THE SURFACE CHEMISTRY OF PITTING CORROSION

by

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ABSTRACT

The use of XPS and AES technique has been explored in the study of the surface chemistry of a whole electrode surface (XPS) and the surface chemistry of natural pits (AES). EDXA and to a small extend SIMS were also used in the investigation of the individual pits. A high resolution Auger electron microscope which has an analytical resolution as small as 0.1 μm enables a newly formed pit of less than 2 μm in diameter to be investigated. By using a Cl/Mg ratio an attempt had been made to correlate the surface chemistry of whole electrodes exposed at different potentials in 1M MgCl₂ solution to the surface chemistry of individual pits naturally produced by means of a simulated metal to metal crevice made of commercial stainless steels (SS316 and SS304) immersed in 1M MgCl₂ solution. The correlation was found to be good and within the expected limit of the data produced by XPS and AES. The estimated value of potentials of the surface of pit and its immediate vicinity was based on a theoretical model of variation of potential around a pit by Melville and also on the potential-current curve of the steel sample in the test solution.

The Cl/Mg ratio was shown to be useful in determining the activity of pits. In repassivated pits in the crevice mouth zone magnesium was a dominant species relative to chlorine, this is in contrast to the pits in the central part of the crevice which were
engulfed in general corrosion. Active pits in the area between the two regions have higher value of Cl/Mg ratio in their surface than that in the surface in their immediate vicinity. The role of chromium in pitting corrosion is suggested to counter the pitting attack by the formation of chromium oxide and oxy-chloride on the surface of pit. Molybdenum when present, also concentrates on the surface of pit. The type of corrosion attacks on sulphide inclusions in stainless steel depend on the copper content of the inclusions. Pitting will be likely to take place on pure MnS inclusions but not on copper enriched-MnS inclusions. The formation of copper sulphide is suggested to be important in reducing the amount of active species of sulphur on the corroded inclusions.
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CHAPTER 1

1 INTRODUCTION

It has been agreed by many authorities [1] that the term 'corrosion' should not only be restricted to the undesirable deterioration of materials, as is commonly held, but covers all aspects of the interaction between materials and its environment irrespective of whether this is deliberate and beneficial or adventitious and deleterious. Nevertheless it is a well known fact that the deterioration of materials caused by a harmful effect of corrosion has resulted a serious impact to the economy and safety of modern industrial plants and human life. For this reason many works have been carried out in the modern age with a two pronged aim i.e to establish the understanding of corrosion phenomena and to combat the bad effect of corrosion. The work involves many areas such as chemical and metallurgical aspects of materials, as well as chemical and physical states of the environment.

The main problem is that many of the laboratory tests and techniques are unable to offer an acceptable way to investigate the practical situation. For example, there is no practical method, so far as has been reported, which is able to monitor localised corrosion attacks in a working industrial plant. Thus it is virtually impossible to discover whether improved operating conditions have led to any improvement in a corrosion incidence. However, sections of the
plant which may be subject to an early failure e.g. tube joints, metal section in contact with a gasket, etc, can be removed at intervals and investigated. This provides updated informations on the level of corrosion attack but from such isolated and infrequent examples it is always difficult to ascertain whether the existing localised corrosion is still active. One possible way to improve this understanding is by making surface studies using electron spectroscopy. This is reasonable to explore since it can provide the surface chemistry of the materials at a shallow depth and even of a very tiny area. This chemical information will relate to the interaction of the surface with the ion of the medium and hence can yield basic information as to the electropotential and pH value in the vicinity of the surface.

It seems that among materials which are classified as corrosion resistant materials, stainless steels are the most popular ones in many major industries particularly chemical, petroleum, process and power industries. They are widely used as condenser tube, nuclear fuel tubing and construction materials. But one of the major concerns of the stainless steel users is its susceptibility to localized corrosion such as pitting and crevice corrosion. Such localized corrosion can cause unexpected and sometimes catastrophic failure while most of the structure remains unaffected.

Stainless steels are iron based alloys containing a minimum of approximately 11 at.% chromium. Their resistance to corrosion is believed to be provided by a very thin surface film which is self-healing in a wide variety of environments. Original discoveries
and developments in stainless steel technology began in England and Germany about 1910. They have undergone many modifications ever since to cope with the uses. Type 304 stainless steel, for example, is the general purpose grade, widely used in applications requiring a good combination of corrosion resistance and formability. The addition of between 2 - 3 at.% molybdenum has much improved its resistance to pitting and crevice corrosion. This modified steel which is known as type 316 is widely used in chemical industry and industries involving marine environments.

The recent development in improving the quality of corrosion resistance of stainless steel seems to focus on the content of chromium, nickel and molybdenum, and also the new entry of other elements such as copper and nitrogen. This leads to the production of new special grades of stainless steel containing more than 20 at.% of chromium and nickel, greater molybdenum content than of type 316, and a little fraction of copper and nitrogen. The steels of this kind like cronifer 2328, cronifer 1925LC, and cronifer 1925hMo produced by Vereinigte Deutsche Metallwerke of Federal Republic of Germany have an excellent corrosion resistance to sulphuric and phosphoric acids even if contaminated with chlorides. They also show good resistance to pitting corrosion, crevice corrosion, and stress corrosion cracking. They have therefore become well established for condenser tubes in nuclear power plant constructions and for other uses e.g offshore industry and phosphate fertilizer plants.

As it was mentioned earlier, localized corrosion is a prime
concern of many stainless steel users and a massive effort was taken by corrosion scientists to investigate it as early as in the early twentieth century. Pitting corrosion alone has been undergoing intensive studies for more than fifty years and in these electrochemical techniques have played a very important role [2-5] especially since potentiostats have been commercially available. Although many corrosion phenomena can be explained in terms of electrochemical reactions there is still a wide area yet to be explored including metallurgical and surface chemical aspects. The discoveries of techniques for surface studies during the past two decades seems to have answered the needs. Now, electron microscopy, X-Ray Photoelectron Spectroscopy (XPS), Auger Electron Spectroscopy (AES), Secondary Ion Mass Spectrometry (SIMS), and Energy Dispersive X-Ray Analysis (EDXA) have become well recognized techniques in corrosion research [6-9]. The study of surface chemistry over a very small area of surface (<5μm), for example, corrosion pits and inclusions, become possible with the availability of a high resolution scanning Auger electron microscope. The use of this instrument has been explored in this work.

