated in vacuum it gives off radiation as from a point source. A continuous spectrum of photons will be created in the range of a few eV to several keV if electrons are continuously circulated in a storage ring at energies about 1 GeV. There are two main advantages of using the synchrotron radiation over those which fall into the first categories. First, it can produce a very high intensity source and second, it can give a variable energy source. Its broad applicability to XPS users has been reviewed [64,65].

The excitation of an electron from a core orbital of an atom by the photoemission process may be presented diagramatically as in Figure 3.1. If the difference between the photon energy $E_{ex}$ and the binding energy of the electron in the orbital, $E_b$ is larger than the
Figure 3.1 Energy diagram in relation to the photoemission of an electron.
work function, $W_m$ of the material, then the electron from the
particular orbital will be emitted from the surface and carries some
kinetic energy. The kinetic energy of the emitted electrons, $E_{k'}$, is
given by

$$E_{k'} = E_{ex} - E_b - W_m \quad (3.1)$$

where $E_{ex}$ is the excitation photon energy and $W_m$ is the work
function of the specimen. The work function for a solid in this
case is defined as the energy separation between the Fermi level of
the solid and the vacuum level.

In practice, an electron may be accelerated or retarded during
its passage from the surface of the specimen to the spectrometer.
The energy between the spectrometer and the Fermi level of the solid
is known as the spectrometer work function. Thus the actual kinetic
energy, $E_k$, of the electron seen at the spectrometer is given by:

$$E_k = E_{ex} - E_b - W_{spec} \quad (3.2)$$

where $W_{spec}$ is the work function of the spectrometer. The binding
energy $E_b$ is the difference in ground state energy computed before
and after the generation of the core-hole state, and it is also
referenced to the Fermi level. By measuring the kinetic energy of
the emitted electron and the work function of the spectrometer, the
binding energy of the orbital emitting that particular electron can
be calculated as given by the following equation:

\[ E_B = E_{ex} - E_k - W_{spec} \]  \hspace{1cm} (3.3)

The excitation energy supplied by a photon beam may be defined within quite narrow limits. As a result of this one may obtain sharp peaks in the kinetic energy spectrum corresponding to the well defined values of \( E_B \) for the core levels of electrons in the elements of the surface layers.

Equations (3.2) and (3.3) hold only if the specimen is in good electrical contact with the specimen holder and thus with the spectrometer. A bad contact will produce an electrostatic charge on the specimen which will in turn result in the uncertainties in the peak positions, i.e. shifts in the peak positions due to surface charging.

To overcome surface charging effect and to estimate the value of the spectrometer work function there is a need to have an energy reference which can be used as a standard. Various methods have been used for the absolute calibration of the spectrometer. In most of the techniques the core level electrons from noble metals, e.g. those of Au 4f7/2 and Ag 3d5/2 are determined relative to the Fermi level. These standards are then used to calibrate the secondary standards. The carbon 1s electron binding energy from adventitious carbon found on most specimen is now widely used as the secondary energy reference in electron spectroscopy. The presence of this
carbon-containing contamination layer on most surfaces was thought as due to hydrocarbons originating from the vacuum pump oil [63]. Most workers [66-68] found the carbon 1s peak from adventitious carbon at 285.0 eV. However from a recent investigation [69] it was revised to be at 284.8 eV. The use of adventitious carbon for energy referencing was reviewed by Swift [70]. Throughout this work the value of 284.8 eV for C 1s is used and any deviation from this value is applied as a correction to the apparent position recorded for all other peaks.

There are two other processes normally accompanying the photoelectron emission by X-ray excitation. First is the emission of the Auger electrons, named after its discoverer, Pierre Auger, and refers to the emission of electrons from the excited atoms as it returns to the ground state. This process can be shown diagrammatically as in Figure 3.2 in which the photoemission of an electron in the K-shell is followed by the ejection of another electron in the L-shell as a result of the transition of an electron from L-shell to fill the hole left in the K-shell. The identification of element may also be made by using the peaks due to these Auger electrons observed in the kinetic, or binding energy, spectrum of the X-ray photoelectron since the kinetic energy of the the electron emitted by this process can be calculated quite easily. Beside that, the kinetic energy of the Auger electron is independent of the excitation X-ray energy used to excite the initial core-hole state. This fact may be used to select the appropriate X-ray source to overcome the problem of overlapping between the photo- and Auger-electron peaks in the XPS spectrum. In this investigation the
Figure 3.2 Energy diagram in relation to the emission of a photo-induced Auger electron.
MgKα X-radiation was used in acquiring spectra from oxide films on Inconel to overcome the problem of overlapping between Ni Auger- and Co and Fe 2p photo-electron peaks which normally arises if AlKα radiation is used (Figure 3.3). The observation of the Auger electron peaks has become the basis of the Auger electron spectroscopy (AES) in which the excitation energy is obtained from the electron beams.

The second process accompanying the X-ray photoelectron is the X-ray fluorescence (XRF) process. The vacancies left in the inner shells following photoelectron emission are filled by electrons from the outer shells and the transitions are accompanied by emission of radiation corresponding to the energy difference between the two shells. The measurement of the characteristic energies of the emitted X-rays forms the basis for X-ray fluorescence spectroscopy (XRF). Since there is no X-ray analyser fitted to the ESCA-3 instrument the measurement of the spectra due to this radiation cannot be made. However the simultaneous measurement of XPS and XRF using VG (Scientific) MA500 instrument done in this research group has been reported [71].

3.1.2.2 CHEMICAL STATE INFORMATION

There are three methods normally used for the recognition of the chemical states of the surface atoms under XPS analysis. These are (a) shift in the peak positions of the main XPS spectra, (b) the presence of satellites to the main peak, and (c) the differential chemical shift in photo- and Auger- electron peaks. For the purpose
XPS Analysis using aluminium radiation

Figure 3.3 Wide-scan showing overlapping peaks.
of this work only the first two will be briefly mentioned.

3.1.2.2(a) CHEMICAL SHIFTS

The peak positions in most compounds differ from those in the parent elements. The loss in electron density around a cation has led to an increase in binding energy, of a few electron volt from the position found for its element. Anions show a corresponding decrease in the binding energy. It is this increase or decrease in the elemental binding energies which are known as the chemical shifts. The higher the valency of the cation or anion the larger will the shift be from its parent element peak. The shifts are sufficiently large to permit clear differentiation of the metal and oxide phases, and further differentiation of the chemical structure within the oxide phase is sometime possible. Figure 3.4 shows spectra of a stainless steel obtained by Castle and Clayton [72] indicating the chemical shifts to lower binding energy in the Cr and Fe 2p3/2 peaks during ion-beam profiling.

3.1.2.2(b) SATELLITE PEAKS

There are four types of satellite that can be observed in an XPS spectrum. The first type are those which arise from satellite radiation in the X-ray spectrum (Kα₂,₃) used to excite the photoelectron spectrum. They are normally observed at a binding energy of about 8.5 eV below the main photoelectron peak with a relative intensity of 10% for MgKα and at 9.5 eV below the main peak with a relative intensity of 6.15% for AlKα. They have no value in
Figure 3.4  Cr and Fe 2p3/2 peaks showing the shift to lower binding energy during ion-beam profiling.
chemical analysis. However, in our attempt to "peak-fit" the transition metals such as that of Cr 2p, the Kα3/4 satellite of the 2p1/2 state has to be subtracted from the 2p3/2 peak. A description giving more detail on how the Cr2p spectra are synthesised will be given and discussed in the next chapter.

The second type of satellites are called shake-up satellites. They are not widely found but are analytically useful in certain special cases [73]. For example such satellites are observed as a characteristic feature of the Cu(II)2p spectrum, but not found in Cu(I) compounds or in the metal [73]. Careful observations of the shake-up satellite fine structures have enabled McIntyre et al. [74] to distinguish Ni2+ in NiO and Ni(OH)2, Figure 3.5. A recent viewpoint believes that it is generated by a charge transfer into the empty 3d of metal state from surrounding oxygen ligands [75].

The third type of satellite are those arising from multiplet splitting [76]. They are widely found than the shake-up satellite and analytically much more useful for this investigation. Such satellites appear in the 2p spectrum of Ni(II) and Co(II) ions but are not prominent in either the metallic or other valence (e.g., Co(III) states, Figure 3.6). This makes the satellites useful in the analysis of XPS spectra in this investigation since nickel and cobalt are two elements normally found in the corrosion film on Inconel. It has also been pointed out by McIntyre et al. [77] that these satellites are useful in distinguishing between the divalent and spinel formation. However they are probably of no use when mixtures of FeO, Fe2O3, and Fe3O4 are present [78].
Figure 3.5 Distinction between NiO and Ni(OH)$_2$ by the careful observations of the shake-up satellite structures (74).
Figure 3.6 Ni and Co spectra showing the presence of satellites associated with Ni(II) and Co(II) ions.
The fourth type of satellites are termed plasmon loss peaks which arise when the emerging electron excites collective oscillations in the conduction electrons of solid and thus suffers a discrete energy loss. They are found on both photo- and Auger-electron peaks within the spectrum, but have little analytical value.

3.1.2.3 SENSITIVITY FACTORS

For a given instrument type and excitation source it is found that not all peaks in the kinetic energy, or binding energy, spectrum have the same height or, more correctly, the same area. In order to quantify the XPS spectra the area from the main peak of each element which is present on the surface has to be normalised by division with the appropriate sensitivity factor. The relative proportion of each element is then obtained as a proportion of the total normalised intensity.

Sensitivity factors are applicable only to a given instrument type and excitation source. They are determined experimentally by running standards, and their determinations form the basis of quantification in XPS. The intensity of an element, \( N_A \), is determined relative to the intensity of a reference element such as fluorine in a compound of known surface stoichiometry. In equation the sensitivity factor, \( F_A \), of an element \( A \) is given by

\[
\frac{N_A}{N_F} = F_A
\]  
(3.4)
where \( N_A \) = intensity of element A
\( N_F \) = intensity of the reference element F
\( n_A \) = stoichiometry of element A
\( n_F \) = stoichiometry of element F

Some early workers used peak heights as the initial measurement of the peak intensities [79,81]. The use of peak heights, although the simplest approach, is unreliable because it is difficult to take account of the effects of peak shift and broadening due to different valence states of an element may have. Apart from these problems, intensity is also lost from the peak by shake-up events (section 3.1.2.2(b)). In principle the use of peak areas may remove many of the problems associated with peak height measurements and has been adopted by many workers [79-84].

The sensitivity factors used throughout this work are those which are based on peak areas obtained from the analysis of standards in this research group some years ago [23,85a-85b]. These values are listed in Table 3.2, and they are similar to the determinations made by Jogensen and Berthou [79].

**Table 3.2 Sensitivity factors.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Sensitivity Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C 1s</td>
<td>0.27</td>
</tr>
<tr>
<td>O 1s</td>
<td>0.60</td>
</tr>
<tr>
<td>Cr 2p3/2</td>
<td>1.10</td>
</tr>
<tr>
<td>Fe 2p3/2</td>
<td>1.80</td>
</tr>
<tr>
<td>Co 2p3/2</td>
<td>2.10</td>
</tr>
<tr>
<td>Ni 2p3/2</td>
<td>1.70</td>
</tr>
<tr>
<td>Si 2p</td>
<td>0.22</td>
</tr>
</tbody>
</table>
3.1.3 ESCA EQUIPMENT

The instrument used in acquiring spectra from all specimens in this investigation is an ESCA-3 MK II X-ray photoelectron spectrometer of VG Scientific Limited, U.K. (Figure 3.7). It comprises two main chambers: preparation and analyser chambers isolated by a gate which could be open or shut by a linear drive mechanism. The specimen holder, with mounted specimens, can be introduced into the analyser chamber also by a linear drive mechanism. Both preparation and analyser chambers are designed with several ports to be used for special purposes. In the preparation chamber one may find an evaporator, a small furnace for heating specimens, and a mass spectrometer head. There are additional ports spared for other additions.

The analyser chamber is fitted with X-ray and electron sources, an ion gun for cleaning and etching specimens, a secondary electron detector, and a photoelectron analyser. It is made out of mu-metal in order to screen out the earth magnetic field. The high vacuum in both analyser and preparation chamber is obtained by using oil diffusion pumps fitted with cold traps. The vacuum levels in both chambers are monitored separately by two vacuum gauges and they are normally better than $10^{-8}$ Torr when the spectrometer is in operation.

The X-ray source is obtained from an X-ray gun fitted with a double anode, magnesium and aluminium, which can generate either MgKα or AlKα characteristic X-radiations. Normal maximum power is
Figure 3.7 Schematic diagram of ESCA 3 MARK II.
The facility for cleaning or etching specimens is provided by AG-2 ion gun housed in the analyser chamber. Argon gas taken from a pure-argon gas cylinder is passed over titanium granules in a small in-line furnace in order to purify it before it is fed into the gun chamber. The heating of the furnace is controlled by a rheostat. The gun is normally operated at an argon pressure of $10^{-6}$ Torr. The use of the ion gun is further discussed in section 3.2.

The most important feature in the ESCA 3 spectrometer is the photoelectron energy analyser. It is a hemispherical analyser (Figure 3.8) which has a constant energy or fixed transmission mode. During its operation a constant potential is applied across the analyser plates so that it acts as a filter to allow only electrons which have kinetic energy above the pass energy, $E_A$. Typical pass energy values available are 10, 20, 50, 100 and 200 eV. The variation in the full width at half maximum of Au 4f7/2 peak with the applied pass energy for different radiations in the VG ESCA3 instrument is shown in Figure 3.9 [82]. Electrons which pass the 'pass' energy potential are then retarded in a retarding field, $E_R$ before passing a variable entrance slits into the hemispherical sector of the analyser. In the hemispherical sector the electrons are constraint to travel in curved trajectory by potentials applied between the inner and the outer plates of the filter to reach a focus at the variable exit slit where a channeltron is mounted. The retarding field, $E_R$, is raised to a value chosen so that its sum with the pass energy, $E_A + E_R$, equals the kinetic energy at the

480W for MgKα and 1KW for AlKα.
Figure 3.8 Diagram of photoelectron analyser.
Figure 3.9 Variation of FWHM of Au 4f7/2 with analyser energy for different X-ray sources (82).
start of the region of the spectrum which it is desired to examine, and then raised in a stepwise movements through the range until the final point on the region is reached. Throughout this work the step potential was set at 0.2 eV for the narrow-scans and at 1.0 eV for the wide-scans. When the retarding field is applied in this way, the electron flux through the entrance slit is reduced in the ratio \( E_A/(E_A+E_R) \) or, if \( E_A \ll E_R \), approximately \( 1/E_A^{1/2} \). As a result of this, the characteristic collection efficiency rises steeply as kinetic energy falls [86]. The retarding field voltage is controlled by a ramp generator which may be driven by the controls on the ESCA or by the datasystem.

As mentioned earlier before entering the hemispherical sector and the channeltron the electrons have to pass through variable slits. The setting of the variable slits may also affect the resolution of the peak. This is because the resolution of the peak not only depends on the geometry of the hemispherical sector and the pass energy but also on the slit width, as given by the following equation:

\[
dE = \frac{WE_A}{2R} \tag{3.5}
\]

where \( dE \) = full width at half maximum height for peak in the spectrum,

\( w \) = slit width,

\( E \) = pass energy,

\( R \) = Mean radius of the hemispherical sector (10 cm).
For this investigation a pass energy of 50.0 eV and a slit width of 0.4 cm was used, giving a nominal resolution of 1.0 eV.

In ESCA-3 the X-rays originate approximately 20 mm from the sample and at 30° from the plane normal to the slit length. Although the illumination is assymmetric the effect on intensity was reported to be less than 0.5% for energies above the pass energy.

The datasystem used for controlling the ESCA-3 comprises a Digital Equipment Corporation (DEC) PDP8e computer with 12K words of memory. It is interfaced to the ESCA-3 through hardware provided by VG Datasystem Ltd. The software for data handling is also supplied by VG. The acquired data from the spectrometer were originally stored in magnetic tapes (old PDP8e), but since December, 1984 it is stored in discs. The acquired data can subsequently be manipulated at a visual display unit (VDU) attached to the system. Data can also be transferred to the University Prime computer for further handling especially for peak fitting and plotting.

Before data acquisition is started a few parameters have to be input. Scanning of the wide region was carried out over 1000-channel span at 0.2 sec per channel of 1.0 eV channel width. Normally at least three scans were made on the wide region. Strong lines were scanned with different span regions according to the elements required. Normally the scanning were made over 100-channel span for C1s, O1s, and Si2p, 120-channel span for Fe2p, 140-channel span for Co2p, and 150-channel span for Cr2p and Ni2p spectra. All
of these narrow region scans were made for a preset period of 0.2 sec at each channel of 0.2 eV width. The preset counting period at each channel will enable the total count to be summed up before the scan on the next channel is made. The acquisition will be stopped after the preset total number of scans or, more correctly, the scanning period, has been reached. For all scans which were made in this investigation pass energy of 50 eV was used.

3.1.4 XPS SPECTRA

As an illustration of certain typical features observed in XPS spectra, Figure 3.10 shows a broad or wide-scan spectrum obtained from an Inconel specimen irradiated with MgKα (1253.6 eV) X-rays. It is displayed over 1000 eV region, and various prominent photo- and Auger-electron peaks, of all elements found, are labelled according to their level of origin. Such a wide-scan is useful as a survey of all those elements which might be present in the surface under investigation.

Figure 3.11 shows a typical high resolution narrow-scan spectrum obtained about the approximate position of Cr 2p energy level from the same Inconel specimen and by using the same X-ray source. While wide-scan is useful in the determination of elements which might be present, the narrow scan is very much useful in the determination of the chemical states of each element. This is clearly shown by the splitting of the Cr 2p3/2 and Cr 2p1/2 peaks in Figure 3.11 which indicates the presence of the chromium trivalent state on the surface. In addition to the chemical state
THE SURFACE ANALYSIS LABORATORY.
University of Surrey.

Spectrum Number - IN2020.0        Date - SUN, 26 MAY 1985

XPS Analysis using magnesium radiation

Figure 3.10 A survey scan of the elements found.

Intensity (Counts.)

Binding Energy (eV.) x10^2

- C = c (XPS PEAKS)
- O = o (AUGER PEAKS)
- CR = y
- NI = z
- CO = +

X10^3

Intensity (Counts.)

Binding Energy (eV.) x10^2
Figure 3.11 A typical narrow-scan for Cr 2p showing the chemical shift.
information, the narrow-scans can also give the peak areas from which the elemental percentage can be calculated. There are two methods of obtaining the peak area, namely by subtraction using linear or S-shape backgrounds. These will be discussed in the next section.

3.1.5 DATA ANALYSIS

The acquired data can be analysed either by using the visual display unit (VDU) which is interfaced to the PDP8e or by using one of the terminals which has a direct access to the University Prime system.

3.1.5.1 PDP8e

The schematic diagram of the layout of the PDP8e with its peripherals is shown in Figure 3.12. It is not only interfaced to ESCA and Prime system but also to an X-Y plotter, a VDU, a teletype for controlling ESCA equipment, and to the most important feature: tapes/discs drive.

3.1.5.1(a) PEAK AREA

Throughout this work the VDU is used mainly for obtaining the intensity, or more correctly the peak area, of the prominent peak of each element. It is obtained by subtracting a linear background from the peak. In defining the background one only has, while displaying the spectrum on the VDU, to set the lower and upper
Figure 3.12 Layout of the PDP8e and peripherals.
binding energy limits of the background. The area under the defined straight line will be automatically subtracted from the area under the original peak by a single-key command. Figure 3.13 shows typical spectra before and after background subtraction. The area obtained after subtraction, together with the peak position, the maximum and minimum counts in the before-subtracted region, will be printed at the teletype. Using the relevant sensitivity factor the normalized area can be calculated for each element, from which the percentage may be obtained.