Combination analysis by more than one analytical surface techniques has been shown to be of significant advantage in characterizing surface film [9]. For the result obtained of each technique will confirm each other and perhaps provide complementary information. Each technique has its own superiority over the others, depending upon analytical depth, focusing ability, and type of interactions between incoming beam and target atom. An example of
combination technique is given by the work of Yahalom and Ives [9]. They used a combination of transmission electron microscopy, electron diffraction, scanning electron microscopy, and X-Ray emission analysis to examine passive film of a stainless steel foil. When using transmission electron microscope they observed two layers of thin film in the corroded area. This has been supported by scanning electron microscope observation which revealed that the film consists of an exposed passive film from the unattacked side and partly broken film from the attacked side lying on the pit walls and on the exposed part of the passive film of the other side of the foil. The electron diffraction works has revealed the structure of the film while X-Ray analysis led to the interpretation that chromium and molybdenum have a very important role in characterizing the quality of the passive film.

In this work now reported, a combination of four analytical surface techniques i.e XPS, AES, EDXA and SIMS has been utilized. XPS was used to study the surface electrochemistry of films formed on electrochemically polarized stainless steel samples. A high resolution scanning Auger electron microscope, in which simultaneous AES and EDXA could be performed, was used to investigate the pitting sites in stainless steels. The results were then supported by results of SIMS. An attempts was made to correlate the results of XPS to AES microchemistry by using an electrostatic theory of the potential variation around a pit.
2 Literature Survey

2.1 Localised Corrosion

All forms of corrosion that attack metal nonuniformly are included in a common term "localised corrosion". These include crevice corrosion, pitting corrosion, intergranular corrosion, bimetallic corrosion, etc. The localised attack is likely to occur whenever either the environment or the metal or both are heterogeneous. A list of various types of heterogeneities can be consulted in a publication by Shreir [1]. Two groups of localisation can be seen, a) those in which heterogeneity of metal and metal surfaces, such as differences in metallurgical structures or geometrical configurations, results in differences in the concentration of the cathodic reactant and b) those involving a heterogeneity of environment, such as differences in aeration [10], differences in pH values [11], and differences in salt concentration [12].

The propagation of localised attack is solely governed by the processes related to the electrochemical reactions namely oxidation and reduction reactions. The oxidation reactions take place at an attacked site (anode) whilst the reduction reactions occur at unattacked area adjacent to the anode. This area will be a cathode.
Oxidation of metal,

\[ M \rightarrow M^{+n} + ne^- \]  \hspace{1cm} (1)

is the only form of oxidation reaction involved in the localised corrosion. The most common reduction reactions to balance the oxidation reaction are:

i. Oxygen reductions

\[ O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \]  \hspace{1cm} (2)

(If the solution is acidic)

or

\[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]  \hspace{1cm} (3)

(If the solution is neutral or alkaline)

ii. Metal ion reduction

\[ M^{+n} + ne^- \rightarrow M^{+(n-1)} \]  \hspace{1cm} (4)

iii. Hydrogen evolution

\[ 2H^+ + 2e^- \rightarrow H_2 \]  \hspace{1cm} (5)

For localised attack, each part of the surface under attack will have its own anodic and cathodic current densities, \( i_a \) and \( i_c \) respectively where \( i_a > i_c \). The total currents of overall localised attack are
where \( I_a \) and \( I_c \) are the total anodic and cathodic currents for anodic area, \( A_a \) and cathodic area, \( A_c \) respectively. The total anodic and cathodic currents will determine the corrosion potential of locally corroded metal.

Considering that an electrolyte contributes an appreciable resistance to the corrosion cell, either because of a high resistivity of the electrolyte or because the anode and cathode are widely separated, then the electrical potential in the electrolyte at the reaction interface will be \( \varphi_{a}^{r} \) and \( \varphi_{c}^{r} \) (\( \varphi_{a}^{l} > \varphi_{c}^{l} \)) at anode and cathode area respectively (Fig. 1). Since the metal is electronically conducting its potential can therefore be considered as everywhere close to a value \( \varphi^{M} \). When a corrosion cell is established the single potential of the cathode, \( E_c \), will be \( \varphi^{M} - \varphi_{c}^{s} \) and of the anode, \( E_a \), will be equal to \( \varphi^{M} - \varphi_{a}^{s} \).

The difference between the two single potentials,

\[
E_c - E_a = \varphi_{a}^{s} - \varphi_{c}^{s}
\]

and

\[
\varphi_{a}^{s} - \varphi_{c}^{s} = I_{corr}R.
\]
where $I_{corr}$ is the corrosion current of the local cell when the electrolyte resistance between anode and cathode is $R$. The release of ions from metal into electrolyte, and consequently the flow of electrons from anode to cathode, will take place when $U_{eq}^s > U_{eq}^s$ and $E_C > E_A$. The local potential difference will be a main driving force throughout the propagation of localised attack in natural condition.

The important environment change during localised corrosion is the change of pH value due to electrochemical reactions. Reduction reactions (oxygen reduction or hydrogen evolution) and dissolution of hydroxides will increase pH value whereas hydrolysis of metal ions will decrease it.

\[ M^{+Z} + zH_2O \rightarrow M(OH)_z + zH^+ \]  

According to Pourbaix [11], differential aeration will change the electrical potential of the anode (lower oxygen concentration) and of the cathode (higher oxygen concentration). He further suggested that a significant increase in corrosion rates of one or both of the aerated and non-aerated zones will only occur when both zones have pH values lower than 10.
The existence of single potentials at anode and cathode of a local corrosion cell.

**Fig. 1** The existence of single potentials at anode and cathode of a local corrosion cell.

**Fig. 2** Factors affecting crevice corrosion.
2.1.1 Crevice Corrosion

Crevice corrosion is a form of localised attack that occurs within crevices or at shielded surfaces where a stagnant solution is present. It was regarded by some authors [13,14] as the most detrimental type of localised attacks in chloride containing media, e.g. seawater [15,16].