3.1.5.1(b) CURVE SYNTHESIS

The acquired spectrum usually consists of peaks from the metal and ionised states which are not clearly resolved due to Gaussian line broadening occurring within the spectrometer. In order to get the chemical information these peaks have to be resolved. A routine is provided in the PDP8e which enables the enhancement in resolution of the spectrum by the use of fast Fourier transforms to remove the broadening. However, this procedure is unsuitable for use when peak broadening occurs for other reasons, for example, owing to multiplet splitting in transition elements as has already been mentioned in section 3.1.2.2: the spectrum is always fitted with peaks of equal width which should not be the case. One way to overcome this difficulty is by using a curve synthesis which could assign different widths, positions and shapes for the peaks to be fitted into the spectrum. This is provided by a routine on the Prime.
Figure 3.13 Typical Cr spectra before (top) and after (bottom) the removal of the linear background.
3.1.5.2 **PR1ME**

3.1.5.2(a) **PEAK FITTING**

As has just been mentioned, one of the advantages of using PR1ME in analysing XPS data is its ability to synthesise the acquired spectrum into peaks with different widths, positions and shapes. The shape of the peak may be chosen from pure Gaussian to pure Lorentzian, or the mixture of the two. Details of this routine, how it works and what effects it has will be discussed in Chapter 4 in which a thorough investigation of its use on characterising spectra from chromium 2p states is carried out.

There are other facilities which are provided on PR1ME. Among these are peak-labelling (section 3.1.4), smoothing and baseline subtraction. All these are well documented in the Ph.D thesis by Richardson [56] to whom all credit should be given for establishing such facilities on PR1ME. For the purpose of this investigation and for comparison with that obtained from using PDP8E the baseline subtraction and smoothing will be briefly described.

3.1.5.2(b) **BACKGROUND SUBTRACTION ON PR1ME**

This method, based on that of Shirley [3], assumes that each photoelectron position is associated with a small constant background to lower energies at the photoelectron energy. In practice, the background at a photoelectron energy is obtained by multiplying the background count on the preset low kinetic energy
side of the peak by the sum of counts from this energy to the preset high kinetic energy end of the peak. The product is then divided by the total counts over the peak in the preset region. Thus the background intensity at any point is proportional to the area under the peak at higher kinetic energies and above the background. The area of the peak can then be calculated by subtracting the area under this S-shape background from the area under the overall peak. The plot of the before-subtraction peak and the background, the peak after subtraction or the background only can be obtained by spooling the processed data to the university CALCOMP drum-plotter. Figure 3.14 shows such plots obtained from a Cr 2p narrow-scan spectrum.

In addition to the baseline subtraction of the narrow-scan spectrum, the routine also enables subtraction on the wide-scan spectrum. This thus enables one to follow the rise in the background from the lowest to the highest binding energy limits in the spectrum. Figure 3.15 shows, for example, peaks from a wide-scan spectrum after the baseline subtraction, and the corresponding background. This feature is much more subjective in its use than when the same routine is used to subtract a background from a narrow scan. However the qualitative enhancement of the wide-scan frequently may be useful.

3.1.5.2(c) SMOOTHING

Generally it is better, in obtaining the chemical state information, to use the first hand spectra obtained by XPS. However, it is often required to extract the information from very
Figure 3.14  Typical Cr spectra before and after the removal of the 'S' shape background.
(a) The wide-scan spectrum obtained after complete removal of the background.

(b) The background used in obtaining the spectrum in (a).

Figure 3.15 The wide-scan background subtraction showing the resulting peaks and the background used.
weak signals, such as that of cobalt, and hence spectra smoothing would probably help. A routine is provided on Prime for such an operation which, in principle, operates on the basis of convoluting the data points with a set of integers, followed by normalisation [86b, 86c]. In practice, the operator only has to specify the interval (in an odd number, n) and the order, m (normally m = 3) of the polynomial, and the number of iteration, p. The rest of the operation will be carried out by the routine. Figure 3.16 shows a three time smoothed spectrum as of Figure 3.15 using 5-point and 3-order smoothing polynomial.

3.2 ION-SPUTTER ETCHING

The power of surface-sensitive techniques such as XPS is markedly increased by the ability to remove material from surfaces in a controlled manner so that the compositions underneath the outermost surface may be revealed layer by layer. Thus the distribution of composition with the depth of the oxide film may be followed, in addition to the chemical state information. For this reason, the coupling of ion etching or sputtering device to an X-ray photoelectron spectrometer has become widely adopted.

In principle ion sputtering techniques require sectioning of the sample and subsequent XPS analysis. By continuous sputtering, layers beneath the topmost layer are subsequently exposed. Compared with the AES, the XPS has a poorer spatial resolution. This means that high resolution depth profiles are only possible with the ion etching beams as uniform as possible over a large area of sample
contributing to the spectrum. Furthermore, in order to get the most benefit from the use of ion sputtering in relation to the quantification of the concentration gradients by XPS, one has to bear in mind several ion beam-induced effects which might arise.

3.2.1 EFFECTS OF ION SPUTTERING

3.2.1.1 PREFERENTIAL SPUTTERING

3.2.1.1(a) SPUTTERING OF ALLOYS

Under ion sputtering atoms are removed from the surface with different efficiencies [87,88]. The removable efficiency is more commonly termed as the sputtering yield which is defined as the total number of secondary particles sputtered per primary ion colliding with the solid surface. Carbon, for instance, has an order of magnitude lower sputtering yield than many metals such that a stoichiometric carbide will be enriched in carbon on sputtering [81]. The sputtering yields obtained by sputtering of pure elements with 0.5 kV argon ions beam have been reported by Wehner [89] and from his data those of steel forming elements can be arranged such that S(Ni)>S(Cr)>S(Fe)>S(Fe)>S(C). However, correction of Wehner data for oxygen contamination by Seah [81] shows that S(Cr)>S(Ni)>S(Fe)>S(Fe)>S(Fe)>S(C).

Ion sputtering of alloys has also shown a preferential removal of one component from the other due to the different sputtering yields of elements in the alloy [90-92]. As a result, the outer
surface will be depleted in component which has the highest sputtering yield. Such a depletion, however, may be significant only in the outermost atomic layers, since the removal of the preferred element eventually leads to a steady-state concentration where both elements are sputtered at a constant rate. The thickness affected by preferential sputtering, assuming diffusion induced by sputtering is low, has been calculated to be in the order of an atomic radius [92-93]. In using ion sputtering to obtain clean surfaces this effect is important since different compositions on the sputtered surface from those in the bulk may affect the oxides to be formed subsequently. The surface compositions after sputtering of a binary alloy A/B in relation to its bulk compositions has been modelled [92-94] and the following equation was derived:

\[
\frac{C_A}{C_B} = \frac{S_{B B}}{S_{A B}}
\]

(3.6)

where \( C_A, C_B \) = surface concentrations of element A and B,
\( B_A, B_B \) = bulk concentrations of element A and B,
\( S_A, S_B \) = sputtering yields of element A and B.

Many workers have observed that the ratio of the sputtering yields of different elements obtained from the sputtering of an alloy differs from that obtained from individual elements [91,95-96]. Anderson and Sigmund model's [97] predicts this as due to the matrix effects, in which the lighter element of a pair in a binary alloy will be preferentially sputtered. Thus, an 'A' atom
surrounded by 'A' atoms will behave differently from an 'A' atom in a 'B' lattice when impacted by a high energy ions beam.

Most of the measurements on the sputtering yields were made by using Auger electron spectroscopy. However, Storp and Holm [98] have reported the evidence of selective removal of chromium after prolonged ion bombardments on steel surfaces by using XPS. This was attributed to the higher sputtering yield of chromium and to the fact that chromium reacts preferentially with oxygen.

3.2.1.1(b) SPUTTERING RATES OF OXIDES

Measurements on the individual sputtering rates of Fe$_3$O$_4$, NiO, and Cr$_2$O$_3$ oxide films have been made by McIntyre and Zetaruk [99]. Under their sputtering conditions they found the sputtering rates of Fe$_3$O$_4$, NiO, and Cr$_2$O$_3$ were 4.0, 4.0 and 1.4 nm/min respectively. In their studies the possibility that ion bombardment of mixtures of Cr$_2$O$_3$ with the other oxides on oxidised Inconel surfaces could lead to preferential retention of the less rapidly removed Cr$_2$O$_3$ was also investigated. Sputtering of the intimate mixture of Cr$_2$O$_3$ and Fe$_3$O$_4$ was carried out and they found that Fe/Cr ratio remains constant which means the lower sputtering rate of Cr$_2$O$_3$ did not cause preferential removal of other oxides. They suggested that the removal rate of the oxide film on Inconel is probably limited by the Cr$_2$O$_3$ rate and that the oxide thickness can be determined from this.
3.2.1.2 **ION-BEAM INDUCED REACTIONS**

Another effect incurred in ion beam sputtering is that of chemical reactions induced by the beam. Types of reactions may be threefold: (a) due to beam or specimen contamination, (b) decomposition or reduction of oxide, and (c) recoil or knock-on reactions. These will be briefly discussed in this section.

3.2.1.2(a) **CONTAMINATION OF THE ETCHING GAS AND SPECIMEN**

Contamination of the etching gas, especially with oxygen, leads to interface broadening when profiling through oxides on metals. Generally the etching rate is reduced [100-101] which means the estimated film thickness becomes higher. This will also decrease the interface, or depth, resolution as etching proceeds. Another form of contamination which may be picked up by the ion beam is the traces of water vapour derived from the analyser vacuum system.

As has been indicated earlier carbon is also found to deposit from vacuum onto specimens undergoing XPS analysis. Under the action of ion beam it could react with other species on the surface to form some compounds. Such a reaction which leads to the formation of chromium carbide has been observed [102].
Ion bombardment of some oxides have been observed to result in the appearance of reduced oxides or metal on the surface \[98,103\]. Kim et al. \[103\], who first observed oxides decomposition by using XPS, found that the behaviour of oxides under ion bombardment is well predicted by the room temperature free energy of formation of the oxide, $\Delta G_f^O$. In their observation they found that all oxides with $-\Delta G_f^O$ below 60 kcal/mole were reduced while all those with $-\Delta G_f^O$ above 108 kcal/mole, except MoO$_3$ and Fe$_2$O$_3$, were stable under the exposure to ion beams. Kim et al used compact oxides in their investigations and among those which were categorized as stable oxides is SiO$_2$. Holm and Storp \[98\], bombarding thin SiO$_2$ film on Si with argon ions of 5 keV energy, observed that SiO$_2$ remains fairly stable only at a primary current density of 1 $\mu$A/cm but reduced to metal when the ion current density reaches 10 $\mu$A/cm or more. Their explanation for the dependency on the primary ion current density is that different recovery times are needed for restoration of the original state. Holm and Storp interpreted the lower limit of $-\Delta G_f^O$ values stated by Kim et al not as a limit in the sense that relatively stable bonds cannot be split by ion bombardment, but rather as a measure of the metal-oxygen affinity, above which the reoxidation processes take place so rapidly that, at a given ion current density, no reduction phenomena can be detected by XPS unless the oxygen is bound in some way.

Regarding the oxides and spinels of Inconel forming elements the existing evidences about their stability and decomposition under
argon ions bombardment will be reviewed.

$\text{Cr}_2\text{O}_3$ was observed to be fairly stable [99,103].

$\text{Fe}_2\text{O}_3$ has been observed by some workers to be reduced to Fe [99,104,105] although the investigation carried out in this research group showed that it is stable [106].

Kim et al. [103] did not observe the reduction of $\text{Ni(OH)}_2$ to NiO or Ni. However, a few workers observed a partial reduction of $\text{Ni(OH)}_2$ to NiO [98,104]. They attributed this to the dehydration of $\text{Ni(OH)}_2$ resulting from moderate heating of a few monolayers beneath the sputtered layer. While Kim et al. [103] did observe the reduction of NiO to Ni, McIntyre et al. [107] and Chuang et al. [105] did not.

Reduction of bulk $\text{Co(OH)}_2$ to CoO and bulk CoO to Co were observed by Chuang et al [105]. They also observed the reduction of $\text{Co}_2\text{O}_3$ to CoO.

Regarding the spinels, McIntyre et al [107] observed the reduction of magnetite ($\text{Fe}_3\text{O}_4$) to FeO, and Chuang et al [105] observed the appearance of Co and Fe(II) on $\text{CoFe}_2\text{O}_4$ on bombardment to ion beam.
3.2.1.2(c) RECOIL AND KNOCK-ON EFFECTS

Ion bombardment may also cause depth resolution loss when ions in the superficial layer are knocked or diffused into deeper layer. This effect which is known as knock-on process is directly dependent on the energy of the primary ions [108]. It has been shown [108] that for low energy ions atoms from one depth are pushed forward to greater depths in the order of 3 nm. One mechanism which has been shown to be responsible for significant motion of atoms in an ion-bombarded solid is a direct momentum transfer process in which an atom is driven deeper into the sample following a collision with an incident ion. This effect could play a vital role when, following the removal of thick oxide layer, the oxide-metal interface is reached. Oxygen, following decomposition of oxides, may be transported into the metal substrate and results in the formation of low valency oxides. As a consequence a sharp interface will be homogenized. This was the argument put forward by Holm and Storp [98] in explaining why they observed the reduction of thin SiO$_2$ film on Si substrate while Kim et al. [103] did not observed such a reduction on compact SiO$_2$ under ion bombardment.

3.2.1.3 OTHER EFFECTS

In addition to the effects cited above, there are a few other problems associated with the use of ion sputtering that could be briefly mentioned.
(a) Non-uniform surface erosion: This effect is due to the non-uniform flux of ions used in the sputtering.

(b) Surface roughness: Surface roughness of the ion sputtered target can be in the form of ridges, steps, cones, or facets. These are due to variation in etch rate from point to point on the surface.

(c) Shadowing effect: This effect arises from the different angles subtended at the sample by the ion gun and the analyser analytical system.

(d) Internal and grain boundary oxidation: This could be the result of oxygen implantation as mentioned earlier.

It is clear from the evidences gathered that sputter-etching process can cause several problems that any compositional profiling using ion sputtering in conjunction with X-ray photoelectron spectroscopy should be treated with extreme caution.

3.2.2 INSTRUMENTION AND ETCH CONDITIONS

The ion gun fitted to ESCA 3 (Figure 3.17) has the ability to generate ions with a variable energy from 0 to 10 keV to choose from. The ion beams can also be focussed by setting up the focussing voltage on the lens from 0 to 10 kV. Argon ions are used as the sputtering ions because an inert gas is less likely to interact chemically with the surface, and argon is readily
Figure 3.17 The AG2 Ion Gun
available. A small trace of oxygen which is normally found in the argon gas 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 x 10^{-6} Pa (10^{-6}\text{Tor}r). The pressure was maintained at this level during the etching period.

Research carried out by Richardson in this laboratory [56] showed that a fairly even etch could be obtained using 3 kV beam energy and 1.5 kV focus. In his investigation thick interference films produced by oxidising stainless steel specimens were etched with argon ion under different conditions. The etch rate and beam uniformity was judged from the changes in the interference colours. Figure 3.18 shows the resulting etched areas, reproduced from the investigation by Richardson [56], using the cited etching conditions. At these conditions the etch rate was estimated to be 1.5 nm/min. With reference to his investigation the same beam energy of 3.0 kV and 1.5 kV focus has been adopted in the etching of all Inconel specimens in this work.

3.2.3 DEPTH PROFILE

Figure 3.19 shows an example of the depth profile which was obtained from a sample exposed to pure water at 473K for 4 hours. In the presentations the elemental distributions are obtained as a function of elapsed etching time. Ion etching (energy = 3 keV, focus = 1.5 kV) was carried out for a fixed time intervals and the ion-sputtered surface was analysed subsequently by XPS scans of the principle peaks, i.e. C1s, O1s, Cr2p, Fe2p and Ni2p. The peak area
Figure 3.1B Uniformity of 3 kV etch on stainless steel specimen [56].
Figure 3.19 Etch profiles for Inconel exposed at 473 K for 4 hours to pure water.
for each element was determined by using straight line background 
(section 3.1.4.1). The peak area data were then corrected for 
relative core-level sensitivities using the sensitivity factors 
which have been listed in Table 3.3, section 3.1.2.3. The 
normalized area were then ratioed to give atomic percentages for 
each element, a, in the sample according to the general 
relationship:

\[
\text{Atomic } \% \text{ of element } a = \frac{N_a / F_a}{\sum_i N_i / F_i}
\]  

(3.7)

where \( N_i \) is the peak area of the principle peak of element \( i \) and \( F_i \) is its corresponding sensitivity factor.

There are two forms of representing the depth profile. In the 
first representation the y-axis of the plot represents the actual 
atomic percentage of an element at a given point corresponding to an 
etch step, Figure 3.19(a). In this presentation, referred to as a 
non-cumulative profile, one may follow at a glance the variation in 
the atomic percentage of a particular element in the oxide film as a 
function of etch time although a little difficulty may arise when 
there are curves close to each other. This difficulty may be 
overcome by plotting the variation via another form of presentation, 
which is referred to as a cumulative profile. This form of 
presentation was originally suggested by Coad and Cunningham [109] 
and has been adopted to be used in this research group and others 
[28,100]. In the representation the atomic percentage of an element 
is assigned by the width of the shaded area at that particular etch
step, Figure 3.19(b); thus the total shaded area will be 100%.

For the purpose of this investigation normally both ways of presenting the depth profile of the oxide film are adopted. Further more, as Figures 3.19(a) and (b) show, the atomic percentage of carbon is not included. The exclusion of carbon is also adopted in presenting most of the depth profiles in this work unless for a specific reason. Carbon always exist on the unetched specimen. This could be due to the contamination from the laboratory air during the transfer from the corrosion cell into the desiccator, during storage in the desiccator and during transfer into the spectrometer of the specimen. It may also arises from the organic material in the water used for the corrosion test [23,85a-b]. It was shown [23,85a-b] to be loosely bound carbon on the surface for it was reduced as the specimen was etched lightly, e.g. 15 sec etch. Another reason for the exclusion of carbon is that it was shown to appear on the surface, normally >30%, even when the metal-substrate interface had been reached. This could be due to the hydrocarbon contamination from the vacuum system [63]. The situation is made worse as one specimen investigated by ion etching technique normally takes not less than two days for the sputtering and data acquisition.
4.1 INTRODUCTION

One of the usefulnesses of the XPS in dealing with corrosion studies is its ability to provide the chemical information of species on the surface under investigation. In interpreting and analysing the electron peaks produced by the interaction of the incoming photons and the electrons at a specific energy state one is also usually interested in the areas associated with the peaks. It is necessary in interpreting these peaks to take into account the electrons which are inelastically scattered during its passage from the point of excitation to the surface of the metal. These electrons register different energies from the elastically scattered ones and thus produce a low kinetic energy background, or in our presentation at higher binding energy region, overlapping with the main peak. The effect could be more pronounced if one attempts to synthesise X-ray photoelectron spectra peaks of transition metals which normally have two peaks very close to each other resulting from two different spin states of the same orbital energy. The broad continuum of loss structure, on which the discrete loss sit, has generally been regarded as a nuisance, to be subtracted from the true peak by whatever method can best be justified. For most group of workers this is interpreted as subtracting a Shirley background [3] which can be fitted assymptotically to the level background
either side of the peak, Figure 4.1. This has the advantage that
the peak area is not sensitive to the start and end position of the
subtraction and, perhaps for this reason more than any other, is
widely used [56].

A difficulty also arises for those specimens which include two
or more chemical states distributed in a layer-like fashion. The
energy loss background from the pure metal may overlap with the main
peak of the oxidised metal due to the relatively wide energy range
of the energy loss electrons emitted. Clearly a Shirley background
gives equal weight to both chemical states within the total peak
envelope whereas common sense suggests that the superficial layer
should have a less pronounced energy loss structure than the
substrate; because the distance travelled by electrons in the
superficial phase is necessarily limited whereas that in the
substrate not. A method of curve fitting was therefore sought which
would enable the energy loss feature of each peak component to be
handled separately and in this chapter will be shown that this then
enables the continuum spectrum to have a useful purpose.