The geometry of a crevice is a very crucial factor for a crevice to function as a corrosion site. Width and size of the crevice and size of metal surface outside crevice are among the major factors that determine the rate of the crevice attack. A variety of factors affecting crevice corrosion can be summarized in Fig.2. Fontana and Greene [17] have put forward an explanation for the mechanism of crevice corrosion in stainless steel in an aerated sodium chloride solution. At the initial state, the stainless steel is assumed to be in the passive state and undergoes corrosion attack uniformly over the entire surface including the ones within the crevice. The oxygen reduction reaction will diminish oxygen content of the crevice. The oxygen consumed is not replenished because of the stagnant condition inside the crevice and a very narrow gap of the crevice restricting the diffusion of oxygen into it. The cathodic reaction within the crevice therefore ceases to operate whereas anodic reaction continues. In order to balance the building up of positively charged metal ions, the negatively charged ions particularly chloride migrate into the crevice. The metal ions will combine with chloride ion to form metal chloride which then hydrolysed by water into hydroxide and acid.
The hydrolysis will increase the acidity of the crevice which will then result in breaking down of passive film. A vigorous attack will take place as soon as the passive film has been broken down.

2.1.1.1 Theoretical Approach of Crevice Corrosion.

Vermilyea and Tedmon [18] have presented a simple theory for concentration charges to explain the current flow into crevice. They used the concept of potential drop in the solution across a crevice as the potential variation determines the migration of ions. The final result of their mathematical treatment represents the relationship between temperature and concentration of anion in bulk solution to potential at any point in the crevice. The theory was in reasonable accord with result of an experiment which was also performed by them. Their experimental result showed that by a small potential different in a crevice can cause large ionic concentration changes. In other words a very high concentration of active anion will result from the large potential different at the bottom of crevice relative to the bulk environment (outside crevice).

An accurate prediction of crevice corrosion behaviour of alloys is almost beyond reach because of the involvement of so many factors as has been shown in Fig.2. However, Oldfield and Sutton [19] have

\[ \text{MCl}_z + z\text{H}_2\text{O} \rightarrow \text{M(OH)}_z + z\text{HCl} \]  

(11)
shown that a reliable prediction could be made by using a mathematical model and programmed it into a computer. Their mathematical model took into account almost all the parameters affecting crevice corrosion. The model was developed by applying four stages of crevice corrosion mechanism as proposed by Fontana and Greene [17], namely:

a) Depletion of oxygen in the crevice solution.
b) Increase in acidity and chloride content of the crevice solution.
c) Permanent break down of the passive film and the onset of rapid corrosion.
d) Propagation of crevice corrosion.

The effects of several parameters in crevice corrosion were successfully predicted by this model. The changes in corrosion potential within a crevice of sufficient tightness to sustain crevice corrosion is also predicted [20]. For example corrosion potential in a crevice of 316 stainless steel in 1M NaCl, pH 6 at ambient temperature has been shown to vary with time. It first remains at a constant value for sometime then drops to a new level and finally increases again slowly. The dropping of the potential is indicative of micropitting taking place whereas the subsequent increase in corrosion potential corresponds to the pits starting to coalesce, leading to a well developed crevice.
2.1.1.2 Experimental Approach of Crevice Corrosion

Differential Aeration

Differential aeration was the very first concept proposed to explain the mechanism of crevice corrosion and was advanced in 1937 by Evans and Mears [21]. A quantitative investigation of this concept was carried out by Rosenfeld and Marshakov [22] using simulated crevices of metal to metal and metal to nonmetal. The role of metal inside and outside crevice to crevice corrosion behaviour were studied by means of polarization and ohmic resistance techniques. They had also constructed a composite electrode to determine current distribution over the metal surface in the crevice. Although they used a rather large crevice gap, between 0.05 mm to 1.0 mm, they managed to show that for a crevice in neutral electrolytes, the anodic process was greatly accelerated whilst cathode process retarded. The result indicated that the faster oxygen concentration is reduced the greater anodic reaction is accelerated. The result of their work had been fully confirmed by Mc Cafferty [23].

pH Values and Potential Changes

The initial oxygen reduction in a crevice will increase pH value due to the formation of hydroxyl ion. The value of the crevice solution then decreases following the hydrolysis of metal ions. This feature had been experimentally proved by Karlberg and Gosta
Wranglen [24] who measured the rise of pH value in a crevice from 6.0 to 9.5 in the first one hour and then fell to less than 4.0. While Suzuki et.al [25] measured the drop of pH values in crevice from 8.0 to 1.0.

Karlberg and Wranglen [24] also measured potential difference between crevice and outer surface. They found the potential difference increased until reach a steady state value. This demonstrates that metal dissolution processes in the crevice are balanced by hydroxide accumulation outside the crevice. The potential across the interface in a local corrosion cell appeared to be in the active part of the anodic polarization curve of the metal. This observation was made by Frankenthal and Pickering [26] by using a microprobe for potential measurement. Potentials less than -44 mV(SCE) were measured during crevice initiation of type 304 stainless steel in 0.5M NaCl + 0.05M H₂SO₄ under natural corrosion condition [27].

A combination of a rubber support and a piece of type 304 stainless steel plate was employed by Bates [28] to form a crevice of area 5 mm² in which the cathode to anode ratio was about 5000 :1. The test environment was 3.5 %NaCl at room temperature. The potential drop in the crevice was monitored using a cotton thread mounted on the rubber support which acted as a salt bridge to a reference electrode. A significant feature of this work is that before a steady state value of the potential drop i.e. ~80 to 150 mV was reached, transitions in the potential drop variation with time occurred. These transitions were postulated to correspond to the different stages of crevice
corrosion development, viz. (a) oxygen depletion, (b) passivity breakdown, and (c) increasing acidity.

Turnbull and Gardner [29] investigated metal/metal crevice made of structural steel, using 3.5% NaCl, artificial and natural seawater as test media. Their results showed that pH value of the crevice solution change independently of the pH value of the bulk.

Effect of Crevise Geometry

The crevice geometry is very essential to promote electrochemical heterogeneity in a crevice since the interior of the crevice functions as anode and the exterior as cathode [22]. The existence of a large potential gradient in crevices during potentiostatic anodic polarization was observed by Greene et.al [30]. This gradient, caused by the high resistance of the narrow electrolyte path, often prevents the passivation of the crevice interior. Thus, although the exterior is maintained in the passive potential region, the interior remains active and rapidly corrodes.

In a separate experiment France and Greene [31] measured the potentials of the crevice exterior and four different points at 0.5 inch intervals within the crevice. They found the crevice potential decreases toward the exterior and the potential gradient across the crevice depends upon the external control potential. Crevice width also has a pronounced influence on crevice potential. By monitoring
the potential at a depth of 0.25 inch at a constant external control potential of 200 mV, they observed crevices less than 0.0015 inch wide to remain active while crevices wider than 0.002 inch are maintained passive to a depth of 0.25 inch. Their results led to a conclusion that crevice potential is not an absolute value, but depends on crevice dimensions as well as anodic polarization characteristics.

Chemical Composition of Surface Film

The passivity of metals is strongly dependence on chemical composition of the passive film. For instance, the critical potential for crevice corrosion initiation of stainless steel increases approximately linearly with the chromium content of the protective film [32,33]. Thus, the resistance to crevice corrosion of stainless steel at polarizing potential well below the critical potential for crevice corrosion initiation is determined mainly by passive film composition particularly chromium content. However, for polarizing potentials close to the critical potential, the resistance to initiation of crevice corrosion is reciprocally dependent on the degree of chromium depletion in the surface film, Cr (Cr = Cr_{bulk} - Cr_{surface}) [33].

Zakipour and Leygraf [34] investigated passive films on stainless steel formed at free surfaces and crevice surfaces where no local crevice been observed. Passive films were formed on a circular rubber ring/stainless steel crevice potentiostatically polarizing at
50 mv in different chloride concentration and pH values. They selected the range for pH values and chloride concentration according to experimental data on artificial and real crevices reported by other workers [25], namely from 8 to 1 for pH values and 0.5M to 4M for chloride concentration. The pH was adjusted by small addition of HCl and NaOH. The surface analysis was performed using AES. Their surface analysis result revealed that the critical film composition for initiation of crevice corrosion was mainly determined by chromium and iron content. The role of nickel and molybdenum on this film was not yet clear. Using a similar type of crevice they also investigated the surface composition of stainless steel during propagation of crevice corrosion [35]. They found the surface layer formed during dissolution in active state is enriched in chromium because of selective dissolution of iron. The film concentration of 50±5 at.% Cr, 40±5 at.% Fe and 9±2 at.% Ni was observed.

Crevice Corrosion Morphology

The surface under crevice will experience a series of morphological changes when subject to localised crevice corrosion attack. Desmond Tromans and Laurel Frederick [36] have reported an observation on morphology of Teflon/metal crevice, using an electron microscope, while Oldfield and Sutton [20] reported on metal/metal crevice. Both observations are similar in their description i.e that micropits are developed at an initial stage, grow, and coalesce to produce a grain boundary and grain orientation etching. When the
corrosion rate becomes severe further metal dissolution will produce a more polished appearance with some evidence of crystallographic dependent corrosion still present.
2.1.2 **Pitting Corrosion**

Pitting corrosion is the localized breakdown of a protective film leading to localized high rates of metal loss which result in the appearance of pits. Pits will initiate on the open surface of materials as well as under crevices. If a crevice is present, the pits will be located within the crevice. The rate of pitting attack in a crevice will be greater than at the freely exposed surface, and once a pit is initiated, it will keep growing by the so called self-sustaining mechanism [17], until the material under attack is completely perforated or the environmental condition has changed to an unfavourable situation for pitting corrosion. The situation will lead to repassivation of the pits present. The self-sustaining mechanism of pitting corrosion is the same as in crevice corrosion which is also governed by electrochemical reactions. Stagnant condition of the environment is a pre-requisite condition for the initiation and the growth of pit, since it will make acid anolyte and alkaline (or less acidic) catholyte concentrate locally at separated areas, i.e anode and cathode. Thus stagnant solutions with the presence of an aggressive anion such as chloride will promote pitting.

The position of pit with respect to the gravity is very important in determining the number of initiated pits and the shape of their growth. More pits grow in the direction of gravity compared to the numbers starting on vertical surfaces or on horizontal surfaces facing downwards [17]. The gravity effect seems to be having a direct influence upon the autocatalytic nature of pitting, because the
concentrated aggressive anion trapped within a pit is necessary for its continuing activity. Such influence of gravity may always be valid for open pits because the open pits allow corrosion products to diffuse easily outwards.

Conversely, Mankowski and Szklarska-Smialowska [37] have found that the covered pits on the surface of a steel electrode facing downwards grow into the metal bulk faster than in the case when the electrode is facing upwards. The rate of deepening is intermediate for the pits growing on a vertical electrode. The widening of the growing downwards pits is much faster than their deepening. This observation has been explained in term of mass transport. Anodic dissolution product in a pit growing upwards is easy to be transported out via the hole in the film covering the pit and under the influence of gravity. Thus the thickening of the corrosion product layer in the pit which inhibits the dissolution process will be restricted. However, the pit grows downwards will have a relatively thick layer which uniformly covers its bottom. The thickening of the layer is caused by restricted transportation of corrosion product from the pit by the film covering its mouth.

2.1.2.1 Potential And Current Distribution Of A Corrosion Pit

The flow of electrons within the metallic phase does not involve significant ohmic potential differences because of the high conductivity of the metal. The flow of current within the aqueous
phase, carried by ions, is associated with small potential changes between the anodic and cathodic areas. The flow of current in the electrolyte from anode to cathode and equipotentials set up around a local corrosion cell can be drawn as shown in Fig. 3.