The spectra of greatest challenge are those of the transition
elements because of their importance in Inconel. Of these chromium
is particularly important. In this chapter therefore results
obtained with the chromium 2p doublet from clean, oxidised and
overlayer deposited chromium surfaces which had been 'curve-fitted'
up to a few electron volts above the 2p3/2 peak will be described.
The purpose is no more than to investigate experimentally the
effects of the presence of the superficial oxide or a material
(a) Negligible difference between two 'S' shaped backgrounds.

(b) Significant difference between two straight line backgrounds.

Figure 4.1 Comparison of background subtraction routines (56).
deposit, on a clean chromium surface, on the energy loss background of the individual components in the Cr 2p peaks. This then, could probably complement the usual way of obtaining quantitatively the distribution of the chemical composition of a surface with depth from the X-ray photoelectron spectra.

4.2 DATA ACQUISITION AND ANALYSIS

X-ray photoelectron spectra of the surfaces were recorded using the ESCA-3 spectrometer of VG Scientific Ltd., U.K., fitted with the preparation chamber and analyser chamber as has been described in detail in section 3.1.3. During the data acquisition the base vacuum of the analyser chamber was around $7 \times 10^{-10}$ Torr and the radiation used for the electron excitation was MgKα (1253.6eV). A pass energy of 50 eV was used in this work in order to obtain good signal to noise ratio [81]. This would give the Au 4f7/2 spectrum a full width at half maximum (FWHM) of 1.8 eV [110].

Analysis of the spectrum was carried out using the Prime terminal located in the ESCA laboratory.

4.3 PEAK FITTING ON PRIME

4.3.1 PEAK FITTING ROUTINE

The program GAMET which has been used for peak fitting in this work was obtained from P. Sherwood of Newcastle University. It was originally developed by C. Laderer at UCLCBL and modified by Baird
at Hawaii University. It has been further modified for the present purposes by Richardson [56] and is run on the Prime 550 computer at this university.

Briefly, the curve fitting provided by this routine is accomplished using a nonlinear least square method. A Gaussian-Lorentzian function is included for defining the shapes of peaks which are to be assigned to the original spectrum envelope. This enables one to choose the shape of the peaks from pure Gaussian to pure Lorentzian. In addition, each peak is associated with appropriate satellite peaks due to the unmonochromatized Mg Kα X-radiation. This is particularly essential for this work as the satellites of the Cr 2p1/2 components occur under the Cr 2p3/2 envelope. Another feature which is provided is the choice of the background tail following every predefined peak. The tail can be fixed to be constant, exponential or the mixture of the two. The baseline slope and intercept can be fixed or left free to be calculated by the program. This enables the variation of the background of each component in the spectrum envelope with the thickness of superficial layer to be followed.

Other parameters associated with each peak that can be fixed or left free are the position, the full width at half maximum, the intensity, its ratio to and separation from other peaks in the spectrum.

Once peaks have been assigned, the program will calculate all the peaks iteratively and fit them to the measured spectrum. The
calculations will be terminated either, a) after all input parameters have been fitted to the best fit, or b) after the maximum preset number of iterations, which is 25, has been reached. The calculated spectrum, which is built as an integral of all fitted peaks and their tails, will be matched to the measured spectrum. The quality of the fit is determined by the value of $\chi^2$ (chi-squared), which is given by

$$\chi^2(\text{calc}) = \sum_{i=1}^{n} \frac{[y_i^{\text{(meas)}} - y_i^{\text{(calc)}}]^2}{y_i^{\text{(calc)}}} \quad (4.1)$$

where $y^{\text{(meas)}}$ is the experimental count rate, $y^{\text{(calc)}}$ the curve fitted count rate and $n$ the number of points in the fitted region of the spectrum.

4.3.2 INPUT FILE

Before the fitting program could be run an input data file has to be prepared. The facility is provided by which through an interactive process a few parameters can be input, fixed or left free, to be fitted later by the routine. This as well will include the raw data recorded by the spectrometer. After the input data file has been set up the input file can still be accessed in order to modify the value of or the constraint on any parameter before it is read into the fitting routine.
4.3.3 OUTPUT FILE

The statistics of the fitted spectrum are output in a file called GOUT.xx where xx represents the code for the terminal used in the fitting process. The file can be accessed in order to obtain whatever fitted parameter that may be needed either by editing the file or by obtaining the hardcopy of it immediately after the fitting process is completed. The plot, which includes a selected number of fitted parameters, such as peaks positions, widths, areas and percentages, of the fitted spectrum is kept in a plotfile called PLOT.xx the hardcopy of which can be obtained by spooling the plotfile to the university CALCQMP drum-plotter or by plotting it using the Hewlett Packard plotter located alongside the terminal.

4.3.4 PEAK FITTING OF CHROMIUM 2P AND ENERGY LOSS BACKGROUND

Using the program described earlier peak fitting of chromium 2p doublet is carried out over a 20 eV region. This range includes the 2p1/2 peaks solely in order that their \( K \sigma_3,4 \) satellites (section 3.1.2.2(b)) can be included as components of known position and intensity in the fitting routine for the 2p3/2 peak. The iteration used peaks of Gaussian shape to which had been added a tail of constant intensity. Two sets of fitting parameters were tried in the process: firstly by fixing only the oxide component width at 3.08 eV and leaving the other parameters free, and secondly, by fixing the metal width at 2.15 eV, oxide width at 3.08 eV, the separation of the 2p3/2 and 2p1/2 components of both metal and oxide features at certain values, and the gradient of the
background slope to zero. By use of a tail of constant intensity on each component peak there is no need to subtract background: this is a built up as the sum of the energy loss tails included in each individual peak of the fitting set. As has been mentioned earlier, the quality of match between the envelope constructed and the acquired data is determined by the chi-square value available from the program. This is brought to a minimum as the tail intensity, which will be referred to as the energy loss background height (ELTH), was varied systematically for both metal and oxide peak components. As an example, the manner in which the degree of the fit \( \chi^2 \) varies with the chosen metal and oxide tail heights is illustrated in Figure 4.2. In the final step of the analysis a Shirley function [3], as has been described in section 3.1.5.2(b), is used to strip the background tail from each individual peak. Thus the peak intensities and the loss intensity can be quoted for each chemical state.

4.4 Phase Distribution

Knowing the peak intensity of the individual chemical state on the surface the thickness of the superficial layer on the chromium surface can be calculated approximately. For this purpose, the general intensity which could be observed from a surface with different phase distribution [111] will be reviewed. To have a direct application to the present work all of the formulation will be referred to the chromium substrate with superficial oxide and overlayer deposit or contaminant.
Figure 4.2 Variation of the chi-square with energy loss background height.
The intensity observed from a chromium metal substrate in the presence of a reaction product of thickness $d_{ox}$ is given by the relationship

$$I^{(1)}_{Cr(0)} = I^{0}_{Cr(0)} \exp\left(\frac{-d_{ox}}{\lambda(E) \sin \theta}\right)$$  \hspace{1cm} (4.2)

where $I^{0}_{Cr(0)}$ is the intensity of the metal substrate when in a clean condition, $\lambda(E)$ is the mean free path of the electron from substrate and $\theta$ is the take off angle.

The intensity of the reaction product, $I^{(1)}_{Cr(III)}$ of thickness $d_{ox}$ is given by

$$I^{(1)}_{Cr(III)} = I^{0}_{Cr(III)} \left[1 - \exp\left(\frac{-d_{ox}}{\lambda(E') \sin \theta}\right)\right]$$  \hspace{1cm} (4.3)

where $I^{0}_{Cr(III)}$ is the intensity from a thick reaction product, and $\lambda(E')$ is the inelastic mean free path of the electron from the superficial layer.

Provided the standard values are known, either equation (4.2) or (4.3) may be solved for the thickness of superficial laminar material, which, in our case could be that of chromium oxide.
If the surface which has already have a superficial oxide of thickness \( d_{ox} \) is further covered by an overlayer, e.g., a titanium deposit or contamination carbon, of thickness \( d_d \), the intensity of the chromium metal signal will then be given by

\[
I^{(2)}_{Cr(0)} = I^{0}_{Cr(0)} \exp\left(\frac{-d_{ox} - d_d}{\lambda(E) \sin \theta}\right)
\]  

(4.4)

while that of chromium oxide will be given by the relationship

\[
I^{(2)}_{Cr(III)} = I^{0}_{Cr(III)} \left\{ \exp\left(\frac{-d_d}{\lambda(E') \sin \theta}\right) - \exp\left(\frac{-d_d - d_{ox}}{\lambda(E') \sin \theta}\right) \right\}
\]  

(4.5)

By combining equation (4.2) and (4.4) and provided that the intensity of the substrate signal before and after deposition of the overlayer material are known, the thickness \( d_d \) of the overlayer deposit can be obtained using the relationship

\[
\frac{I^{(2)}_{Cr(0)}}{I^{(1)}_{Cr(0)}} = \exp\left(\frac{-d_d}{\lambda(E) \sin \theta}\right)
\]  

(4.6)

The thickness obtained by equation (4.6) can always be checked using the intensity ratio of the superficial signals, i.e., that of the oxide layer, which is given by

\[
\frac{I^{(2)}_{Cr(III)}}{I^{(1)}_{Cr(III)}} = \exp\left(\frac{-d_d}{\lambda(E') \sin \theta}\right)
\]  

(4.7)
4.5 SPECIMEN PREPARATION

4.5.1 CLEAN CHROMIUM

A flat chromium surface was obtained by polishing a pure 0.8 cm x 1.0 cm chromium specimen to one micron finish with diamond paste and was then degreased in acetone. It was then cleaned by etching with the argon ion in the analyser chamber of the spectrometer in order to remove some oxide left on the surface after polishing. The energy of the bombarding ion was 3.0 kV at focusing voltage of 1.5 kV. Before etching the argon gas was let into the analyser chamber to give a pressure of $10^{-6}$ Torr as has been described in section 3.2.2.

4.5.2 OXIDISED CHROMIUM

Oxidised chromium surfaces were obtained by two methods. In the first method an ion cleaned chromium surface was oxidised by bleeding pure oxygen, taken from a flask mounted on the preparation chamber, into the spectrometer at room temperature. The oxidation was monitored in Langmuirs (1 Langmuir (L) = $10^{-6}$ Torr.s). In the second method an ion cleaned specimen was exposed to air in a tube desiccator for ten days.

4.5.3 ALUMINIUM EVAPORATION

In order to investigate the effect of different thickness of overlayer on the energy loss background of the chromium 2p spectrum
attempts were made to deposit thin layer of aluminium on a clean chromium surface. Aluminium was chosen as the depositing material because Al 2p photoelectron peaks occur at the binding energies far below those of chromium 2p peaks, and hence, no interference of its background on the chromium peaks is anticipated.

The first attempt to evaporate aluminium on clean chromium surface was carried out in the analyser chamber of the X-ray spectrometer. An evaporator with a long nozzle of half a centimeter diameter was mounted in the chamber. The evaporation material was made by placing a small piece of pure aluminium wire in the helix of the tungsten filament of the evaporator. The chromium was first cleaned by ion etching and then positioned against the evaporator nozzle hole. The current passing through the evaporator filament was switched on and increased gradually to a certain maximum value and maintained at that value for a period of time. At the same time the vacuum level of the analyser chamber was monitored in order to ensure some aluminium was being evaporated. During evaporation the pressure rose to $10^{-8}$ Torr but fell immediately after evaporation to $10^{-9}$.

There were some disadvantages to having the evaporation in the analyser chamber:

(1) a longer time would be needed to pump down the analyser chamber to a reasonable vacuum for analysis when the filament needs recharging with new evaporation material,
(2) there is a difficulty in positioning the specimen to be exactly against the nozzle hole when the evaporator was mounted in the analyser chamber,

(3) there is uncertainty that the detection was really made on the deposited area because of the very small area of the deposition region as a result of using a small hole nozzle.

For these reasons the evaporator was transferred to the preparation chamber, and its long nozzle removed, for the later attempts. The same evaporation procedure was then followed as before.

4.5.4 TITANIUM EVAPORATION

There were further problems in the use of aluminium as an overlayer material:

(1) the melting aluminium made the filament more brittle and caused it to break frequently,

(2) a series of chromium surfaces with different aluminium overlayer thicknesses could not be obtained because of the interruptions mentioned in (1),

and (3) the tenaceous oxide makes evaporation difficult.

Attempts were made to evaporate titanium, instead of aluminium, onto chromium. Titanium has the same advantage as aluminium as the
depositing material i.e. that Ti 2p peaks are well separated from those of chromium such that the background arising from these peaks is anticipated not to interfere with the chromium 2p peaks to be analysed. In these attempts, the tungsten was replaced with a titanium wire of 0.1 cm diameter, with an advantage that the depositing material came directly from the filament itself. The same procedure was then followed as in the aluminium evaporation but higher filament currents were used to make the deposition more successful. A current higher than 30A, but always less than 45A, was used at different evaporation periods. The vacuum level of the spectrometer preparation chamber during evaporation was about 10^-7 Torr.

4.6 RESULTS

4.6.1 CLEAN CHROMIUM

Figure 4.3 shows a typical wide scan obtained from a very clean chromium surface and Figure 4.4 shows the corresponding peaks after background subtraction from the same spectrum. A piece of information which is thought to be useful that can be obtained from the peaks-only spectrum such as that shown in Figure 4.4 is the pronounced appearance of the plasmon peaks, with decaying tails, on the high binding energy side of the photoelectron peaks of the chromium. This is a characteristic which is often observed whenever chromium is present as a clean surface.
Figure 4.3 A typical wide-scan of a clean chromium surface.

Figure 4.4 A typical spectrum obtained by subtracting the 'Shirley' background from the wide-scan in Figure 4.3.
The chromium spectra obtained from clean chromium surfaces with wide scans as that in Figure 4.3 were fitted using the routine mentioned in section 4.4. The difficulty to get a very clean chromium without a monolayer of chromium oxide left on the surface made the fitting with only one singlet in each state of the Cr 2p spectrum yield a poor quality fit as shown in Figure 4.5. Apparently it is clear that one peak per spin state does not adequately describe the peak envelope. Thus a set of two Cr 2p spectra from clean chromium surfaces were fitted by the inclusion of a second component in each spin state. The second component is attributed to the presence of superficial oxide of a monolayer thickness. Results confirming the presence of surface oxide on clean chromium will be given in section 4.6.1.1.

Results of four-peak fitting of the Cr 2p spectra are shown in Table 4.1. The range of the fitted region was fixed between 566 to 589 eV in CR.1, and, between 568 to 588 in CR.2. Results in the table were obtained with the width of the oxide component fixed to 3.08 eV in accordance with the value observed previously [85b], for each pair of the metal and oxide energy loss tail heights (ELTH). The metal width and the positions of both metal and oxide components as well as the slope of the background baseline were all left free. It seems that the metal width slightly varies from 2.10 to 2.14 eV for CR.1, and 2.04 to 2.05 eV for CR.2. The binding energy of the metal component for the CR 2p3/2 of all spectra is apparently at the same position, i.e at 573.0 eV, but that of the oxide component seems to vary from 1.6 to 2.0 eV for CR.1, and from 1.4 to 1.5 eV for CR.2 above the metal component binding energy in each spectrum. The
Figure 4.5 Chromium 2p spectrum fitted with two peaks showing the requirement for other peaks.
Table 4.1 Four-peak fits using sloping backgrounds of chromium 2p spectra of clean chromium surfaces.

(a) Spectrum CR.1

<table>
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<tr>
<th>Metal ELTH (%)</th>
<th>Oxide ELTH (%)</th>
<th>Metal FWHM (eV)</th>
<th>Metal B.E. (eV)</th>
<th>Oxide FWHM (eV)</th>
<th>Oxide B.E. (eV)</th>
<th>Metal Sep. (eV)</th>
<th>Oxide Sep. (eV)</th>
<th>Metal 3/2:1/2 ratio</th>
<th>Oxide 3/2:1/2 ratio</th>
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(b) Spectrum CR.2

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<th>Oxide ELTH (%)</th>
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<th>Metal B.E. (eV)</th>
<th>Oxide FWHM (eV)</th>
<th>Oxide B.E. (eV)</th>
<th>Metal Sep. (eV)</th>
<th>Oxide Sep. (eV)</th>
<th>Metal 3/2:1/2 ratio</th>
<th>Oxide 3/2:1/2 ratio</th>
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<td>3.00</td>
<td>1.40</td>
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separations between the metal and oxide components of the 2p3/2 state and those of 2p1/2 also appeared to vary. The metal components separation varies from 9.1 to 9.2 eV for CR.1 and from 9.1 to 9.2 eV for CR.2. For the oxide component the separations are from 8.7 to 9.2 eV for CR.1 and 8.6 to 8.7 eV for CR.2. Metal 2p3/2 to metal 2p1/2 and oxide 2p3/2 to oxide 2p1/2 intensity ratios do not seem to give two to one ratio but rather vary and these are clearly shown in Table 4.1.

Another observation which should be mentioned is the variation in the value of the chi-square at a specific ELTH of the metal component as the ELTH of the oxide component is varied. For CR.1 the chi-square value seems to become smaller, indicating a better quality of the fit, as the ELTH of the oxide component of the oxide component is reduced from 15% to 5% and 0.1% when the ELTH of the metal component is at 30% and 25% respectively. The best fit seems to be given by 25% metal and 0.1% oxide ELTHs pairs. The fitted spectrum for CR.1 is shown in Figure 4.6(a). The same trend is also observed for CR.2. The best fit, indicated by the smallest chi-square value, for CR.2 is given by the pair 25% metal_0.1% oxide. The best fitted spectrum of CR.2 is shown in Figure 4.6(b). Calculation by percentage ratio gives the oxide thickness of 0.26 nm on the specimen represented by CR.1 and 0.27 nm on that represented by CR.2.

Having succeeded in obtaining good fits with only the oxide width fixed, the attempt was made to fix a few more parameters in the program. It was started by fixing the metal and oxide ELTH pair.
(a) Spectrum CR.1 fitted by using 25% metal; 0.1% oxide energy loss tail heights.

(b) Spectrum CR.2 fitted by using 25% metal; 0.1% oxide energy loss tail heights.

Figure 4.6 Spectra of Cr 2p for clean chromium surfaces fitted with four peaks using sloping backgrounds.
at the values which give the best fit for each spectrum in the last results. Another parameter which was expected to play an important role in determining the effect of the ELTH is the slope of the baseline of the spectrum. In this second attempt the slopes of the background of the fitted spectra were fixed at zero while its intercepts with the intensity axis were left free. Table 4.2 shows the results obtained by fixing the metal width, the separation between metal 2p3/2 and 2p1/2 components, the separation between the oxide 2p3/2 and 2p1/2 components, and oxide width at 2.15 eV, 9.2 eV, 9.2 eV and 3.08 eV, respectively, for both spectra CR.1 and CR.2. It seems that by setting the ELTH of the oxide component to the smallest value, i.e. 0.1% of the oxide main peak height, the best quality fit is obtained with the ELTH of the metal component at 29% and 26% for CR.1 and CR.2 respectively. Figure 4.7 shows the best fitted spectra of CR.1 and CR.2 by imposing constraints on the mentioned parameters. Calculation by percentage ratio shows that the thickness of surface oxide is 0.26 nm on both samples. This is in agreement with the value calculated earlier.

From the peak fittings of the CR.1 and CR.2 spectra it appears that a superficial layer of about 0.2 nm thickness, or approximately a monolayer, on a chromium sample is not thick enough to give an energy loss background of the oxide component in the chromium 2p spectrum.
Table 4.2  Four-peak fits using constant backgrounds of chromium 2p of clean chromium no. 1.

Fixed parameters:

Metal FWHM = 2.15 eV.

Oxide FWHM = 3.08 eV.

Cr 2p3/2 and 2p1/2 peaks separation = 9.2 eV.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>Metal ELTH (%)</th>
<th>Oxide ELTH (%)</th>
<th>Metal B.E. (eV)</th>
<th>Oxide B.E. (eV)</th>
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(a) Spectrum CR.1 fitted by using 29% metal; 0.1% oxide energy loss tail heights.