A comprehensive study was carried out by Rosenfeld and Danilov [39] on potential and current density on the surface around an active pit in stainless steel. The test solution for their experiment was $0.04M \text{FeNH}_4(\text{SO}_4)\cdot12\text{H}_2\text{O} + 0.56M \text{NH}_4\text{Cl}$. Pits were naturally developed in the open surface. The size of the typical active pit used in their investigation was 0.4 mm diameter. The anodic current density measured by them was about $112 \text{mA/cm}^2$. It was found to be having the same value for any position inside pit. The cathode current density (current density outside pit), in contrast, undergoes degradation from $6 \text{mA/cm}^2$ at edge of the pit to a constant value of $0.4 \text{mA/cm}^2$ for areas surrounding the pit have radii greater than 2 mm relative to the pit centre. From potential measurement, inside pit shows having active potential values whereas area outside pit, further away from edge of the pit has a constant passive potential. Potential gradient has a zero value at about the same area as the cathode current is constant.

Pickering and Frankenthal [40] have compared experimental results to a theoretical prediction of potential variation in the electrolyte within an active pit. A flat bottom and passivated wall pit was used as a model for the theoretical treatment of potentials. For experimental data, large pits were developed at constant
Fig. 3  Schematic drawing of a local corrosion cell showing:
(a) current paths in the electrolyte flowing from the anode to the cathode,
(b) equipotential lines in the electrolyte.
(After reference 38)
potentials between 850 to 1200 mV(SHE) in a solution of 0.5mM $\text{H}_2\text{SO}_4 + 0.5\text{M Na}_2\text{SO}_4 + 3\text{mM NaCl}$. The potential at the opening of the pit was found to be the same as that set by the potentiostat but the potential shifted in the less noble direction for the position in electrolyte closer to the pit bottom. Their theoretical prediction failed to verify the experimental results for potential near pit bottom. This theory has however been modified later by Lau and Chang [41] by incorporating reduction of hydrogen ion as an additional cathodic reaction in pit at high applied potential. The result of their refinement to the theoretical model of Pickering and Frankenthal [40] seems to be agreed well to the experimental data.

The distribution of potential and current can be theoretically determined from the Laplace equation

$$\nabla^2 P = 0 \quad (12)$$

$$i = -\sigma \nabla E \quad (13)$$

where $P$, $i$, and $\sigma$ are the potential, current density and solution conductivity respectively. The product of polarization resistances, $(\frac{\partial V}{\partial i})$ and the electrolyte conductivity has the dimension of length

$$L = \sigma \frac{\partial V}{\partial i} \quad (14)$$

and has been used to determine the potential variations in corroding systems [42-44]. This parameter is known as Wagner's polarization
parameter. It can be calculated by inserting the slopes of the anodic or cathodic polarization curves into equation (14), i.e

$$L_c = \sigma h_c \quad \text{or} \quad L_a = \sigma h_a$$

(15)

$L$ is Wagner's polarization parameter, $h$ is the slope of polarization curves at Tafel region. Indices, $a$ and $c$ indicate anodic and cathodic for the parameters respectively.

A mathematical model for variation of potential around a pit has been developed by Melville [44], with assumptions that pit is very small and is in a cylindrical system. He obtained a solution for equation (12) in Bessel functions. He also related the electrode potential, $E(r)$, which measures the potential drop across the electrode surface, to the electrostatic potential, $P(r,z=0)$, as

$$E(r) = V - P(r,z=0)$$

(16)

where $z$ is distance above electrode surface, $V$ is some constant and $r$ is distance from pit centre.

By assuming the current density over the pit region, $J_a$ is constant and very large,

$$J_a = \frac{I}{\pi a^2} > \sigma \left[ \frac{P + (E_c - V)}{L_c} \right]$$

(17)

where $I$ is the total current flowing from the pit and $a$ is pit radius,
he then defined a reduce potential [43] of electrode surface around a pit as,

\[ p(r, z=0) = \frac{\sigma}{I} [P(r, z=0) - (E_c - V)] \]  

(18)

\( E_c \) is free corrosion potential over the unpitted surface (cathode). If radius of the pit, \( a \) is far less than Wagner's polarization parameter of cathode, \( L_c \), the potential will be independent of the polarization parameter. The potential distribution of zeroth order in \( a/L_c \) will be

\[
P(v, z = 0) = \frac{1}{\pi a} \left\{ \begin{array}{ll}
\frac{2}{\pi} E\left(\frac{r}{a}\right) & ; \ 0<r<a \\
\frac{2}{\pi} \left[ \frac{r}{a} \right] \left[ E\left(\frac{a}{r}\right) - \left(1 - \frac{a^2}{r^2}\right) K\left(\frac{a}{r}\right) \right] & ; \ a<r<\infty
\end{array} \right.
\]  

(19)

where \( K\left(\frac{2}{r}\right), E\left(\frac{2}{r}\right) \) and \( E\left(\frac{2}{r}\right) \) are complete elliptic integrals of the first and second kind respectively.

As \( E_c \) and \( V \) are constant (Equation 18), \( p(r, z=0) \) also appears as the distribution of potential along the electrode surface containing a pit. A plot of \( \Pi p \) against \( r/a \) as in Fig. 4 shows that potential falls rapidly from a maximum at centre of pit and become about constant at the area greater than two pit radii away from centre of pit.
Fig. 4 Variation of potential with distance from the centre of a pit of radius \( a \) for potential along the electrode surface. \( a \ll L_0 \), zeroth order approximation. After Melville [44].

\[ \text{Potential, } \varphi = \frac{\pi \sigma I}{a} \left( E - V \right) \]

- \( a = \) pit radius,
- \( r = \) distance from pit centre.
2.1.2.2 Initiation of Pit

Pit initiation was suggested to begin with the breakdown of passive film [1]. It was at first speculated that there is a competition of chloride ion and oxygen to replace the adsorbed oxygen of the passive film. The film breakdown occurs when chloride ions successfully compete with adsorbed oxygen of the passive film and effect an exchange or displacement of oxygen in an oxygen-metal bond by chloride ions [45]. The presence of chloride has been established in the total composition of films in the area of breakdown. This has lead to a suggestion that halide ions adsorption on the surface of the passive film would lower its surface energy sufficiently to cause the film to fracture at its weaker points and loosen its adhesion to the substrate [45].

Uhlig [46] has pointed out three factors probably enter the breakdown mechanism of the passive film:

1) Affinity of the metal for oxygen compared to chloride ion.

2) Composition and structure of a transient surface metal halide complex, e.g. $M(Cl)_2$ enrich may also contain OH radicals and $H_2O$ molecules.

3) Ease of ionic exchange with adsorbed oxygen of the passive film.

While Wilde [47] proposed that initiation of pitting occurs at defects or holes in the passive film. The electrostatic adsorption of chloride ions occurs as the potential of the surface is raised, until a critical $\lambda$electrolyte interface of the defects is reached which...
follows by a local anodic dissolution take place at the defect sites. Janik-Czachor et al. [48], in a review on pit nucleation emphasised on the association of pre-existing flaw with the passivity breakdown leading to pit nucleation. The flaw modelling has also been related to the salt accumulation and pH reduction theories.

The passive film breakdown leading to pitting initiation has been related to a critical pitting potential, $E_{cp}$. The incidence of pitting at this potential was observed by Leckie and Uhlig [49]. The examination of the test electrode was carried out under a low power microscope, thus the pitting potential can be interpreted as meaning the necessary condition for the initiation of fairly large pits [50]. This interpretation matches with the result of Steigerwald [51] showing that pitting can take place at potentials active to $E_{cp}$. Current blips have been observed at potentials less noble than the pitting potential by several workers [52,53]. Microscopic examination revealed some very small depressions occurred at these potentials. The depressions, nevertheless, did not propagate if the potentials were held constant. This observation lead to a suggestion by Hisamatsu [50] that at these potentials film breakdown and metal dissolution can occur but the propagation of the small depressions can only take place when the potentials exceed $E_{cp}$. In other words, the film breakdown is necessary but not sufficient for pit initiation.

Increasing of applied potential towards noble direction will attract more chloride ions to the metal surface. Wilde [15] has shown that there is a local surface concentration of Cl$^-$ as potential
increases to $E_{cp}$. Another evidence for this is from the work of Janik-Czachor et.al [54] which showed the chlorides do agglomerate on the surface of the pure iron at potential even below $E_{cp}$ in the form of thick chloride salt "islands". These salt islands are presumably the nucleation sites for pitting as $\text{Cl}^-$ will destroy passivity by displacing adsorbed oxygen of the passive film [46].

The critical pitting potential will shift in the negative (active) direction as chloride concentration increases [49]. This is one of the reason why at initial stage of crevice attack was in the form of separated pits, that is due to crevice harbour higher concentration of $\text{Cl}^-$ compared to the bulk solution.

2.1.2.3 Propagation of Pit

Once a pit was initiated, a secondary process known as the pitting propagation stage becomes operative. The propagation of pit is very dependent on hydrogen ion concentration and accumulation of $\text{Cl}^-$ in pit cavity [3]. The decrease of pH in pit cavity will promote more rapid anodic dissolution of its surface. A study by Mankowski and Szklarska-smialoska [55] on pits grown under potentiostatic condition indicates that chloride ion concentration in slowly growing pit is higher than of quickly growing pit. Highest concentration of chloride ions observed in the pits were about 12N. In the case of closed pits (film covered pits), the further growth of the pits will be followed by a gradual decrease of $\text{Cl}^-$ concentration to about 2N. This is
expected due to the decreasing tightness of the film covering the pit in which also convection and diffusion of the contents increases. Their result, which shows the rate of pit growth decreases with the increases of Cl$^-$ concentration in pit, has altered the general belief that the solution filling a pit, in steel, when enriched in Cl$^-$ will lead to a severe dissolution of pit wall. Their results also indicate that the pit growth is controlled by diffusion.

The behaviour of chromium and molybdenum in the propagation process of localized corrosion in steel has been investigated by Yang et al [56]. Oxygen-free FeCl$_2$ and/or CrCl$_3$ solution were used. The corrosion conditions were set as those existing inside occluded corrosion cells in steel. The surface films formed in these conditions were analysed by means of AES and XPS. Their results show that chromium is passive at pH values higher than 1.8 in ferrous chloride and/or chromic chloride solutions. It suggests that Cr has a retarding effect on the propagation of pit in steels at its early stage. A subsequent increase in Cl$^-$ concentration and a decrease of pH as a result of hydrolysis of Cr$^{+3}$ may occur at a later stage. The chromium may therefore increase the rate of pitting in the advance stage of propagation. A similar behaviour of Cr in Cr-containing, Mo-free steels was observed by Schultze and Wekken [57]. The role of Mo in the propagation of localized attack is however suggested as an effective retarding element in more advance stages of pitting corrosion [56]. This is attributed to the formation of an extremely thin but very protective film of MoO$_2$ (or hydrated oxide) at highly acidic conditions.
The limitation of the propagation of pit is also associated with the electrochemistry in term of protection potential, $E_{prot}$ [58]. $E_{prot}$ is defined as the potential below which existing pits cannot propagate. It is usually determined by a cyclic polarization procedure. $E_{prot}$ is not a unique property of an alloy but depend upon experimental procedure. Pourbaix [59] has suggested that $E_{prot}$ of a corroding electrode is very near to the actual potential of the surface at the bottom of the pit, therefore it varies with acidity and Cl$^-$ concentration. This hypothesis has then been supported by experimental data of Wilde and Williams [13], and reaffirmed by Suzuki and Kitamura [60] work which revealed that $E_{prot}$ decreases with time as pit propagates.

Another worker [61] has shown a similar result while working on a freely corroding sample. He found that the pit or crevice anode is polarized only a few milivolts, while the passive external cathode is polarized to over 150 mV relative to the overall corrosion potential of the specimen. These observations are parallel to those by Kitamura and Suzuki [62] who also concluded that pit growth occurs only at potentials more noble than the open circuit anode potential of the pit interior.

2.1.2.4 Repassivation of Pit

In natural condition, newly formed pits are very unstable and often become inactive because of the inward migration of chloride ions
is insufficient to alter the acidity of pit. For example, Aziz [63] discovered that one half of the pits initially formed on an aluminium surface exposed to tap water become inactive in two weeks. Whilst May [64] found some of artificial pits developed in copper sample become inactive at the early stage of their growth. Frankenthal and Pickering [26] reported that pits not associated with inclusions do not grow to an appreciable size. Their reason for this phenomena is that the entire pit cavity is exposed to the bulk solution and mixing of the solutions facilitates repassivation. In contrast, repassivation is less likely to occur in the covered pits.