(b) Spectrum CR.2 fitted by using 26% metal; 0.1% oxide energy loss tail heights.

Figure 4.7 Spectra of Cr 2p for clean chromium surfaces fitted with four peaks using horizontal constant intensity backgrounds.
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4.6.1.1 ANGULAR WORK

In order to show that the second component of the chromium spectrum is a surface rather than a bulk feature the spectra of a very clean chromium surface were obtained at the take off angle of 25° and 55°. The spectra were fitted by fixing the oxide and metal widths at 3.08 and 2.15 eV respectively with a zero gradient background slope. Figure 4.8 shows the best fitted spectrum obtained at each take off angle. The fitted spectra clearly show a higher oxide to metal ratio on the 25° spectrum compared with the one at 55°. This indicates the existence of a surface feature on a clean chromium surface which is attributed to the surface oxide of chromium. The spectra also show the increase in the ELTH for both components in which for the metal component it increases from 25 to 30% and for the oxide from 0.1 to 18%.

To have a better understanding on the behaviour of the energy loss background of the oxide component on the increasing oxide thickness on a chromium surface a thin and thick layer of oxide films were developed on clean chromium surfaces. The results obtained from the peak synthesis of these spectra are given in the next two sections.

4.6.2 THIN OXIDE LAYER

One sample was ion cleaned and exposed to 40L oxygen. The spectra were very similar to the previous set and results of fitting for this sample are shown in Table 4.3(a) in which only the oxide
Figure 4.8 Spectra of Cr 2p obtained at 25° (top) and at 55° (bottom) take-off angles showing the presence of a surface component.
Table 4.3(a) Fits of Cr 2p spectrum using sloping backgrounds of chromium exposed to 40 L oxygen.

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<th>Metal ELTH (%)</th>
<th>Oxide ELTH (%)</th>
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<th>Metal B.E. (eV)</th>
<th>Oxide B.E. (eV)</th>
<th>Oxide B.E. (eV)</th>
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width was fixed at 3.08 eV. Again the quality of fit consistently improves as the tail height of the oxide component is reduced to zero with the metal tail height at 25%. The spectrum is shown in Figure 4.9(a). The thickness of the oxide film was calculated to be 0.33 nm.

Results obtained by fixing the metal width at 2.15 eV, the separation between the 3/2 and 1/2 peaks at 9.2 eV for both components and the slope of the background to zero are shown in Table 4.3(b). The best quality of fit at these conditions is given by 28% of metal and 0.1% of oxide tail heights, Figure 4.9(b). The oxide thickness was calculated to be 0.31 nm using the results at these fitting conditions. The thickness of the oxide seems to increase approximately 15% from the clean samples but still - two monolayer thick. Thus it appears that an oxide film of a couple of monolayers thickness is not enough to contribute to the energy loss background of the oxide component, and that the metal tail height is always maintained at or lower than 30%.

4.6.3 THICK OXIDE LAYER

Table 4.4 shows the results obtained from the peak fitting of the Cr 2p spectra of the chromium surface with thicker overlayer chromium oxide films. CRO.1 is the spectrum obtained from the specimen which was exposed in 1800L oxygen in the analyser chamber of the spectrometer while the CRO.2 is that obtained from specimen exposed at the atmospheric pressure in a glass tube desiccator for about ten days. Again, both spectra were fitted with four singlets,
(a) Fitted with four peaks using sloping backgrounds.

(b) Fitted with four peaks using horizontal backgrounds.

Figure 4.9 Spectra of Cr 2p obtained from chromium exposed to 40L oxygen showing negligible oxide tail heights.
Table 4.3(b) Fits of Cr 2p spectrum using constant intensity backgrounds of chromium exposed to 40 L oxygen.

Fixed parameters:

Metal FWHM = 2.15 eV.
Oxide FWHM = 3.08 eV.
Cr 2p3/2 and 2p1/2 peaks separation = 9.2 eV.

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Table 4.4 Four-peak fits using sloping backgrounds of Cr 2p spectra of chromium covered with thick oxides.

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two in each energy state. The results presented in Table 4.4 were obtained by fixing only the width of the oxide component for both spectra at 3.08 eV as was in the fitting of the Cr 2p spectra from clean chromium surfaces. Assuming our initial suggestion, that the ELTH due to electrons coming from the chromium substrate is always higher than that from the chromium oxide overlayer is correct, the fitting was carried out in such a way that the ELTH of the oxide component was always set equal or smaller than the ELTH of the metal component. The variation in the chi-square value was followed as the ELTH of the metal component was varied to a higher value at a fixed value of the ELTH of the oxide component. From Table 4.4 it seems that as the ELTH of the metal component increases at a certain value of the ELTH of the oxide component the chi-square value becomes smaller. It seems that this trend is followed in both spectra. For CR0.1 the best quality fit was given by the pair 30$ metal_20$ oxide ELTHs with the chi-square value of 364 while for CR0.2 it was given by 30$ metal_25$ oxide with the chi-square value of 123. The fitted spectra are shown in Figure 4.10. It also appears that by having a slightly higher proportion of oxide on the surface, represented by CR0.2, the fitted spectrum seems to give a slightly smaller value of the metal component width and higher value of the metal 2p3/2_metal 2p1/2 and oxide 2p3/2_oxide 2p1/2 separations when these are compared with the values fitted for the spectrum from surface with slightly less oxide, CR0.1. For both spectra the oxide 2p3/2_ oxide 2p1/2 separation are always higher than that of the metal 2p3/2_metal 2p1/2 components, but the metal 2p3/2 and oxide 2p3/2 separation seems to be maintained between 2.3 to 2.4 eV. The intensity ratio of the 2p3/2 metal peak area to that
(a) Fitted using 30% metal; 20% oxide tail heights.

(b) Fitted using 30% metal; 25% oxide tail height.

Figure 4.10 Spectra of Cr 2p obtained from chromium exposed to 1800L oxygen (top) and atmosphere (bottom); fitted with four peaks using sloping backgrounds.
of the 2p1/2 component varies between 2.36 and 2.54, while that of the oxide components varies between 1.93 and 2.16. This again shows a disagreement with the 2:1 ratio calculated theoretically. The thickness of oxide film was calculated to be 0.68 nm on CRO.1 and 1.33 nm on CRO.2.

By following the same fitting procedure, using a horizontal baseline, as used in section 4.5.1 for clean metal, the spectra CRO.1 and CRO.2 were refitted. The metal width, oxide width, metal 2p3/2_metal 2p1/2 separation and oxide 2p3/2_oxide 2p1/2 separation were fixed respectively at 2.15, 3.08, 9.4 and 9.8 eV for both spectra. Results from the refitting of CRO.1 and CRO.2 are presented in Table 4.5. It appears that the best quality fit for CRO.1 is given by setting the metal and oxide ELTH to 30% and 24% respectively while for CRO.2 it is given by 30% metal_27% oxide ELTHs. The best fitted spectra for CRO.1 and CRO.2 are shown in Figure 4.11. It seems that by forcing the baseline of the background to be horizontal the ELTH of the oxide increases to 24% and to 27% for CRO.1 and CRO.2 respectively. The ELTH of the metal component in each spectrum remains at the same value as that obtained from the fitting with sloping baseline; with a very small increase from that set for the spectra of clean chromium surfaces.

The results obtained from the fitting of spectra of oxidised chromium surfaces seem to show an increase in the ELTHs of both metal and oxide components from those obtained a) from surfaces which are very clean, or, b) from surfaces with superficial oxide film of a monolayer thickness. In addition, the oxide tail height
Table 4.5 Fits using constant intensity backgrounds of Cr 2p spectra of chromium covered with thick oxides.

Fixed parameters:
Metal FWHM = 2.15 eV.
Oxide FWHM = 3.08 eV
Metal 2p3/2 and 2p1/2 peaks separation = 9.4 eV.
Oxide 2p3/2 and 2p1/2 peaks separation = 9.8 eV.

(a) 1800 L exposure

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Table 4.5 (cont.)

(b) Atmospheric exposure

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(a) Fitted using 30% metal; 24% oxide tail heights.

(b) Fitted using 30% metal; 27% oxide tail heights.

Figure 4.11 Spectra of Cr 2p obtained from chromium exposed to 1800L oxygen (top) and to atmosphere (bottom); fitted with four peaks using horizontal backgrounds.
is comparable with that from the metal component. In order to support the evidence that the increase in the energy loss background with respect to the zero loss intensity for both metal and oxide components is due to the presence of a surface layer of certain thickness, a series of spectra obtained from chromium surfaces with overlayer deposit of different thicknesses were studied. Results of such attempts are presented in the following sections.

4.6.4 ALUMINIUM EVAPORATION

Attempts to evaporate aluminium on the chromium surface, as has been described in section 4.4.3, were first carried out in the analyser chamber of the spectrometer. Typical Cr 2p signal of an ion cleaned chromium surface is shown in Figure 4.12(a). An almost flat tail at the higher binding energy side of the spectrum could be used to indicate that a clean surface had been obtained. After the spectrum of Cr of this sort was obtained the chromium surface was ready to be deposited with aluminium. The first evaporation was carried out with the filament current set at 8A for a period of not longer than 20 sec, after which the filament had broken. In spite of a very short evaporation period the aluminium was managed to be deposited on the chromium surface, although it was not as thick as had been aimed for. This is indicated by the Cr spectrum monitored just after the evaporation, Figure 4.12(b). It seems that the slope of the energy loss background of Cr after evaporation is steeper than that from clean chromium.

Another series of evaporations were continued after the
(a) Cr 2p from a clean chromium.

(b) Cr 2p from chromium covered with a thin aluminium.

Figure 4.12 Spectra of Cr 2p showing slightly rising tail following deposition of a very thin aluminium overlayer.
tungsten filament was replaced with a new one. However, no other successful results were obtained when the evaporation was carried out in the analyser chamber until the filament had broken again. The reason for not obtaining good aluminium deposition could be due to a very low pass current used as a precaution measure to keep the filament at a longer lifetime. After the filament broke for the second time and due to some other reasons as have already been mentioned in section 4.4.3 the evaporation was carried out in the preparation chamber.

Evaporation in the preparation chamber was first carried out using low passage current. After a series of attempts no promising results were obtained. These were shown by the absence of Al 2p peaks in the widescan spectrum from every attempt. To overcome these failures, the passage current was increased to 10 A at a period of 10 minutes. The current was just about to be brought back to zero when the filament broke again. However, the surface was analysed and from the wide scan, Figure 4.13(a), it can be seen that some aluminium has been deposited onto the chromium surface. Intensity ratio calculation gives the thickness of the aluminium deposit as 3.63 nm or about 3Å. From the wide scan one may still notice the presence of Cr 2p peaks which are followed by a sharply rising background at the higher binding energy. The information on, (a) the elements which were present, and, (b) the background following the peaks of the elements after aluminium evaporation can be enhanced by Figures 4.13(b) and (c) respectively, which were obtained from the wide scan shown in Figure 4.13(a). Figure 4.14(a) shows the Al 2p3/2 spectrum fitted with two components; metal and
Figure 4.13 (a) The wide-scan, (b) the peaks after background subtraction of (a), and (c) the corresponding background used to obtain (b) for chromium covered with thick aluminium deposit.
Figure 4.14  Al 2p3/2 and O 1s spectra obtained from chromium surface covered with a thick layer of aluminium deposit.
oxide. A good fit, as shown, was obtained when the metal energy loss tail was set at 11% for the metal component and and 0% for the oxide. The corresponding O 1s and C 1s spectra from this surface are shown, respectively, in Figure 4.14(b) and 4.15(a). The narrow scan of Cr 2p obtained from this surface is shown in Figure 4.15(b). The sharp rise of the lower binding energy side of the zero-loss Cr 2p3/2 peak may still be observed but the rise in the energy loss background is so sharp that makes the 2p1/2 component of the spectrum almost disappear as if all electrons coming from this spin state have been driven away towards the higher binding energy region. Even though the signal to noise ratio of this spectrum was not as good as aimed for attempts were made to synthesise it using the fitting program which was used previously. Figure 4.15(b) shows the best fitted spectrum attainable. It seems that only one singlet, i.e. that of the metal, in each peak of the chromium spectrum is needed for a good fit. Metal width was fixed to 2.05 eV and the slope of the baseline was allowed to vary.

4.6.5 CARBON EVAPORATION

In spite of the unsuccessful work on the aluminium evaporation it is worth noting a series of wide scans obtained from the failed attempts to evaporate the aluminium. This is shown in Figure 4.16. No aluminium signal could be observed from any of the spectrum but one may notice the increase in the C 1s intensity which is followed by an increase in the slope of the energy loss background trailing the Cr 2p signal which has been attenuated. The presence of an increasing thickness of carbon layer can also be noted from Figure
Figure 4.15 Carbon 1s and chromium 2p spectra obtained from a chromium surface covered with a thick aluminium deposit.
Figure 4.16 Wide-scans obtained from a chromium surface covered with different thicknesses of carbon deposit.
Figure 4.17(a) Spectra obtained by background subtraction of the wide scans in Figure 4.16.
4.17(a) which shows the peaks of elements which are present after the background was subtracted from each wide scan in Figure 4.16. Figure 4.17(b) shows the corresponding backgrounds used in the subtraction. The deposited carbon is thought as due to the contamination from the vacuum system as well as from the heated evaporator. Intensity ratio calculation yields the thickness of the deposited carbon for the final stage (Figure 4.16(c)) as 0.63 nm or about 0.5 Å. Peak fitting of carbon 1s gives three peaks at the binding energies of 282.8, 284.8 and 286.4 eV. These peaks could be assigned to that of the carbide and the contamination carbon respectively. Figure 4.18 apparently shows an increase in the hydrocarbon component over the carbide component of the C1s spectra corresponding to the wide scans shown in Figure 4.16. This may be used to indicate the increase in the thickness of the contaminant carbon covering the clean chromium surface. These observations support the reason for obtaining a series of Cr 2p narrow scan spectra from a chromium surface on which had been deposited with different thicknesses of the overlayer material. In section 4.6.6 results obtained from the synthesis of Cr 2p of a chromium surface which was covered with differing thickness of titanium overlayer will be presented.

4.6.6 TITANIUM EVAPORATION

For the reasons already mentioned in section 4.4.4 a titanium wire was used as the filament of the evaporator in order to deposit some titanium on an ion cleaned chromium surface. Figure 4.19 shows a series of wide scans of the surface arranged in the order of the
Figure 4.17(b) Corresponding backgrounds used in the subtraction of the wide scans in Figure 4.16 to obtain spectra shown in Figure 4.17(a).
Figure 4.18 C 1s spectra corresponding to the wide scans in Figure 4.16; showing an increase in the contaminant carbon.
Figure 4.19 Wide-scans obtained from a chromium surface covered with different thicknesses of titanium deposit; showing the attenuation in the Cr 2p peaks followed by rising backgrounds.
titanium thicknesses. It obviously shows an increase in the zero loss peak of titanium and a decrease in that of Cr 2p followed by a steadily sloping energy loss background at higher energy as the thickness of the titanium overlayer is increased. A sharp fall in the energy loss background at the higher binding energy region of the titanium 2p spectrum could be used to suggest that a clean layer of titanium was deposited on the chromium surface. Figure 4.20 shows the fitted spectra of titanium 2p from the chromium surface at each stage of the titanium evaporation. X-ray photoelectron peaks of both titanium carbide and oxide are apparent in the titanium spectra. The presence of titanium oxide and carbide on the surface is also indicated by the oxygen 1s and carbon 1s spectra as shown in Figure 4.21 and 4.22 respectively.

In order to see the effect of the titanium thickness might have on the ELTH for both metal and oxide components of the Cr 2p spectrum, peak components were fitted to the Cr spectrum obtained at each stage of the evaporation. Again, the attention was focussed on the background rise in the region up to 15 eV from the chromium 2p3/2 peak.

Starting with only the oxide width at 3.08 eV fixed, the values of the other parameters obtained for the best fits to the spectra for chromium 2p of a clean surface before evaporation (CRTI.0), and of those with differing thickness of deposited titanium films, represented in the order of the titanium thickness as CRTI.1, CRTI.2 and CRTI.3, are shown in Table 4.6. Again, the best fit for the chromium 2p doublet from the ion cleaned surface
Figure 4.20 Spectra of Ti 2p corresponding to the wide scans shown in Figure 4.19 fitted with four peaks.
Figure 4.21  O 1s spectra for chromium surfaces with different titanium overlayer thicknesses.
Figure 4.22 C 1s spectra for chromium surfaces with different titanium overlayer thicknesses.
Table 4.6 Fits of Cr 2p using sloping backgrounds of chromium surfaces with varying thickness of titanium overlayers.

(a) Spectrum CRTI.1

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(b) Spectrum CRTI.2

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Table 4.6 (cont.)

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(o) Spectrum CRTI.3

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</table>

| 50             | 2.30           | 573.8           | 575.8           |                | 2-113      |
| 30             | 3.31           | 573.7           | 575.7           |                | 2-114      |
| 40             | 2.34           | 573.8           | 575.8           |                | 115        |
requires the presence of a surface feature, probably an oxide. The best quality fit also requires only a very small tail on this peak and a value of metal, 29%; oxide, 4%, was adopted. The best quality fit for each spectrum after the titanium evaporation appeared to be given by the ELTH pairs of 25% metal - 15% oxide for CRTI.1, 30% metal - 25% oxide for CRTI.2, and 50% metal - 40% oxide for CRTI.3. The corresponding fitted spectra for all stages are shown in Figure 4.23. The results in Table 4.6 and Figure 4.23, show an increase in both metal and oxide ELTHs as the thickness of the material deposit is increased. The peak position of the metal component is maintained between 573.5 and 573.8 eV while that of the oxide component is between 575.3 and 575.8 eV.

As confidence increased in the fact that the computer iterations converged on a narrow range for the parameters left free they were fixed so as to reduce the degree of freedom in the fitting procedures. Table 4.7 shows a set of results obtained by fixing the metal and oxide widths at 2.15 and 3.08 eV respectively, and the metal 2p3/2 - metal 2p1/2 and oxide 2p3/2 - oxide 2p1/2 separations both at 9.2 eV. The background for all components was also fixed to a constant intensity. Figure 4.24 shows the variation of the chi-squared value with the ELTH of the oxide component at a fixed ELTH of the metal component for each fitted spectrum. Based on the assumption that the metal component tail height should always higher than that of oxide component because of its greater depth, the best quality fit of each spectrum appears to be obtained by fitting the ELTH pair of 25% metal - 23% oxide for CRTI.1, 30% metal - 26% oxide for CRTI.2, and 50% metal - 40% oxide for CRTI.3. Figure 4.25 shows
Figure 4.23 Cr 2p spectra fitted with sloping backgrounds.
Table 4.7 Fits of Cr 2p spectra using constant intensity backgrounds of chromium with different thickness titanium overlayers.

Fixed Parameters:

Metal FWHM = 2.15 eV.

Oxide FWHM = 3.08 eV.

Cr 2p3/2 and 1/2 peaks separation = 9.2 eV.

(a) Spectrum CRTI.1

<table>
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<tr>
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<th>Metal B.E. (eV)</th>
<th>Oxide B.E. (eV)</th>
<th>Metal 3/2:1/2 Ratio</th>
<th>Oxide 3/2:1/2 Ratio</th>
<th>Chi Square</th>
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Table 4.7 (cont.)

(c) Spectrum CRTI.3

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Figure 4.24 The variation of chi-square with oxide energy loss tail height at certain metal tail heights resulting from the fitting of Cr 2p spectra of chromium with differing titanium overlayer thicknesses.
Figure 4.25 Four-peak fits using horizontal backgrounds of Cr 2p spectra for chromium surfaces covered with titanium overlayer of increasing thicknesses.
the corresponding fitted spectra. By comparing these results with the observations on the spectra fitted with only the oxide width fixed, it seems that equally well fitted spectra could still be obtained when the values of the ELTHs were fixed at the values set for those with sloping backgrounds.