The phenomena that pitting corrosion would stop if the pit and the rest of the surface were equally accessible to the electrolyte was first predicted and experimentally confirmed by Rosenfeld and Danilov [39]. Current density in the solution over pit dropped dramatically to zero when the protecting layer of the pit is destroyed. The same characteristic was observed for the potential in the pit. Its value becomes equal to that of passive surface outside the pit about 20 minutes after the destruction of the protecting layer. The destruction of the shielding layer over the pit has resulted in free access of the solution from the bulk which leads to a direct passivation of the pit and to the equalization of the potentials.

An active pit will stop propagating if its potential decreases to below \( E_{\text{prot}} \). This is due to the pit loosing high \( \text{Cl}^- \) concentration [46], and the metal surface within the pit repassivates.
Although $E_{\text{prot}}$ is related to the conditions necessary to repassivate a growing pit, it actually varies with the degree of pit growth. $E_{\text{prot}}$ decreases with increasing extent of propagation [15].

It has been widely accepted that $E_{\text{prot}}$ varies with pit depth [15,65] because a deep pit retains its altered environment more easily than a shallow pit. However, if one considers that a solution resistance controls the dissolution rate in pit [66] then $E_{\text{prot}}$ would not necessarily vary with pit depth. This controversy inspired Newman and Franz [67] to conduct an experiment investigating the nature of $E_{\text{prot}}$ for pitting. They used 1M NaCl containing 0.04M Na$_2$S$_2$O$_3$ and developed single corrosion pits potentiostatically. Taking $Q^{1/3}$ (Q is the charge) as a pit depth parameter, they showed that $E_{\text{prot}}$ was independent of $Q^{1/3}$. $E_{\text{prot}}$ is therefore not a systematic function of pit volume, although it is somewhat dependent on pit shape. They [67] have also concluded that $E_{\text{prot}}$ in a pure sodium chloride solution should be independent of pit size in the absence of random factors, e.g. spontaneous repassivation.
2.2 Sulphide Inclusions In Stainless Steel

Generally sulphur improves mechinability in steel. This effect is most often seen in terms of higher allowable machining speeds for any given value of tool life. The presence of sulphur, however also produces some deleterious effects on some service properties. Those most greatly affected being forgeability, ductility, toughness, weldability, fatigue and corrosion resistance.

In stainless steel, sulphur usually exists as sulphide because its solid solubility in stainless steel is less than 0.01 at.% at room temperature. The sulphide inclusions formed during solidification of steel are predominantly manganese sulphide. According to Wranglen [68,69] inclusions of Fe are more harmful than those of MnS owing to higher electrical conductivity and higher solubility of FeS in steel matrix. FeS inclusions are very effective cathodes for hydrogen evolution and strongly promote hydrogen embrittlement [70]. Fortunately, under proper metallurgical conditions sulphur will combine with Mn rather than Fe to form MnS [68]. Nevertheless, MnS is also detrimental since it will act as active anodic sites particularly in a stainless steel surface at the presence of aqueous chloride ions [71].

Smialowski, et al. [72] have observed that sulphide inclusions and complex oxide-sulphide inclusions in particular are the most susceptible spots for pit nucleation compared to other type of inclusions in stainless steel. They have not observed any nucleation
of pit at separate oxide inclusions. Microprobe analysis results of Smialowska, et al. [73] have also supported this observation. The sulphides undergo dissolution during corrosion, but oxides do not. The microprobe analysis revealed only oxide inclusions present in highly developed pits without any traces of sulphide.

Mechanism of Pitting Attack On Manganese Sulphide inclusions

The existence of inhomogeneties such as inclusions in or near a surface of metal will make the surface composition of that spot slightly different from the rest of the surface. Sulphide inclusions are also known to have relatively high electronic conductivities as compared to the surrounding oxide film and a lower electronic conductivities than the stainless steel matrix [74]. All this means that a potential difference will exist between the sites of inclusions and the rest of the surface. This will increase the tendency of preferential adsorption of anions, eg. Cl\textsuperscript{-} at the inclusions sites. The preferential adsorption of Cl\textsuperscript{-} has successfully been shown by Overman [75] in his investigation on stress corrosion cracking in 304 stainless steel by means of a radiochemical method. The preferentially adsorbed chloride ions will facilitate the pit nucleation process. The acidification due to hydrolysis of chloride salts will result in dissolution of active sulphides and bare metal will be disclosed.

Anodic dissolution of MnS will form elementary sulphur if the
electrode reaction take places as suggested by Wranglen [69],

\[ \text{MnS} \rightarrow \text{S} + \text{Mn}^{2+} + 2e^- \]  \hspace{1cm} (20)

Whereas Eklund [74] who observed discrete sulphur particles at the attacked areas suggested that the particles were precipitated from the solution. He proposed a mechanism for the dissolution of MnS as follows,

\[ \text{MnS} + 4\text{H}_2\text{O} \rightarrow \text{Mn}^{2+} + \text{SO}_4^{2-} + 8\text{H}^+ + 8e^- \]  \hspace{1cm} (21)

\[ \text{MnS} + 2\text{H}^+ \rightarrow \text{Mn}^{2+} + \text{H}_2\text{S} \]  \hspace{1cm} (22)

\[ \text{H}_2\text{S} \rightarrow \text{S} + 2\text{H}^+ + 2e^- \]  \hspace{1cm} (23)

At the edge of the inclusions the attack will be prominent because of different electronic conductivity at inclusion/metal interface. The attack will expose bare stainless steel under oxide film for further microcrevice attack. The mechanisms mentioned above seem to agree with a model (Fig.5) outlined by Wranglen [69] in 1974, explaining the pitting mechanism in stainless steel at MnS inclusions.

The most recent model was proposed by Szklarska-Smialowska [76] for pitting mechanism at a near-surface MnS inclusions covered by a defective passive film. Her model also seems to be consistent to many
(a) Schematic illustration of MnS inclusion in stainless steel.

(b) First stage of the initiation of pitting on stainless steel.