The above 'best fits' still appear to be subjective however since, as Figure 4.24 shows, it seems that other combination of metal-oxide ELTHs also could give equally good fits for each titanium coverage. Having noted this, the loci of points which would give equally good fits were examined for each evaporation stage. These are plotted as in Figure 4.26. It is found that the curve representing equally good fits at one stage is almost parallel with that for such other stage, and each curve has two extreme points, a) a point with the metal ELTH at a maximum while that of oxide is at a zero value, and b) a point with the oxide ELTH at a maximum while that of metal is at a zero value. Such plots obtained from two extremes for the last stage of the evaporation are shown in Figure 4.27. Apparently both show equally well fitted spectra. Examining the spectra fitted at the extreme points of each stage, it was found that the metal to oxide area ratio: another parameter which was left free to vary, varies between the end points, compensating the change in background distribution. For example, in the case of the two extreme points shown in Figure 4.27, the upper curve yields a metal/oxide area ratio of 2.9 whereas the lower curve yields an area ratio of 4.7. Having noted this the apparent intensity ratio between the oxide and the metal components of the chromium 2p3/2 peak and the way in which this would apparently alter
Figure 4.26 Loci of equally good fits and the lines of 'constant composition'.

a: CRTI.0
b: CRTI.1
c: CRTI.2
d: CRTI.3
Figure 4.27 Cr 2p spectra for the final stage of the titanium evaporation showing equally good fits at two extremes of the metal-oxide tail heights.
as this substrate is coated with titanium was considered as the next procedure in searching for a unique fitting to the spectrum representing each different thickness of titanium. This leads to the use of equations (4.2) to (4.5) which gives the apparent ratio, \( R_a \), as

\[
R_a = \frac{I_{\text{Cr}^{(III)}}^{(2)}}{I_{\text{Cr}^{(0)}}^{(2)}} = \frac{I_{\text{Cr}^{(III)}}^{(1)}}{I_{\text{Cr}^{(0)}}^{(1)}}
\]  

(4.8)

which is equal to the apparent ratio before evaporation, \( R_i \). Thus the oxide to metal ratio is appeared not to be affected by the thickness of the titanium deposit on the chromium surface.

From this viewpoint two sets of spectra were selected, giving the range over which the oxide to metal intensity ratios were equal to that of clean chromium surface before evaporation. The metal-oxide tail heights which give these sets are thus illustrated by lines of 'equal composition', 1 and 2, in Figure 4.26 and are listed in Table 4.8. Figure 4.28 shows the fitted spectra representing points on the line of 'equal composition' 1. By using data within these sets the thickness of the titanium deposit and the total overlayer on the surface can be calculated using the mean free path \( \lambda \), of the electrons contributing to the zero-loss peak, and, using any of the methods which will be described below. The tail heights obtained are unique for the fixed parameters and compositions.
Table 4.8 Sets of 'constant composition'.

Set 1

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<th>Oxide</th>
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<td>ELTH (%)</td>
<td>(%)</td>
<td>(%)</td>
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<th>Oxide</th>
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<td>ELTH (%)</td>
<td>(%)</td>
<td>(%)</td>
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<td>28.88</td>
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</table>
Figure 4.28 Cr 2p spectra corresponding to points on 'equal composition' line 1 in Figure 4.26.
The first method, (a) is by using the combination of equation (4.2) and (4.3) and assuming $\lambda(E') = \lambda(E) = 1.3 \text{ nm}$ and $I_{Cr(0)}^O = I_{Cr(III)}^O$, which leads to equation

$$\frac{I(1)_{Cr(III)}}{I(1)_{Cr(0)}} = \exp\left(\frac{d_{ox}}{\lambda \sin \Theta}\right) - 1 \tag{4.9}$$

Substituting the computed areas of the metal and oxide components from the fitted spectrum of CRTI.O, and $\lambda = 1.3$ for electrons from chromium 2p orbital, and the take off angle $\Theta = 45^\circ$, gives the thickness of thin oxide on the clean chromium before titanium evaporation as 0.30 nm. Substituting this value into equation (4.2) the intensity of the metal component from an oxide free surface can be calculated, and using this intensity value in equation (4.4) the total thickness of overlayer on the chromium surface after each stage of evaporation can then be obtained.

The second method, (b) is by using the equation (4.6), and, the third method, (c) is by using equation (4.7).

The thicknesses of the titanium deposit and the total overlayer calculated for both sets are given in Table 4.9. It seems that the thicknesses of the total overlayer and titanium deposit agree well between the methods used.

Having calculated the overlayer thickness for each case the opportunity was taken to examine the attenuation of both the energy
Table 4.9 Titanium thicknesses.

Set 1

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<th>$\overline{d}_{Ti}$</th>
<th>$\overline{d}<em>{Ti} + d</em>{ox}$</th>
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Set 2

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<th>$\overline{d}<em>{Ti} + d</em>{ox}$</th>
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<tr>
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</table>
loss background and the zero loss peak intensities with increasing thickness of the titanium deposit.

4.6.7 ATTENUATION CHARACTERISTIC LENGTH

Assuming, a) the intensity of the inelastic energy loss background following a zero loss peak is constant over 20 eV range and b) its attenuation with the overlayer thickness is given approximately by

\[ ELTH' = ELTH \exp\left(-\frac{d}{A \sin \theta}\right) \]  (4.10)

where \( ELTH' \) is the intensity of the energy loss background of chromium 2p with overlayer of thickness \( d \), \( ELTH \) is the intensity of the energy loss background from a clean surface, \( \theta \) is the take off angle and \( A \) is the attenuation characteristic length, or the inelastic mean free path of the electrons which are inelastically scattered during its passage to the surface. By plotting \( \ln ELTH' \) versus \( d/\sin \theta \), \( A \) can be obtained from the gradient of the line.

From Tables 4.8 and 4.9, \( ELTH' \) for the metal and oxide components and \( d/\sin \theta \) for each spectrum in both sets can be calculated. The plots of \( \ln ELTH' \) vs \( d/\sin \theta \) for both metal and oxide components are illustrated in Figure 4.29, which show that the logarithm of the calculated tail heights for both metal and oxide components decrease linearly with the thickness of the titanium deposit. This agrees well with our assumption that the energy loss background is attenuated exponentially with a factor determined by
Figure 4.29 Exponential attenuation of the energy loss background with the thickness of the titanium layer.
an attenuation characteristic length, \( \lambda = 1.44 \text{ nm} \) which was obtained from the gradient of the line. It seems that the characteristic attenuation length of the electrons which have lost energy inelastically from the chromium 2p doublet of the chromium surface is 10% higher than that of zero-loss electrons.

4.7 DISCUSSION

4.7.1 GENERAL EFFECTS OF THE FITTING ROUTINE

It has been shown that it is feasible to handle peak fitting on chromium 2p doublet from chromium samples with a very thin (0.2\( \lambda \)) and thick (1\( \lambda \)) superficial oxide layer and with overlayer deposit of varying thickness (up to 3\( \lambda \)). It appears that in the case involving spectra from clean chromium surfaces the use of two components in each spin state gives better quality fits compared with those when only one component is included. The presence of a second component in each of the main chromium peak was shown by a series of spectra obtained from the angular experiment to be a surface rather than a bulk feature, e.g. due to electron and core-hole interaction, and it is suggested to be chromium oxide.

In all X-ray photoelectron spectra of chromium 2p investigated the computed peak position of the fitted 2p3/2 metallic component occurs at 573.0 ± 0.2 eV. This agrees well, although slightly less than, the values measured by other groups of workers [115] without the metal and oxide components fitted in the chromium 2p doublet.
When only the oxide width was fixed at 3.08 eV, the separation between the Cr 2p3/2 and the Cr 2p1/2 metal components was ~ 9.2 eV for spectra obtained from clean surfaces. This separation increases to 9.4 eV for the oxidised specimen. As for the separation of the oxide components, the value obtained seems to vary between 8.6 and 9.8 eV.

4.7.2 EFFECTS OF CONSTANT INTENSITY BACKGROUNDS

The investigation also shows the feasibility of handling energy loss features as individual elements of a spectrum corresponding to each component in a complex peak. A constant intensity background was assumed for each component over a range of < 20 eV from the chromium 2p3/2 binding energy position. This procedure is the equivalent of using a Shirley inversion formula

\[ F(E) = j(E) - \int dE' F(E') k \]  

(4.11)

where \( F(E) \) is the shape of the primary photoelectron peak and \( j(E) \) is the measured peak shape and \( k \) is a constant which matches the background to the measured spectrum at the lower energy end of the primary peak, and hence, yields the value of the constant energy loss tail.

Tougaard and Sigmund [112] show that a single scattering approximation

\[ j(E) = F(E) + \int dE \ F(E_o) \ K(E_o-E) \]  

(4.12)
gives a reasonable match to the line shapes obtained by inversion of empirical method (4.11). In Tougaard and Sigmund approximation, $K(E)$ is the probability of scattering as a function of electron energy $E$ and thus the case of (4.11) assumes $K(E)$ a constant, independent of energy over the peak width. The energy loss tail is also assumed to remain constant over an interval of <20 eV in our fits. This is shown by Tougaard and Sigmund to imply uniform straight line motion in the electrons whose energy loss is proportional to their distance of travel across the interval: their calculations suggest this is justified, providing, as in the present case, no discrete losses e.g. plasmon generation or satellite peaks occur. In the present case, it has been shown experimentally that, by imposing a Shirley background and a constant intensity energy loss tail up to 20 eV region over the width of each component of the spectrum, that the oxide component has a zero relative tail height for a sample with a superficial layer of a monolayer or 0.2Å thickness. For this particular case the energy loss tail height for the metal component is 29% of the zero loss peak height. The presence of this background is due to electrons coming from a distance of a mean free path, $\lambda$, which have lost energy inelastically during its motion to the surface.

By increasing the oxide thickness on the chromium surface to the order of the mean free path, the relative tail height of the oxide component increases whereas that of the metal remains constant. For this case it has been shown that the tail of the oxide component has increased from no height at all to 27% of the zero-loss peak height. This is in agreement with the earlier
observation on the tail height of the metal component of a clean chromium surface.

The fact that constant tails are suitable for fitting over an energy range of 20 eV implies that the stopping power of the material for electrons, i.e. the rate of energy loss for an electron travelling in a uniform medium, is greater than 20 eV/Å nm or 15 eV/Å. Tougaard and Sigmund [112] assumed a value of 10 eV/Å in their calculations. None of these findings are in any way contentious. However, as has been mentioned earlier, it was observed that during the formation of thick oxides the energy loss tail on the metal feature also increased relative to its peak height. This can only mean the attenuation of the zero-loss peak for a given overlayer thickness is greater than that of the out-of-peak energy loss feature; it is prediction of Tougaard and Sigmund [112] that, at thickness greater than the inelastic mean free path, $\lambda$, the mean free path length for the angular deflection, $\lambda'$, would become increasingly important and the opportunity was taken to investigate this by the evaporation of overlayers onto the surface of chromium.

The presence of overlayer materials on ion cleaned chromium surface does attenuate the peak height and increase the relative tail height of both metal and oxide features in the chromium 2p doublet. This was observed in the presence of aluminium, carbon or titanium overlayer on chromium. A thorough investigation by the method of peak synthesis on the spectra obtained from the chromium covered with titanium overlayers of increasing thickness showed that
the relative energy loss tail height increases with the thickness of the overlayer. It was also shown that for titanium overlayer of less than 2.0 nm thickness, the energy loss tail height of the metal component remains at about 30%. This, together with the earlier results obtained from the 1800L and atmospheric exposure specimens could be a guide in determining the energy loss tail height of the metal component of the chromium substrate covered with overlayer of less than 2.0 nm thickness. In addition to that the relation between the energy loss tail height and the overlayer thickness also yields the characteristic scattering length of the electrons which have lost energy, as 1.44 nm, a 10% increase in the value adopted for scattering without energy loss. According to the observations of Tougaard and Ignatiev [113] the energy loss tail height is fairly constant over the quantum shell and kinetic energy ranges normally used in XPS. Thus the ratio of peak area to tail height ought to be usable as an indication of overlayer thickness for all elements. The fact that ten percent change in peak to tail attenuation, as is shown by the present result, is equivalent to the relative change in intensity of two peaks of the same element separated by a twenty percent difference in kinetic energy. This is usable although spectroscopists would normally be looking for a bigger change from which to estimate overlayer thickness.

The observations made on the spectra obtained from the evaporation of carbon, aluminium and titanium show that aluminium and carbon have less effect on chromium 2p ELTHs than titanium. Further, it was observed that the well fitted spectra of carbon 1s and aluminium have themselves smaller ELTHs, i.e. 5% and 11%,
respectively. This could mean ELTH varies with stopping power of each element i.e. be proportional to density of element. This observation is in disagreement with the idea of Tougaard and Sigmund [112] that the ELTH is constant for all elements.

4.7.3 WIDE SCAN BACKGROUND STRIPPING

The information in the background could perhaps be made more readily available by suitable manipulation of the wide scan spectrum and initial steps have been taken to achieve this. The Shirley background function used to strip the individual peaks can also be used across the entire spectrum (although the iterations converge more rapidly if this is done in at least two parts). This has been shown useful in order to show the coverage of aluminium, carbon or titanium on chromium surface. Figure 4.30 obtained by evaporating titanium onto chromium could be used to show a better example in the use of the wide scan background stripping. These show the combined peak and background for the clean chromium merged with the background of the subsequent substrates. This presentation focuses well on the increasing slope of the post-peak energy loss background and could be a useful method of enhancing information available from XPS. The stripped peaks (Figure 4.31) also give a better focus on the elemental concentrations than is usually obtained from a set of wide scan spectra in which peak intensity and energy loss data overlap and sometimes interfere.
Figure 4.30 The total removal of peaks from the wide scan spectra of Figure 4.19 using a 'Shirley' function: curves all normalised at Ti 2p position.
Figure 4.31 Spectra obtained after complete removal of the backgrounds from clean chromium (a), and from chromium at the first (b) and the second stage of titanium evaporation.
From the work discussed in this chapter the following conclusions were drawn:

(i) It is feasible to use constant intensity background for the individual components fitted in the chromium 2p spectra.

(ii) The energy loss tail height of the metal component remains at 30% as the clean specimen was covered with oxide or any other overlayer of less than 2.0 nm thickness.

(iii) The characteristic length of the electrons which have lost energy in the range of 20 eV of the fitted region was obtained as 1.4 nm.

(iv) The energy loss tail height varies with the density of the depositing element.

(v) The Shirley background subtraction of the wide scan spectra could be used in enhancing information available from XPS.
5.1 INTRODUCTION

High temperature and high pressure introduce a number of experimental difficulties which must be overcome if meaningful measurements are to be made [114]. A point of primary concern is the design required to withstand the pressure and temperature conditions, and the nature of the corrosion cell material which may be necessary if the solution can be contaminated by dissolution of the cell wall.

In this chapter the preparation of the specimens to be exposed in high temperature water, (a) at 473 K and (b) at 573 K, and the set up employed will be presented. Then a typical procedure followed in developing the oxide film on an Inconel specimen at each of those temperatures will be described.

5.2 SPECIMEN PREPARATION

All of the Inconel 600 specimens, provided by AERE, Harwell, were cut into elliptical coupons of 1.5 x 1.0 cm diameters and 0.1 cm thickness. The chemical analysis of the as received specimen gives the composition of the Inconel in weight percent as shown in
Table 5.1: Chemical composition of Inconel 600 (weight %).

<table>
<thead>
<tr>
<th>Cr</th>
<th>Fe</th>
<th>Co</th>
<th>Mn</th>
<th>Mo</th>
<th>Zr</th>
<th>Al</th>
<th>Ti</th>
<th>Nb</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>15.70</td>
<td>8.64</td>
<td>0.14</td>
<td>0.40</td>
<td>0.02</td>
<td>&lt;0.01</td>
<td>0.19</td>
<td>0.22</td>
<td>0.01</td>
<td>0.10</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Si</th>
<th>C</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.40</td>
<td>0.06</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Before each test the specimen was mechanically polished with SiC paper under cold water to grade 1200 and then to 1 micron finish with diamond paste. Then it was degreased in acetone and rinsed thoroughly with pure water. It was then transferred into ESCA where it was cleaned by argon ion etching to overcome the modified surface which would have resulted from the polishing. The conditions of the etching used were as cited in section 3.2.2. The etched specimen was kept immediately after it was taken out of the spectrometer in a sealed container for a few days, normally not longer than two days, before it was then exposed to the corrodent in the corrosion cell. Figure 5.1 shows the depth profile of a specimen after keeping it two days in a sealed container immediately after it had been cleaned by ion etching.
Figure 5.1 Depth profiles of Inconel specimen exposed for 2 days to desiccator air after cleaned by ion etching.
5.3 WATER PURITY

Water which was used in this work was prepared from deionised water which was multiply distilled using the apparatus shown in Figure 5.2. The conductance of the distilled water was monitored regularly and the water was only collected into the spherical glass container when the conductance was between 0.3 and 0.6 μS/cm. The spherical container may take up to 2 litres of distilled water when full. The water was kept in the container normally not longer than a week before it was used for the test solution. However, since all part of the distilled apparatus is made of silica glass the uptake of silicon into the prepared pure water is anticipated.

Cobalt-dosed water was prepared by dissolving appropriate amount of cobaltous carbonate into a certain quantity of the pure water to give the desired level of cobalt in the solution for each particular test. In order to permit monitoring of the cobalt present in the oxide film on Inconel the amount of cobalt in the dosed solutions was always made higher than 0.1 mg/l.

The simulated PWR water chemistry was prepared by dissolving a certain amount of boric acid and lithium hydroxide to give the desired level of boron and lithium in the solution. For all exposures in the simulated PWR water the prepared solution contained 1000 mg/l boron and 2 mg/l lithium. This level is in the range of the recommended B-Li coordination in PWRs [33,40].
Figure 5.2 Cyclic Water Purification Unit

- Condenser
- Temperature Controllers
- Reservoir
- Heater
- Transfer Vessels
- Conductivity Meter
5.4 EXPOSURE AT 473 K

5.4.1 CORROSION CELL

A cell for high temperature and high pressure aqueous corrosion requires a special attention to the avoidance of contamination of the solution to which the specimen is to be exposed. In this work a PTFE cell was chosen to reduce the silicon pick up by the specimen which occurred when the silica cell was used [85b]. All specimens at 473 K were exposed in the PTFE cell as shown in Figure 5.3. It can contain only a small volume of water, ca 15 ml, which makes the heating and cooling periods smaller. The design of this cell was based on the previous cells [56,85b] which were used in investigations of the interaction of stainless steel with high temperature water in this laboratory. A slight modification was made especially on the supporting base of the cell. In the previous cell the heater rod was enclosed in a very thick wall cylindrical aluminium body which was withdrawn from this later design. Instead the heater rod is now enclosed only by a thin wall copper cylinder and it was held right up beneath the cell base by a bolt type aluminium support. The purpose of the present base design was to avoid time lag during cooling which was experienced in using the previous cell. In the cell the solution was only exposed to the specimen, a gold disc, a thermocouple and the PTFE cell wall and the thermocouple sheath. The solution in the cell is heated by a Watlow Fire-rod of 1.5" length and 0.25" diameter placed beneath the copper cell base. To overcome the copper pick-up previously experienced [85b] a thick gold disc is placed between the copper base and the
Figure 5.3  PTFE Corrosion Cell
solution, a measure which was also adopted by Richardson in his work [56].

The temperature of the solution is measured by a fine chromel/alumel thermocouple sheathed with stainless steel. Specimens exposed in a PTFE cell with this thermocouple had been observed to show no sign of nickel pick-up [56] previously experienced in Clayton's work [85b]. The surface area of the thermocouple exposed to the corrodent is made less by sheathing it further with a PTFE tube extending up to its end.

5.4.2 PRESSURE VESSEL

To attain a high temperature (above 373 K) without boiling the solution ought to be pressurised. This was made possible in this work as well as in the previous ones [56,85b] by the availability of a cylindrical mild steel high pressure enclosure. The vessel was manufactured by Lintott Engineering Ltd. and could stand a safe working pressure up to 2.3 MPa (330 psi). At this pressure a maximum temperature of 483 K may be achieved before boiling the water.

Figure 5.4 shows the schematic diagram of the vessel and Figure 5.5 shows the set-up used. The size of the vessel is approximately 90 cm long and 37 cm inner diameter. It has a large door at one of its ends which enables the easy setting up of the corrosion cell, water reservoir, thermocouple and heater rod. A glass viewing window is placed on its top for the operator to have a
Figure 5.4 Pressure Vessel

PRESSURE AND VACUUM CONNECTIONS

OBSERVATION WINDOW

PINCH VALVES

GAS DOSING

WATER OUTLET
Figure 5.5 Set-up for 473°K exposure.
good view of the inside when a test is in progress. On its side are placed four ports, two at each side. The thermocouple and heater rod wires are connected through one port which carries all the electrical connection wires while the PTFE/glass outlet valve is mounted at another port which also carries the dosing gas pipes. The vessel is also equipped with a graphite bursting disc to allow it to be pumped down, using an attached Speedvac single stage rotary pump, to a rough vacuum, which is adopted as the procedure in reducing the oxygen level in the solution. Two other features of the vessel ought to be mentioned are (a) the inlet valve for nitrogen purging and (b) the outlet valve for releasing the gas pressure after each test run has been completed. For a safety reason another valve was installed connecting the pipe from the vessel to the nitrogen gas cylinder placed inside a rack outside the laboratory. In the rack two gas cylinders could be connected to an inlet valve such that the operator always have one spare full cylinder in hand in case the other one runs out of gas. The pressure in the vessel is measured with a Budenberg gauge or via an Intersonde Ltd. PR-350 pressure transducer to one of the two Kent Mk III multichannel recorders.

The flow system which was used throughout this investigation is shown in Figure 5.6. A two litre glass reservoir containing the solution was connected to the corrosion cell via a silicon rubber tube. Another piece of silicon rubber tube was used to join the corrosion cell to the outlet glass/PTFE valve which was mounted through the wall of the vessel. A gas dosing unit was also available and may be connected between the reservoir and the
Figure 5.6 Flow System
corrosion cell. However, since the dosing unit was not used in this work it is not included in the set up.

5.4.3 A TYPICAL RUN AT 473 K

Exposures at 473 K were run in the PTFE corrosion cell which was explained as in section 5.4.1. A 2 litre glass reservoir containing the pure water or solution was placed in the pressure vessel. It was then followed by placing the corrosion cell with the specimen already mounted in it into the vessel. The flow circuit was then connected and was doubly checked to ensure the flow was really on and the connections of the thermocouple and the heater rod were alright before the enclosure door could be tightly closed. The pressure vessel was then roughly pumped down to a vacuum for two to two and a half hour period. At an early stage of pumping bubbles might be seen coming out of the water in the reservoir which ceased at the end of the pumping period. It was shown by Richardson [56] that the oxygen level in the solution may be reduced down to 0.2 mg/l after 150 minute pumping, Figure 5.7. After vacuum pumping the vessel was then pressurised with oxygen free nitrogen to a low pressure at first, ~350kPa (50 psi), to check the flow system. At this stage the corrosion cell should be filled with the water and a few drops might be seen coming down of the PTFE/glass outlet valve. The vessel was then fully pressurised and the rate of flow of the water through the system was set to approximately 0.5 ml/min. Also at this stage the heater rod placed underneath the base of the corrosion cell was switched on. It normally took between approximately 20 and 25 minutes for the water temperature to reach
Figure 5.7 Comparison of nitrogen purging and vacuum degassing [56].
473 K. In one or two occasions an attempt was made to reduce the heating time but it was found that the water temperature then dropped due to the sudden ingress of cold water from the reservoir. The disruption of the water flow could be due to nitrogen bubbles forming downstream from the corrosion cell as a result of boiling of the water in contact with the gold disc at the base of the corrosion cell.

After the exposure period had been reached the cell was cooled rapidly by switching off the heater but maintaining the water flow. At the same time the pressure was released gradually as to keep the temperature down without boiling the water. After the water temperature was slightly below 373 K the pressure was fully released so that the corrosion cell could be removed out of the vessel and the specimen can be taken out of the cell as soon as possible. The total cooling time was in the order of 10 to 15 min. As soon as the specimen was taken out of the cell it was held vertically such that it stood on its edge on a piece of wipe paper in order to dry the excess water left on its surface. The total time normally taken from start of cooling to the time the specimen was successfully removed into a desiccator was between approximately 20 and 25 minutes.

Specimens were mounted for XPS analysis and then stored in the glass tube desiccator (Figure 5.8) before being transferred into the ESCA 3 preparation chamber. The storage time for specimens were kept to a minimum to minimise the change in the oxide films by keeping them in a desiccator although only little change was
Figure 5.8 Tube Desiccator
anticipated. The oxide films formed have proved to be stable in the UHV of the ESCA. Using the ion etching technique which was described in Chapter 3 the oxide was examined. It normally takes two days for acquiring data from each specimen.

5.5 EXPOSURE AT 573 K

5.5.1 TITANIUM AUTOCLAVE

In addition to the work at 473 K the opportunity was taken to expose a few specimens at a higher temperature using a titanium autoclave as shown schematically in Figure 5.9. This facility was provided at the Atomic Energy Research Establishment (AERE), Harwell, U.K.. The autoclave may contain up to a maximum volume of 15 ml water and may be pressurised up to a safe working pressure of 3100 psi. This enables a maximum temperature of 643 K to be achieved without boiling the water.

The heating of the system is provided by a large heating unit surrounding the autoclave and it can be removed quite easily as needed, to bring down the temperature of the autoclave after every exposure. The water temperature in the autoclave is measured by a thermocouple sheathed with titanium.

In addition to the gas inlet/outlet valve, the autoclave is also equipped with a bursting disc in order to allow rough vacuum pumping. At the base of the specimen chamber a tube of 1/8" bore is made through an outlet valve in order to remove the solution after
Figure 5.9 Titanium autoclave.
5.5.2 A TYPICAL RUN AT 573 K

The only difference between the exposure at 473 K and that at 573 K is the nature of the environment surrounding the specimen. In the 473 K exposure the water environment was allowed to flow through an outlet valve and thus the specimen was always exposed to a fresh environment. This was not so in the exposure at 573 K in which the specimen was exposed to a static water environment which itself constantly being pressurised as a solid state. Hence the initial volume of water to be put into the autoclave chamber has to take into consideration the volume of the specimen, the specimen holder and the part of thermocouple sheath inserted into the autoclave as well as the the volume occupied by the expansion of water at 573 K. The following data were used in calculating the volume of water required for a typical run at this temperature:

Volume of specimen = 0.15 ml (was neglected).
Volume of specimen holder = 2.0 ml.
Volume of water at 573 K ~ 1.5 x volume at room temperature.
Volume of water in the unheated base outlet ~ 2 ml (was considered as a dead volume)

Thus the minimum water required to cover the specimen and also for allowing a room for the expansion is 7.5 ml (57% fill).

After placing the specimen holder with a mounted specimen in
the autoclave chamber, 10.5 ml of water was poured into the chamber. Then 3 ml was allowed to drain through the base outlet valve leaving 7.5 ml of water in the autoclave needed for the exposure at 573 K. The autoclave was then closed and the securing bolts were sufficiently tightened. The heating unit was then replaced surrounding the autoclave and the inlet gas valve was opened to let an initial nitrogen overpressure of 1000 psi on the solution. At about the same moment the the heating unit was switched on. It normally took about an hour for the water temperature to reach 573 K. After the required exposure period was achieved the heating unit was switched off and lowered down immediately thus allowing the solution to cool down. It took about an hour for the solution to reach below 373 K so that the pressure could be released and the specimen be removed out of the autoclave. The drying method and the storage of the specimen after every exposure were kept the same as for the 473 K exposure.

The results obtained by the methods as developed and described in this chapter are presented and discussed in Chapter 6 following.
CHAPTER 6

AQUEOUS OXIDATION OF INCONEL: RESULTS

6.1 INTRODUCTION

This chapter describes results obtained from Inconel specimens which were exposed to pure and reactor chemistry simulated water, with and without the presence of cobalt ions in the solutions, at 473 K and 573 K. Since different cells and methods were used at these two temperatures, the chapter is divided into two main sections, namely, (a) exposures at 473 K, and, (b) exposures at 573 K.

6.2 RESULTS AT 473 K

6.2.1 EXPOSURES IN PURE WATER

6.2.1.1 VARYING EXPOSURE PERIOD

Figure 6.1 shows the cumulative depth profiles of specimens exposed to pure water for 4, 24 and 48 hour exposure periods. As mentioned in section 3.2.3, in these presentations carbon was not included in the normalisation of the elements in the film. It seems that a much thinner film was formed on the 4 hour exposure specimen. This is indicated by a rapid drop in the oxygen profile which reaches 40 at.% after only 2.5 minutes etching; which is
Figure 6.1 Cumulative depth profiles of Inconel specimens exposed for 4 and 24 hours at 473K to pure water.
Figure 6.1(c) Cumulative depth profile of Inconel specimen exposed for 48 hours at 473K to pure water.
approximately equivalent to 3.75 nm of oxide thickness. The 24 and 48 hour exposures give slightly thicker oxide films which were shown by the oxygen profiles, in both cases, reaching 40 at.% after 3.75 minutes etching, which is approximately 5.6 nm oxide thickness, Figure 6.2. It is also noted that in the 24 and 48 hour exposures the oxygen profiles look very similar but the quantity of nickel on the extreme outer region of the oxide film on the 48 hour specimen is slightly higher than that on the 24 hour specimen.

Analysis of the X-ray photoelectron spectra of the elements found in the oxide films reveals that in 4 and 24 hour exposures nickel can hardly be seen on the unetched surface. However, it is observed entirely in its metallic state after 0.5 minute etching. For 48 hour exposure nickel is present in its oxidised state on the unetched surface (Figure 6.3(a)) and quickly changes to the metallic state after 0.5 minute etching (Figure 6.3(b)). The method of curve fitting described in Chapter 4 was used to identify the components in the Ni 2p spectrum obtained from the unetched surface of the 48 hour specimen (Figure 6.3). The fitted spectrum clearly shows the presence of Ni(II) and the metallic state. Such a good fit was obtained by using constant intensity background of 30% metal; 15% oxide. This seems reasonable as it takes only 30 sec. of etching for the oxidised state to change to metallic. The third component appeared at the higher binding energy shoulder of the oxidised component is the multiplet splitting satellite, a characteristic of the Ni(II). The presence of the oxidised nickel on the outer surface of the 48 hour exposure specimen makes it rather difficult to use the nickel signal to calculate the film thickness as was used
Figure 6.2 Oxygen distributions on Inconel specimens exposed for 4, 24 and 48 hours at 473 K to pure water.
(a) From the unetched surface; fitted using 30% metal; 15% oxide energy loss tail heights.

(b) From surface after 30 sec etching; fitted with 25% metal; 15% oxide energy loss tail heights.

Figure 6.3 Ni 2p spectra from the unetched and after 30 sec. etching of Inconel exposed to pure water at 473K for 48 hours.
by Clayton [85b] and Richardson [56] in determining the thicknesses of the oxide films on stainless steel specimens.

For the 4 hour exposure the proportion of nickel increases as etching starts; for the 24 hour exposure specimen the nickel proportion decreases and then increases again after 0.5 minute etching; and for the 48 hour exposure, it is present in a constant quantity for up to 2 minutes etching then sharply increases, in its metallic state, to its substrate level. This can be seen clearly in the depth profile when only metal elements are used in the normalisation, Figure 6.4.

On the outer surfaces for the 24 and 48 hour exposures the nickel to chromium ratio is between 0.28 and 0.57 which then decreases at deeper layer to the minimum level of 0.13, Figure 6.5. It then increases again to the nickel to chromium substrate ratio. In the 4 hour exposure only the increasing trend in the nickel to chromium ratio was observed from the start of etching. The nickel to iron ratio, Figure 6.6, also shows an increasing trend starting from the unetched surface to around 3.5 minutes of etching after which it forms a plateau indicating that a substrate level has been reached. Except in the region between the unetched and 30 seconds etching, for both 24 and 48 hour exposures, the nickel to iron ratio increases, as etching continued, until the substrate ratio is reached, indicated by a constant ratio, after 6 minutes etching. On the other hand the iron to chromium ratio decreases to a minimum then increases to a plateau, Figure 6.7. This trend was noted for specimens at all different exposure periods. The difference is only
Figure 6.4 Cumulative depth profiles of Inconel exposed at 473K to pure water for 4 and 24 hours without oxygen in the normalisation.
Figure 6.4(c) Depth profile of Inconel exposed at 473K for 48 hours to pure water without oxygen in the normalisation.
Figure 6.5 Variations of Ni/Cr ratio on Inconel specimens exposed for 4, 24 and 48 hours at 473K to pure water.

Figure 6.6 Variations of Ni/Fe ratio on Inconel specimens exposed for 4, 24 and 48 hours at 473K to pure water.
Figure 6.7 Variations of Fe/Cr ratio on Inconel specimens exposed for 1, 24 and 48 hours at 473K to pure water.
in the etching time at which the minimum occurs, which shows an increase with exposure period. They are respectively at 1.0, 2.0 and 6.0 minutes etching for the 4, 24 and 48 hour exposures. These could be used to indicate that the relative proportion of iron to chromium at the oxide/solution interface increases as the exposure period is increased. On the 48 hour specimen the quantity of iron observed at the oxide/solution interface is almost twice that of the chromium.

On the unetched surface of the 4 hour specimen the iron spectrum shows a mixture of the trivalent and divalent states, Figure 6.8(a). As etching started it changes entirely to a divalent state and the metal component begins to appear after 1 minute etching, Figure 6.8(b). For the 24 and 48 hour specimens the mixture of the divalent and trivalent species are also observed on the unetched surface, Figure 6.9; the shoulder due to the metallic component on the Fe 2p spectrum appears only after 2.5 minutes etching for the 24 hour specimen and 3.0 minutes for the 48 hour one, Figure 6.10.

For all exposures chromium was observed in its trivalent state in the oxide film, Figure 6.11. The fitted Cr 2p spectra (Figure 6.11) shows a consistency in the peak position of the oxide component (575.6 eV) with that obtained from a pure chromium exposed to air (Chapter 4). For the 4 hour exposure the metal component in the chromium spectrum starts to appear after 2 minutes etching (Figure 6.12) at which the iron is almost entirely in its metallic state. Again, the fitted Cr 2p spectrum shows no change in the peak
Figure 6.8 Fe 2p3/2 spectra obtained at the unetched and etched surfaces of Inconel exposed to pure water at 473°K for 4 hours.

(a) Fe 2p3/2 on the unetched surface showing a mixture of Fe(II) (with 45% ELTH) and Fe(III) (with 45% ELTH).

(b) Fe 2p3/2 from surface after 1.0 min. etching showing the appearance of the metallic component (with 45% ELTH).
Figure 6.9 Fe 2p3/2 spectra obtained from the unetched surfaces of Inconel exposed at 473°C for (a) 24 hours and (b) 48 hours to pure water; both show a mixture of Fe(II) and Fe(III) in the absence of the metallic iron.
Figure 6.10 Fe 2p3/2 spectra from Inconel exposed at 479°K showing the appearance of metallic iron after certain periods of etching.
Figure 6.11 Cr 2p spectra observed on the unetched surfaces of Inconel exposed at 473°K to pure water for different exposure periods.
(a) Cr 2p with the metallic starts to appear. The spectrum was fitted with 35% metal; 30% oxide energy loss tail heights.

(b) Fe 2p corresponding to the surface as (a).

Figure 6.12 Cr and Fe spectra from Inconel exposed to pure water at 473°K for 4 hours after 2 min. etching. Note the occurrence of almost metallic iron when the metallic chromium starts to appear in the Cr spectrum.
positions from those observed previously (Chapter 4) which suggests that no shift in peak position has resulted from the ion beam etching. For the 24 and 48 hour exposures the chromium metallic state begins to appear after 3 and 4 minutes etching respectively (Figure 6.13). It seems that for each specimen when metallic chromium starts to appear in the chromium spectrum the oxygen proportion on the surface is about 40 at.%. The etch time corresponding to this point was taken as the definition point of the oxide-metal interface on stainless steel [85b,56].

On the outer surface for all specimens the oxygen spectrum shows a mixture of oxide and hydroxide (Figure 6.14). As etching starts the intensity of the hydroxide component decreases quickly, and the oxygen spectrum typically obtained for that of transition metals appears, Figure 6.15.

6.2.1.2 EFFECTS OF COBALT ON OXIDE FILM

Having decided to adopt the 24 hours as the exposure period, as it gives an oxide film of practicable thickness for analysis by XPS, investigation was undertaken to look into (a) the effect of cobalt ions in the solution on the oxide formation and (b) the uptake of cobalt ions into the oxide film on Inconel. The amount of cobalt in the solution prepared for each run was slightly higher than that observed in a typical reactor plant cooling system. Such a high amount was adopted in order that the level of cobalt expected to be found in the oxide film would always be above the sensitivity of the XPS detection on cobalt.
Figure 6.13 Cr 2p spectra obtained from the 24 and 48 hour exposure specimens after they are etched for certain periods. Both spectra show the presence of the metallic Cr component.
Figure 6.14 O 1s spectra obtained from the unetched surfaces of Inconel exposed at 473K to pure water for (a) 4, (b) 24 and (c) 48 hours.
Figure 6.15 Typical O 1s spectra obtained after certain etching period for Inconel exposed to pure water at 473°K for different exposure periods.
Figure 6.16(a) shows the cumulative depth profile of the oxide film on Inconel exposed to pure water dosed with 0.6 mg/l cobalt as cobaltous carbonate. It shows that the proportion of oxygen detected reaches 40 at.% level after 3.50 minutes etching indicating that an oxide film of 5.25 nm thickness was formed on this specimen. It also appears that cobalt is distributed through the oxide film. However, cobalt is also observed beyond the oxide/metal interface. The maximum amount of cobalt was observed to be 5.0 at.% after 30 seconds etching. The distribution of cobalt in the oxide film is such that it is highest at the oxide/solution interface and decreases as etching continues. This is self-evident from Figure 6.16(b) in which only the metal elements were included in the normalisation. From such a depth profile the maximum amount of cobalt recorded is 18.5 at.% and this occurred right on the unetched surface.

On the outer part of the oxide film cobalt was observed in the divalent state but started to change to the metallic state after 1.0 minute etching. The Co 2p spectra observed are shown in Figure 6.17. The appearance of the multiplet splitting satellite in the each of the spectra confirms the presence of the cobalt divalent state. The change from the divalent to the metallic state could also be due to the ion beam reduction. Comparing the cumulative profile for this exposure with that obtained from the specimen exposed to cobalt free water (Figure 6.1(b)) it seems that the presence of cobalt in the solution has no effect on the depth profile of the oxide film formed. The chemical states of chromium, iron and nickel were also similar to those formed on the pure water
(a) With oxygen in the normalisation.

(b) Without oxygen in the normalisation.

Figure 6.16 Depth profiles of Inconel exposed at 473K for 24 hours to pure water containing 0.6 mg/l cobalt.
Intensity (Counts.)

Intensity (Counts.)

(a) After 15 sec. etching.

(b) After 1.5 min. etching.

Figure 6.17 Typical Co 2p spectra observed. Note the presence of the satellite due to Co(II).
A second specimen was exposed to pure water dosed with 0.1 mg/l cobalt. Unaware of the great effect the trace of cobalt left from the previous exposure would have on the succeeding specimen, the flow circuit was not flushed thoroughly before this exposure was carried out. The depth profile of the specimen at this exposure is shown in Figure 6.18(a) in which the oxygen was included in the normalisation. As might be expected the amount of cobalt incorporated into the oxide film is almost as high as that found in the oxide formed at 0.6 mg/l exposure and for this specimen a maximum amount of 3.32 at.% is detected. Cobalt is also distributed quite evenly through the oxide film in the divalent state on the extreme outer surface and begins to appear in the metallic state after 1.5 minutes etching.

Another specimen was exposed to pure water containing 0.35 mg/l cobalt. Figure 6.19 shows the depth profiles for this specimen. It seems that the amount of cobalt in the oxide film is slightly lower compared to the previous specimens but again, is distributed through the oxide film reaching the metal/oxide interface. The maximum amount of cobalt detected is 3.1 at.% at 2.0 minutes etching using the profile with the oxygen included. The chemical information shows that in the outer part, as in the previous specimens, cobalt exists in the divalent state. This changes to metallic state after 1.0 minute etching. The overall elemental depth profile is not very much different from the previous ones (Figures 6.16 and 6.18). The chemical states for chromium,
Figure 6.18 Depth profiles of Inconel exposed at 473K for 24 hours to pure water containing 0.1 mg/l cobalt.
(a) With oxygen the normalisation.

(b) Without oxygen in the normalisation.

Figure 6.19 Depth profiles of Inconel exposed at 473K for 24 hours to pure water containing 0.35 mg/l cobalt.
nickel, iron and oxygen are also similar with those observed on the previous specimens.

To investigate the effect of longer exposure period on the cobalt uptake, a specimen was exposed to pure water containing 0.2 mg/l cobalt for 48 hours. Figure 6.20 shows the profile for this specimen. It seems that a slightly different profile was obtained for this specimen compared to the specimens at 24 hour; that a slightly thicker oxide might have formed on this specimen with the outer surface containing a slightly greater proportion of nickel. However, the depth profile looks very much similar to that obtained from the 48 hour exposure in plain water. Again, this shows the reproducibility of the results at 48 hour exposure. The higher quantity of nickel on the extreme outer region of the oxide film occurs at the expense of the total quantity of iron and chromium. The maximum cobalt observed is 2.18 at.% at 30 seconds etching. The profile also shows that cobalt is distributed to a great depth. Cobalt is initially in the divalent state and changes to the metallic state as etching continues. Although a slightly thicker oxide was formed it makes not much different in the cobalt distribution and the maximum amount incorporated compared with the specimens at 24 hour exposure. The slightly thicker film formed is suspected to be due to the longer exposure period rather than the presence of cobalt in the solution. The metal component of the chromium 2p spectrum seems to appear after 5.0 minutes etching at which the iron is entirely in its metallic state. It seems that the general trends in the chemical states of the elements found on the previous specimens are also followed on this specimen.
FIGURE 6.20 Depth profiles of Inconel exposed at 473K for 48 hours to pure water containing 0.2 mg/l cobalt.

(a) With oxygen in the normalisation.

(b) Without oxygen in the normalisation.
It appears that the overall view obtained from the cumulative depth profiles of all specimens exposed to cobalt dosed pure water show the reproducibility of the results in the respect that the oxide thickness and formation are not affected by the cobalt concentration in the solution.

6.2.2 EXPOSURES IN SIMULATED PWR WATER CHEMISTRY

As an approximation to the current practice in the PWRs a few specimens were exposed in modified water containing 1.0 g/l boron as boric acid and 2.0 mg/l lithium as lithium hydroxide. The pH of this solution is 6.5 at 25 C.

6.2.2.1 COBALT-FREE ENVIRONMENT

For the first specimen no cobalt was dosed to the solution. The 24 hour exposure period was still adopted for this specimen as well as for the later exposures. Figure 6.21, with and without oxygen, shows the etch profiles for the specimen at this exposure. Compared with the specimen exposed to pure water at the same temperature and exposure period it seems that a slightly thicker oxide was formed on this specimen. This is indicated by the total etch time needed, which is 6.25 min., i.e. equivalent to 10.13 nm thickness, to reach the 40 at.% oxygen level. At the extreme outer surface nickel is present at a greater proportion when it is compared with that found on specimen exposed to pure water at the same temperature and for the same exposure period. The total proportion of chromium and iron seems to be reduced at this region
Figure 6.21 Cumulative depth profiles of Inconel exposed at 473K for 24 hours to water containing 1000 mg/l boron and 2 mg/l lithium.
and becomes 20 at.% only after 2 minutes etching. After this stage the total proportion of chromium and iron stays slightly above 20 at.% throughout the oxide film. This is slightly lower than that observed on the specimen exposed to pure water at the same temperature and exposure period. The proportion of nickel seems to be high at the unetched surface, decreases as etching starts and forms a small plateau before increasing to its substrate proportion (Figure 6.21(b)). Nickel is present in its oxidised state at the outer surface (Figure 6.22) and changes to entirely metallic after 3.5 minutes etching. The chemical states of chromium and iron were also observed to follow the general trends as those in the pure water exposure specimens.

6.2.2.2 COBALT-DOSED ENVIRONMENT

Following the undosed cobalt exposures a few specimens were exposed to the simulated PWR water chemistry dosed with various cobalt concentrations. The range of the amount of cobalt dosed in the solution is kept the same as that adopted for the pure water exposures.

The first specimen in this series was exposed to the simulated reactor water containing 0.5 mg/l cobalt. The 40 at.% oxygen level was reached after the specimen was etched for 6.0 minutes indicating that an oxide of 9.0 nm had been formed on the specimen. Figure 6.23 shows the etch profiles obtained from this specimen. Cobalt seems to be distributed evenly through the oxide film extending up to the oxide/metal interface. The maximum amount of cobalt recorded
Figure 6.22 Ni 2p spectra of Inconel exposed at 473°K for 24 hours following ion-beam etching.
Figure 6.23 Depth profiles of Inconel exposed at 473K for 24 hours to simulated PWR water containing 0.5 mg/l cobalt.
is 3.9 at.%, obtained after 4.0 minutes etching. On the extreme outer surface cobalt occurs in the divalent state and its metallic state starts to appear after 1.5 minutes etching. Cobalt, which is present in the metallic state, may still be observed until the last stage of etching has been reached, i.e. 19.0 minutes, at which the analysis was stopped. The proportion of nickel was observed to be constant from the most outer surface up to 6.0 minutes etching. Nickel was observed in its divalent state at the extreme outer surface and became entirely metallic after 6.0 minutes etching. A sharp increase in nickel proportion was observed after this stage. Also at the stage when nickel proportion starts to increase sharply, metallic chromium begins to appear on the lower binding energy shoulder of the Cr 2p divalent state peak. Iron was found as a mixture of the ferrous and ferric on the extreme outer surface of the specimen and changed to ferrous and metallic as etching went on.

Another specimen was exposed to solution dosed with 0.3 mg/l cobalt. Figure 6.24 shows the etch profiles for this specimen. Due to the failure of the PDP8 on the first day of the scheduled booking days to use the instrument the specimen could only be etched and analysed half way through the oxide film. This is obvious from Figure 6.24 in which the profile is terminated at only 8.0 minutes etching. Nevertheless some results from this specimen may be reported. From the nickel and oxygen profiles it seems that a thicker film was formed on this specimen compared with the previous specimens. Cobalt seems to be distributed more evenly through the oxide film which was able to be analysed. The maximum amount of cobalt detected on this specimen is 4.1 at.%. At the last stage of
Figure 6.24 Depth profiles of inconel exposed at 473K for 24 hours to simulated PWR water containing 0.3 mg/l cobalt.
etching only nickel appears to be entirely in the metallic state. As for cobalt, it was only partly reduced to its metallic state from its divalent state, whereas for chromium and iron none of the X-ray photoelectron spectra of these elements had shown the metallic state.

Figure 6.25 shows the etch profiles of the specimen exposed to water containing 0.2 mg/l cobalt. The profile seems to be similar to that at 0.3 mg/l exposure although there is a slightly lower chromium proportion on the outer region of the film. The amount of cobalt distributed appears to be less than that in the previous specimens but still spans the entire oxide depth. Its maximum amount was detected to be 2.9 at.%. In the similar trend cobalt occurs in divalent state on the outer region of the oxide film and changes to metallic as etching continues. At the end of the etching period the metallic state of nickel and iron managed to appear whereas chromium was still left in its trivalent state.

Another specimen was exposed at 0.1 mg/l cobalt. Again, only one day analysis work available for this specimen. This was due to time taken to clean the ion gun from carbon which had accumulated between its cathode and anode that made the ionisation of the argon gas impossible. The specimen could only be etched up to 12 minutes and the depth profile obtained is shown in Figure 6.26. Except some depletion in chromium and enhancement in nickel on the extreme outer region of the oxide film the profile looks very similar to that at cobalt free exposure indicating a slightly thinner film was formed compared to those formed at 3.0 and 2.0 mg/l cobalt. Cobalt was
Figure 6.25 Depth profiles of Inconel exposed at 473K for 24 hours to simulated PWR water dosed with 0.2 mg/l cobalt.

(a) With oxygen in the normalisation.

(b) Without oxygen in the normalisation.
Figure 6.26 Depth profiles of Inconel exposed at 473K for 24 hours to simulated PWR water containing 0.1 mg/l cobalt.
still distributed evenly but in a much lower proportion through the oxide film. The maximum amount of cobalt detected for this specimen is 2.1 at.%. The general trend in the variation of the chemical state of cobalt, chromium, nickel and iron is also followed in this specimen.

Figure 6.27 shows the etch profile of the specimen exposed at 0.6 mg/l cobalt. The sharp rise in the nickel profile and the similarity of the overall profile with that obtained from specimen exposed to cobalt free solution seems to indicate a thin film was formed on this specimen. A maximum of 3.7 at.% cobalt was detected. Chemical state information reveals that cobalt, nickel, iron and chromium follow the general trends as indicated by other specimens exposed to the simulated PWR water.

6.2.3 COBALT UPTAKE VERSUS COBALT IN Solution

Cobalt uptake into the oxide film was observed to vary with the cobalt concentration in the pure and simulated PWR water. Since nickel occurred in its divalent state right from the unetched surface for all specimens exposed at this temperature it is impossible to determine the exact position of the metal / oxide interface and the thickness of the oxide film. Thus it is intended to show only the maximum amount of cobalt observed as the oxide film was etched away. Figure 6.28 shows the way in which the measured maximum amount of cobalt in the oxide films on specimens varies with the amount of cobalt dosed in the pure and reactor simulated water. For pure water exposures, ignoring the point at 0.1 mg/l cobalt
Figure 6.27 Depth profiles of Inconel exposed at 473K for 24 hours to simulated PWR water containing 0.6 mg/l cobalt.
Figure 6.28 Maximum cobalt observed in the oxide versus cobalt concentration in solution.
which might be due to some scatter in the depth profile at this concentration, the relationship seems to be linear. For the simulated PWR water exposures the points look more scattered but may also give an almost linear dependency of maximum amount of cobalt in the oxide film on cobalt concentration in the solution. It also seems that the maximum amount of cobalt does not become zero for both pure and simulated PWR water exposures. For confirmation another specimen was exposed to pure water free of cobalt and the depth profile is shown in Figure 6.29. It appears that cobalt could still be detected in the oxide film at the metal substrate. The maximum amount of cobalt detected for this specimen is shown in Figure 6.28 at the point of 0.0 mg/l cobalt. The presence of cobalt in the oxide film formed on this specimen suggests the strong influence of the traces of cobalt left in the flow system on the amount of cobalt incorporated into the oxide film. The maximum cobalt recorded for the double exposure specimens (section 6.2.4) are also included in Figure 6.27 for comparison. Another point worth noting is that a change from pure to simulated PWR water does not seem to increase the maximum amount of cobalt incorporated into the oxide film on Inconel for the same cobalt concentration in the solution.

6.2.4 DOUBLE EXPOSURES

The effects of prefilming in pure water at 473 K on the cobalt uptake was investigated by double exposure experiments. At first two specimens were run in these experiments. The first one was exposed firstly in cobalt free pure water at 473 K for 24 hours and
Figure 6.29 Depth profiles of Inconel exposed at 473K for 24 hours to pure water showing the effects of traces of cobalt in the system on the uptake of cobalt.
then in pure water dosed with 0.5 mg/l cobalt for another 24 hours. The temperature of the solution seemed to fluctuate during the prefilming exposure. This could be due to the sudden ingress of cold water from reservoir downstream which could also indicate the leak somewhere at the cell. For this reason during the interval between the first and the second exposure the cell was checked thoroughly for leakage. As a result of this inspection the specimen had to be removed out of the cell and left to dry in air. It took about 25 minutes before the specimen could be reposition in the cell for the second exposure. In the second exposure the vessel was also pumped down to a rough vacuum for 2 hours. In the second stage the temperature was very steady indicating the leakage was successfully cured. Figure 6.30 shows the etch profiles for this specimen. In the extremely outer region of the oxide film the proportion of nickel, iron and chromium seem to be similar to that in thin film at single pure water exposures. Deeper in the film the profile seems to follow that of thick film at simulated PWR water exposures. Until the end of the analysing period was reached no sign of the metal/oxide interface had occurred. It seems that a very thick film was formed on this specimen. Cobalt seems to be distributed through that part of this oxide film which was possible to etch.

The second specimen was exposed firstly to pure water for 24 hours and then to simulated PWR water dosed with 0.5 mg/l cobalt for another 24 hours. Again, during the switch over of the solution between the first and the second exposure the specimen was taken out of the cell and let to dry in air. It took about 30 minutes before the specimen could be ready for the second exposure. Figure 6.31
(a) With oxygen in the normalisation.

(b) Without oxygen in the normalisation.

Figure 6.30 Depth profiles of Inconel exposed firstly to pure water at 473K for 24 hours and then to pure water containing 0.5 mg/l cobalt for another 24 hours at 473K.
Figure 6.3 Depth profiles of Inconel firstly exposed for 24 hours at 473K to pure water and then another 24 hours at 473K to simulated PWR water dosed with 0.5 mg/l cobalt.

(a) With oxygen in the normalisation.

(b) Without oxygen in the normalisation.
shows the depth profiles obtained for this specimen. The profile seems very much similar to that of double exposure in pure water. In the outer region nickel was depleted whereas iron and chromium were enhanced. In deeper region the profiles follows that of thick film. Until the last stage of etching period was reached only nickel has shown its metallic component, but only slightly. For iron and chromium no sign that they change to metallic state has been observed. Cobalt seems to be in a slightly greater proportion in the outer region and decreases slightly towards deeper region in the film. The maximum amount of cobalt detected is 4.06 at.% with oxygen; and 14.91 at.% without oxygen in the normalisation. Cobalt is present in the divalent state and until the last stage of etching no metallic cobalt has been observed on the surface which was able to be analysed.

In order to understand the reason for obtaining much thicker oxides on the double exposure specimens which might have arisen because they were left to dry in air between the exposures, a specimen was rerun; in undosed pure water and then in cobalt dosed water for 24 hours in each exposure. Again, 0.5 mg/l cobalt was dosed in the solution used for the second exposure. In between the exposures the specimen was kept immersed in water left in the cell from the first stage. Figure 6.32 shows the depth profile obtained from this specimen. Using the 40 at.% oxygen level as an indication of the oxide/metal interface the thickness of the oxide film formed is estimated to be 13.5 nm. This thus shows that the oxide film on this specimen is thinner than those formed on the previous two specimens, Figures 6.30 and 6.31. Cobalt is observed to be present
Figure 6.32 Depth profiles of Inconel exposed firstly for 24 hours at 473K to pure water and for another 24 hours at 473K to pure water containing 0.5 mg/l cobalt.
throughout the film, initially in the divalent state and changes to the metallic state as etching continues. The maximum cobalt detected is 5.39 at.% with oxygen; and 21.75 at.% without oxygen in the normalisation.

6.2.5 DISCUSSION

6.2.5.1 OXIDE THICKNESS

The results obtained from the specimens exposed in plain water at different exposure periods at 473 K appear to show the dependence of oxide thickness on the exposure period. It was shown clearly that at 4 hour exposure a very thin oxide film, mainly of chromium oxide, of 3.75 nm thickness was formed and the thickness increased to approximately 6.0 nm as the exposure period was increased to 24 and 48 hours. The thickness of the oxide film obtained in pure water exposures is comparable with that observed by McIntyre [30] on Inconel formed after 3 hour exposure in pH 10 solution at 280 C under the hydrogen overpressure.

The presence of 1000 mg/l B as boric acid and 2 mg/l Li as lithium hydroxide in the solution, to simulate the reactor coolant, seems to thicken the oxide film slightly reaching up to 10 nm. However, the thicknesses of the oxide films observed at this temperature are still much thinner when they are compared with those formed on the Inconel specimens exposed to a real reactor coolant, such as those observed by Pick [35]. In his studies Pick observed oxides of not less than 0.5 μm thick which is almost 50 times of
that observed in this work. This is not at all surprising since in a real situation specimens were normally exposed at much higher temperatures, and had been taken from plants which had been in operation for not less than one effective full power year.

The oxide films observed on Inconel at this temperature can also be considered as thin oxides when they are compared with those formed at the same temperature and solution conditions but shorter exposure periods on stainless steel specimens, studied by Richardson in this laboratory [56]. This is still true when they are compared with the thinnest oxide observed on the stainless steel which was 25 nm thick. The only exception in the present work is for those films on specimens from the double exposure experiments in which the specimens were left to dry in air in between the exposures. These specimens yield oxide films of thicker than 45.0 nm, judging from the final etching time reached.

6.2.5.2 CHEMICAL STATES

On the 4 and 24 hour pure water exposure specimens, nickel is hardly observed in the extreme outer region of the oxide film. It seems that nickel is buried underneath the chromium rich layer formed on these two specimens. The wide scans taken at various etch periods from these specimens (Figures 6.33 and 6.34) probably could be used to support this. Attention is focussed at the slope of the post-peak energy loss tails (p-p) following the Cr 2p and Ni 2p peaks. It is apparent from both figures that p-p of the Cr 2p is sloping steeply down towards higher binding energy region as etching
Figure 6.33 Wide-scans obtained after a series of etchings of specimen exposed at 473°K for 4 hours. Note the sloping down of the post-peak (pp) backgrounds of the Cr 2p peaks and the rising pp backgrounds of the Ni 2p peaks.
Figure 6.34 Wide-scans obtained after a series of etchings of specimens exposed at 473°C for 24 hours to pure water. Again, note the same pp phenomenon as observed from Figure 6.33.
starts. This may indicate that a clean chromium oxide is present on both surfaces. By contrast, the slope of the p-p of the Ni 2p peaks is increasing. As has been suggested in Chapter 4 this characteristic may be used as an evidence that nickel is buried underneath a superficial layer which on these specimens is the chromium oxide.

The presence of oxidised nickel on the outer region was only observed in the 48 hour exposure specimen. Its proportion is increased but only slightly on specimen exposed to simulated PWR water chemistry. The depth profile at 48 hour exposure to pure water looks very much the same as that exposed to simulated PWR water for 24 hour exposure. It seems to suggest a same mechanism of oxide formation in both cases. It seems that for these cases more nickel ions were able to be transported through the passive chromium oxide film which was the only oxide observed at 4 hour exposure specimen. For some reason the nickel ions which have entered into the solution were deposited back onto the chromium oxide film to then form a very thin outer layer, on the 48 hour sample. The other possible source from which nickel ions could have come is the stainless steel sheathed thermocouple. The increase in nickel content of the outer layer at the oxide/solution interface was also observed by Clayton [85b] and Richardson [56] on stainless steel specimens exposed to pure water in the PTFE cell. 5 to 20 at.% of nickel observed on the outer surface by Clayton was interpreted as due to the solution transport from the chromel/alumel thermocouple which was used [85b]. Replacement of that type of thermocouple by stainless steel sheathed thermocouple had succeeded in reducing the
amount of nickel present in the outer layer as was observed by Richardson [56]. He then interpreted the presence of nickel in the outer layer to have come from a corroding stainless steel surface. In the present work the XPS spectrum of Ni 2p observed on the outer surfaces of the specimens exposed to simulated reactor water reveals that nickel is present in the divalent state which changes quickly to the metallic state as etching starts.

Iron seems to follow the same transport path as nickel. This was shown by the presence of slightly higher proportion of iron in the extreme outer region of the oxide film formed on the 48 hour exposure in pure water and 24 hour exposure in simulated PWR water specimens. The high proportion of iron to chromium and iron to nickel in the film compared with that in the substrate indicates that a considerable amount of iron enters the solution. The Fe 2p spectrum obtained from the outer surface shows a mixture of Fe(II) and Fe(III). As etching continues metallic iron begins to appear in the spectrum.

Chromium was observed to be present in Cr(III) state. The appearance of its metallic state is only apparent when the Fe 2p spectrum is entirely in the metallic state. Interestingly, at that stage the oxygen found on the surface is about 40 at.%. It is also noticed from the etch profiles without oxygen in the normalisation that at the point where the proportion of oxygen is about 40 at.% the metals composition is approximately of the alloy. Thus it seems that the use of the 40 at.% oxygen level as an indication of the metal/oxide interface is justified. This, in turn, has been the
basis used in estimating the oxide thickness in accord with that used previously [85a, 85b, 56].

The observations thus seem to suggest that it is possible for Inconel to produce two layered structure oxide film as has been found on mild steel [4] and stainless steel [21, 22, 56, 85b]. However, the outer layer on Inconel is very much thinner. The inner layer is rich in chromium and the outer region contains nickel, iron and chromium. Interestingly, the oxide formed on Inconel at 473 K in pure water was observed to be very similar to that formed on stainless steel at 393 K [85b], where in each case nickel has hardly been observed on the extreme outer region of the film.

6.2.5.1 COBALT UPTAKE

It is evident from the results obtained that the maximum amount of cobalt observed both in pure and reactor simulated water exposures at 473 K is proportional to the concentration of cobalt ions in the solution (Figure 6.28). However, the maximum amount of cobalt found in the oxide film depends only on the concentration of cobalt in the bulk solution, and not strongly dependent on time of exposure, temperature, or of water chemistry (i.e. 'PWR' or pure water).

The proportionality of the maximum amount of cobalt in the oxide film and cobalt concentration in the solution agrees well with the cobalt uptake in the oxide film of stainless steel observed by Richardson [56]. In his work he showed that this is true for the
exposures in pure water at 413 K and 473 K and also for the exposures in the simulated PWR water at 473 K. However, in his observations the maximum amount of cobalt found in the oxide film increases as a change is made from pure to the simulated PWR water at the same amount of cobalt dosed in the solutions. He also observed the suppression of the amount of chromium when cobalt present in the oxide film, which was shown not to occur in this work.

It is also evident from the depth profiles obtained by excluding oxygen in the normalisation from specimens exposed to solutions dosed with cobalt that the proportion of cobalt with respect to the other metal ions is highest at the oxide/solution interface and decreases towards the deeper depth in the oxide film. However, cobalt is also observed, in its metallic state, beyond the metal/oxide interface in the etch profiles. This may be evidence of the poor sputtering rate of cobalt ions and for beam mixing. In order to support this conjecture the Cr 2p spectrum obtained after 20.0 minutes etching of the third prefilmed specimen was fitted with four peaks. The surface at this stage is probably beyond the metal/oxide interface as the oxygen found is 27 at.% which is less than the proportion of oxygen representing the metal/oxide interface (see above). Figure 6.35 shows the good fit obtained by assigning 43% tail height to the metal component and 30% to the oxide components. From the results in Chapter 4 it has been suggested that the tail height of the components fitted to the Cr 2p spectrum is always less or equal to 30% when the overlayer oxide or deposit is less than 2.0 nm. From the oxide/metal ratio of the fitted Cr 2p
Figure 6.35 Cr 2p spectrum from the base of the oxide and was fitted using 43% metal; 30% oxide energy loss tail.
spectrum as shown from Figure 6.35 it is apparent that the oxide left on the Inconel surface at that stage is less than 2.0 nm. One possible explanation for obtaining good fit with such high tail heights would be the presence of metallic overlayer covering the chromium oxide. The appearance of metallic cobalt after bombardment of bulk CoO and cobalt ferrite by ion beam was observed by Chuang et al [105]. The observation of Chuang et al and the possibility of the poor sputtering rate and beam mixing of cobalt ions under the ion beam could probably account for the occurrence of metallic cobalt beyond the metal/oxide interface, as has been observed in this investigation.

The chemical state of cobalt in all specimens at 473 K was initially in the divalent state (Figure 6.17). None of the observations at 473 K has shown the presence of the trivalent cobalt. However trivalent cobalt was observed on stainless steel specimen which was allowed to cool overnight in the corrosion cell [56]. As etching continued the divalent cobalt changed to the metallic. The fact that Co(II) has been observed to reduce to the metallic cobalt [105] makes it rather difficult to suggest whether the change from Co(II) to metallic cobalt observed is a true chemical state within the film or whether it is a result of ion beam induced effect. However the fact that the cobalt metal is on top of the Cr₂O₃ (see above) suggests the latter.
6.3 RESULTS AT 573 K

The opportunity was also taken to expose a few specimens in the titanium autoclave at 573 K in order to investigate further the behaviour of the aqueous oxidation of Inconel and the cobalt uptake into the oxide film at this temperature close to that of an operating reactor plant coolant.

A specimen was exposed to pure water at this temperature for 10 minutes. This was originally intended as a familiarity experiment. However, it probably worth reporting the results obtained from this specimen. Figure 6.36 shows the depth profile of this specimen. As clearly shown by the rapid decrease in the oxygen profile, the oxide film obtained is quite thin, approximately 9.0 nm. However, this is relatively thick compared with that formed at 473 K. Further, in spite of the very short exposure time, the proportion of nickel seems to be quite high at the oxide/solution interface.

Following the previous specimen another sample was exposed to pure water at this temperature for 4 hours. Figure 6.37 shows the etch profiles obtained with and without oxygen in the normalisation. As expected, a much thicker film was formed compared with the previous one. Using the oxygen profile, the thickness of the oxide formed is estimated to be thicker than 37.5 nm. Nickel proportion is high at the outer/region with respect to other metal ions.
Figure 6.36 Depth profiles of Inconel exposed for 10.0 minutes at 573K to pure water in the titanium autoclave.
Figure 6.37 Depth profiles of Inconel exposed at 573K for 4 hours to pure water in the titanium autoclave.

(a) With oxygen in the normalisation.

(b) Without oxygen in the normalisation.
A specimen exposed for 4 hours to pure water containing 0.5 mg/l cobalt at this temperature produces etch profiles as shown in Figure 6.38. Again, an oxide of thicker than 37.5 nm was formed on this specimen. The maximum amount of cobalt detected is 1.80 at.% with oxygen; and 7.15 at.% without oxygen in the normalisation. This is lower than that observed in the oxide films at 473 K exposures. However, cobalt is distributed throughout that part of oxide film which was able to be etched.

Figure 6.39 shows the depth profiles obtained from a specimen exposed to the simulated PWR water without the presence of cobalt in the solution. Again it shows the formation of a thick film, thicker than 30.0 nm judging from the etching time which gives the percentage of oxygen close to 40 at.% It also shows cobalt distribution through the oxide film which could be attributed to traces of cobalt left from the previous exposure to pure water containing cobalt. Nickel is again shown to be a stable oxide constituent right from the solution/oxide interface. The inner layer which is rich in chromium is apparent from the profile without oxygen in the normalisation (Figure 6.39(b)).

Another specimen was exposed to simulated reactor water which was dosed at room temperature with 0.5 mg/l cobalt (Figure 6.40). Again, the oxide formed is thick, approximately 45.0 nm and the proportion of nickel is almost constantly high right from the outer surface towards the deeper depth. Cobalt is distributed throughout the oxide film but, again, at a slightly lower proportion compared with that in 473 K exposure.
Figure 6.38 Depth profiles of Inconel exposed for 4 hours at 573K to pure water containing 0.5 mg/l cobalt in the titanium autoclave.
Figure 6.39 Depth profiles of Inconel exposed for 4 hours at 573K to simulated PWR water in the titanium autoclave.
**Figure 6.40** Depth profiles of Inconel exposed for 4 hours at 573K to simulated PWR water dosed with 0.5 mg/l cobalt in the titanium autoclave.
It is evident from the results obtained at 573 K that the oxide films formed are much thicker, 45.0 nm or more, compared with those formed at 473 K in the PTFE cell. The oxygen profiles of all specimens, except that exposed for 10 minutes at this temperature show similarity that 40 at.% oxygen content was obtained after 28.0 to 30.0 minutes etch (Figure 6.41). This thus show a consistency of the oxide thickness formed at this temperature for the same exposure period.

Nickel is observed to be present at a high proportion in the outer region of the oxide film on all specimens exposed at 573 K. There is no other sources from where nickel may have been transported; the thermocouple used at this temperature was sheathed in a titanium pocket. One possible explanation is that a high proportion of nickel ions enter the solution and quickly builds up a high concentration. This is because of the limited volume and the static nature of the solution in the autoclave. The high solution concentration of nickel ions would enhance the deposition of nickel in the film. Additionally, there may be some further deposition during cooling which normally takes one hour or more.

The observations also show that an inner layer which is rich in chromium was formed at the metal/oxide interface. This layer and that observed on the 473 K specimens was formed by the oxidation at the metal/oxide interface during the oxide growth. Thus the formation of the oxide film on Inconel exposed at this temperature
Figure 6.41 Oxygen profiles obtained from Inconel specimens exposed at 573°K for 4 hours compared with that obtained at 10 min. exposure.
involves the formation of two-layer oxides, an inner layer which is rich in chromium and an outer layer which contains nickel, iron and chromium in approximately the concentrations found in the alloy.

It is also evident from specimens exposed to solution containing cobalt that the cobalt is distributed through the oxide film reaching the oxide/metal interface as was observed on the 473 K specimens. As has been suggested earlier in the case of the 473 K specimens, the observation of cobalt at or near the metal/oxide interface in the profiles may be attributed to the poor sputtering rate of cobalt ions and to the oxide mixing under ion beam. Again, the synthesis of the Cr 2p spectrum obtained from the surface close to the metal/oxide interface of the specimen at this temperature has proven to be helpful. Figure 6.42 shows such a typical spectrum which has been fitted with metal and oxide components of 50% and 38% tail heights respectively. The proportion of cobalt was also observed to be slightly lower in the 573 K specimens than those observed on the 473 K specimens. This is hardly surprising as the amount of cobalt available from the solution at 573 K is limited whereas in the 473 K exposure cobalt is continuously supplied from the refreshing solution.

6.3.1.1 MASS TRANSPORT PROCESSES

At higher temperature films are thicker and also dependent on time. Thus mass transport processes over a layer thicker than normal passivation film are now important. Clues to the type of controlling mechanisms are therefore sought in the spectra.
Figure 6.42 Cr 2p spectrum obtained at the metal/oxide interface of Inconel exposed at 573°K to pure water containing 0.5 mg/l cobalt for 4 hours: fitted with the use of 50% metal; 38% oxide tail height to show the presence of cobalt on top of the Cr₂O₃ layer.
From the profiles obtained at 573 K it has been suggested that an inner layer rich in chromium was formed on specimens at this temperature. Figures 6.43 and 6.44 show respectively the nickel to chromium and iron to chromium ratios found throughout the films. They clearly show the enrichment of chromium in the inner layer at the expense of both iron and nickel. In the inner layer chromium is present in the trivalent state. This is clearly shown from Cr 2p spectrum taken from the specimen exposed to the simulated PWR water containing cobalt at 573 K after it had been etched for 5 minutes (Figure 6.45). The surface at this stage is probably close to the division between the inner and the outer layers of the film formed. This is also evident from the Ni/Cr ratio plot (Figure 6.43) where at this point the ratio starts to form a plateau. The Cr 2p spectrum shown has been fitted with three components in each spin state with the use of constant energy tails. The spectrum clearly shows the present of Cr(III) in the form of mainly oxide and a small proportion of other component. Such a good fit was obtained with the metal tail height set at 40% and those of the oxide and the other high energy component were at 28% and 8% respectively.

The enrichment of chromium in the inner layer at the expense of nickel and iron may arise from selective dissolution of both iron and nickel species during the formation of the inner layer or alternatively, from selective oxidation of chromium. Since no evidence of chromium depletion in the alloy has been found it is assumed, following the reasoning of Asami et al [116], that selective dissolution occurs. It is also shown from Figure 6.43 that at the oxide/solution interface the ratio of nickel to chromium
Figure 6.4.3 Ni/Cr (atomic ratio) versus etch time for specimens exposed for 4 hours at 573K.

Figure 6.4.4 Fe/Cr ratio (atomic ratio) versus etch time for specimens exposed for 4 hours at 573°K.
Figure 6.45  Cr 2p spectrum obtained after 5 min etching of a specimen exposed at 573K for 4 hours.

<table>
<thead>
<tr>
<th>Binding Energy (eV)</th>
<th>CHI SQ. = 237</th>
</tr>
</thead>
<tbody>
<tr>
<td>578.8</td>
<td>2.10 15.88 3.88</td>
</tr>
<tr>
<td>578.3</td>
<td>2.08 10.88 3.88</td>
</tr>
<tr>
<td>579.5</td>
<td>2.16 15.88 3.88</td>
</tr>
<tr>
<td>579.3</td>
<td>2.08 10.88 3.88</td>
</tr>
<tr>
<td>586.6</td>
<td>3.08 16.88 4.88</td>
</tr>
</tbody>
</table>

Intensity (Counts)
is approximately that in the alloy. The X-ray photoelectron spectrum of Ni 2p obtained from the unetched surface (Figure 6.46) shows that nickel is present in the divalent state. Comparing such a spectrum with those observed by McIntyre [74,77] in his attempts to differentiate Ni(II) in Ni(OH)₂ from that in nickel ferrite it seems that nickel observed in the oxide film at this temperature is in the form of a spinel. This is in accord with the general belief in the mass transport processes that in an oxygen-free and limited volume solution in which the condition is reducing only spinel of type, MFe₂O₄, where M may either Fe(II) or Ni(II) or the mixture of both, may be deposited to form the outer layer. However, in view of the excess of chromium in the complete film, deposition must also have occurred elsewhere in the titanium autoclave.

6.4 CONCLUSIONS

The following conclusions were drawn from the results both at 473 K and 573 K.

(a) At 473 K:

(i) Cobalt is incorporated in a divalent state.

(ii) Cobalt is distributed throughout the oxide film. The presence of metallic cobalt beyond the metal/oxide interface in the profiles may be evidence of poor sputtering rates for cobalt ions and for ion-beam mixing.
Figure 6.46 Ni 2p spectrum obtained from the unetched surface of Inconel exposed at 573°C for 4 hours to simulated PWR water containing 0.5 mg/l cobalt.
(iii) The maximum cobalt concentration in the oxide film is proportional to the cobalt concentration in the solution.

(iv) The addition of boric acid and lithium hydroxide to the water does not increase cobalt uptake.

(v) The cobalt uptake in the oxide film on Inconel is less compared to the uptake on stainless steel with the same exposure conditions.

(b) At 573 K:

(i) Much thicker films were formed on Inconel at this temperature compared with those formed at 473 K.

(ii) Two-layer films were formed, a chromium rich inner layer and an outer layer containing nickel, iron and chromium. The iron is in the form of a Fe(II)/Fe(III) mixture. Chromium is in the Cr(III) state.

(iii) Nickel is a stable constituent at the extreme outer surface of the oxide film. At this temperature it is present as a Ni(II) compound, possibly a spinel.

(iv) Cobalt is distributed throughout the oxide film in the divalent state.

(v) There is a net loss of iron and nickel from the alloy and its oxide.
In this investigation two pieces of work, the synthesis of the Cr 2p doublet and the investigation of the aqueous oxidation of Inconel at high temperature and its interaction with cobalt ions dissolved in the solution, have been undertaken by way of the experimental objectives outlined in section 2.6.

A few observations do emerge from the work on the fitting of the X-ray photoelectron spectra of the chromium 2p peaks. With the use of constant energy loss backgrounds in the range of 20 eV over the Cr 2p spectra it has been shown that good fits can be obtained by assigning a lower relative tail height to the superficial component than that assigned to bulk component. Apparently no tail height should be assigned to the superficial component when the overlayer is in the order of one monolayer thick. As the thickness of this layer increases the tail height of the superficial component increases but always lower than 30%, when the overlayer is thinner than 2 nm. By contrast, the relative tail height of the metal component is always close to or at 30% when the superficial layer is in the order of one monolayer thick; and it remains almost unchanged when the superficial layer is still below 2 nm in thickness. The increase in the tail heights for both components is only apparent when the metal is covered, by means of evaporation.
The results obtained by depositing the clean chromium surface with overlayer materials of differing thicknesses clearly show the attenuation of the zero-loss peaks and an increase in the relative energy loss tail heights of the substrate components. These features have been used to calculate the attenuation characteristic length of the electrons which have undergone energy loss during its passage to the surface over the range of the chromium 2p peaks. The value was obtained as 1.4 nm, a 10% increase from that calculated from the zero energy loss electrons.

The observations obtained from the initial steps taken to synthesise the X-ray photoelectron spectra of the elements other than the chromium show the difference in the relative tail heights of different elements. This has been suggested as due to the difference in the stopping power of the elements; that the energy loss tail height be proportional to the density of the element. In addition to this, an initial step was also taken to use the Shirley background to strip background in the wide scan spectra and this has been shown useful in enhancing the information which can be obtained from such spectra. Both of these observations are still open for investigation in any further investigations.

Ion etching is damaging and therefore one important need is to be able to place components in order on the basis of the non-destructive spectroscopy. In future investigations ELTH analysis should play an important role in this. As an example it
was possible to show that ion damaged cobalt lay on top of Cr$_2$O$_3$ at the base of an ion-etch sequence. Turning to the oxidation of Inconel the basic information on depth of oxide and distribution of species within it has been obtained by ion etching.

The oxide films formed on Inconel are much thinner than those found on stainless steel at 473 K using the same exposure conditions [56]. Films are thicker on longer exposure periods at the same temperature, and, on Inconel exposed at 573 K in the static titanium autoclave. The thin film at 473 K is mainly a chromium rich layer which is overgrown by a thin outer layer containing nickel, chromium and iron species, in the proportion approximately that in the alloy, when Inconel is exposed at 573 K.

Cobalt is distributed throughout the oxide film in a higher proportion at the oxide/solution interface and decreasing towards deeper depth in the film. Cobalt was observed beyond the metal/oxide interface and this is interpreted as due to the poor sputtering rate of cobalt and to the beam mixing under the bombardment of ion beam. The method of peak fitting was used to reach at this interpretation.

The maximum amount of cobalt observed in the oxide film seems to be proportional to that in the solution. However, it is apparently unchanged when additions of lithium as LiOH and boron as H$_3$BO$_3$ are made to the solution to simulate the reactor water chemistry.
The enrichment of chromium ions in the oxide is interpreted by the selective dissolution of nickel and iron. The dissolution and transport of iron is known to play a dominant role, determining the oxidation rate of steel in high temperature aqueous media. It would seem that Inconel is not fundamentally different in this respect. However, the transport mechanism of iron and nickel across the chromium oxide-rich layer has not been established. In the case of steel, the inner layer is known to be porous and this information should be sought for the much thinner films formed on Inconel.

The rate of oxidation of Inconel is much less than on steel. This could be due to the very high resistance of the chromium-rich layer formed on Inconel which acts as a barrier between oxidising species in solution and the unoxidised substrate.

The observation of formation of very thick films, rich in chromium, on specimens left to dry in air between the exposures in the prefilming experiments suggests that initially a glassy or gel-like layer is formed. On dehydration this film crystallises to form a crystalline layer which could be more porous than the gel-like film. On exposure to water at the later stage the high porosity of the crystal-like layer may enhance the dissolution of iron and nickel leaving the protective layer very rich in chromium.

The use of curve fitting with constant intensity tails on the spectra obtained from the Inconel specimens has proved useful in identifying the chemical states of the elements found in the oxide films.
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269, (1972).


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