(c) Continued anodic attack on sulphide inclusion in stainless steel.

Fig. 5 Pitting attack on MnS inclusion [69].
experimental evidences as discussed earlier. Pitting processes covered by her model are, a) Diffusion of metallic ions through the defective film. b) Formation of a salt (chloride) layer over the defective area. c) Acidification. d) Dissolution of the defective film and the attack at inclusion/matrix interface by acid. e) Propagation stage. The rest of the MnS inclusions dissolved in the very highly acid pit solution. An occluded cell is then formed by the formation of a film of corrosion product at the pit mouth.
2.3 Corrosion Properties of Stainless Steel

2.3.1 Composition of The Surface Film.

The excellent corrosion resistance of stainless steels is attributed to the presence of a passive film on their surfaces. The amount of protection afforded by this film depends upon its solubility, adherence, and defect structure. The film comprises only a few molecular layers, i.e. 10 to 65 Å for iron-chromium alloys [77,78].

The passive films formed on austenitic and ferritic stainless steels have been found enriched in chromium [79-82]. Hashimoto and Asami [81] have suggested that Cr exists in the form of a hydrated chromium oxy-hydroxide. They have also suggested that the passive film is not uniform but contains micro-pores which repeatedly form and repassivate. Olefjord and Elfstrom [82] believe that the film consists mainly of chromium oxide and hydroxide. The passive films of both 19Cr and 19Cr-2Mo Ferritic stainless steels, formed by polarizing in 1N HCl, have been analysed using XPS technique by Hashimoto and Asami [81]. Their XPS result shows that the composition of the passive film of both steels is the same, with only very little Mo was found for the latter. This result is consistent with the AES results of other workers [79,80] which also reported very little Mo in the passive films of stainless steels. The XPS work on passive film of stainless steel carried out by Olefjord and Elfstrom [82], however, produced a contradictory results. They claimed Mo is enriched in the
passive film as also did by Sugimoto and Sawada [77] who found the Mo content of the films increases almost linearly with the increase of Mo content in the bulk alloy.

The passive film not only consists of metallic compounds or oxides of iron, chromium and some extent of nickel and molybdenum, but also contains bound water. The presence of bound water in passive film has been confirmed by many workers [83,84]. Saito, et al [84] has found that the amount of bound water in the passive film of 304 stainless steel varies with surface preparation and passivation temperature. The amount of bound water decreases as the passivation temperature increases. The authors suggested two kinds of bound water exist in the passive film. The first ones consists mainly of aquo and hydroxyl group, (\(-M-OH\) or \(-M-O-OH\)), which could be replaced easily by Cl\(^-\). This bound water acts as an effective species to capture the released metal ions to form hydroxylated metallic ion, MOH\(^+\), contributing in repairing of the film. The second ones probably consist of \(-M-O-\) or \(-M-O-M-\) type bonds. Its strong bonding to metal ions makes the film better resistant against Cl\(^-\) attacks, but the drawback is its poorer ability to promote self-repair.

2.3.2 Effects of Surface Condition

The importance of surface finish in characterizing the properties of a protective (passive) layer against the onset of pitting can be seen in a review by Sedriks [85]. The work of
Steensland, as quoted in the review, demonstrated that 304 stainless steel in aerated 5% NaCl has a different range of pitting potentials for different surface finishes.

Frankenthal [86], while studying pitting property of Fe-Cr alloys prepared by electropolish~ing and mechanical polishing has noticed that pits grown in the Flade region were always considerably larger on mechanically polished samples than those on the electropolished samples. Samples which were mechanically polished and annealed behaved similarly to the electropolished ones. He also found no correlation between pit density and modes of surface preparation.

Asami and Hashimoto [87] have used XPS to investigate the relationship between surface treatments and surface composition of 304 and 316 stainless steels. The most striking observation has been made is the dependence of chromium in the surface film on surface treatment. This increased in the order: dry polishing < HF treatment < 10% HNO$_3$ treatment < 30% HNO$_3$ treatment. Iron decreases throughout this series. The concentration of nickel in the substrate beneath the film also increases. The nickel content in the film is significantly lowered but Mo remains unchanged compared to the bulk composition regardless of the method of surface treatment. In addition to the study of surface composition, they have also investigated the aging effect. They found the effect was considerable, the thickness and iron content of the surface film dramatically increased during the first day of storage in the air of the desiccator, but slowed down afterwards. This effect is similar in
all surface treatments. Based on the XPS results they then suggested that a magnetite-like compound which has iron to oxygen ratio of about 1.4 was formed during the ageing. This compound may be responsible for further ennoblement of the pitting potential.

2.3.3 Effects of Alloying Elements

It has long been known that Cr, Ni, and Mo increase pitting resistance of stainless steels [52, 88]. The increase of Cr, Ni, and Mo content will make the pitting potential more noble. Critical current density for passivity decreases sharply at all Ni levels with the increase in Mo content [52]. Chromium has been constantly observed to be enriched in the surface film. Its role can be explained in terms of pitting potential of Cr. Because Cr has better pitting resistance than iron which is the main constituent of the surface film, so its enrichment in the film tends to make the film have greater resistance to pitting. Pure Cr does not show pitting in 1N HCl at 25°C and maintains its passivity up to +0.85 V(SCE), before undergoing transpassive dissolution. Whereas pure Fe and Ni show active dissolution and not passivate [77]. Another explanation on the role of Cr was given by Hashimoto and Asami [81] by suggesting that the passive film contains micro-pores, some of which grow into pits. Increases in the Cr content of the alloy will interfere with the development of micro-pores into pits due to a rapid repassivation of the pit sites by the formation of a passive hydrated chromium oxyhydroxide film.
Experimental evidences on the existence of Mo in the surface film is not firm [77,79-82], but for Ni, similar observation was reported i.e Ni content is very low in the passive film. Olefjord and Elfstrom [82] postulated that the beneficial effect of Ni and Mo has no relation to their occurrence in the passive film. Instead the alloying elements on the surface lower the dissolution rate in the active phase and thereby provoke formation of passive film during passivation and repassivation of locally attacked sites. A similar suggestion has again been made by Hashimoto and Asami [81] on the role of Mo, viz. Mo does not repassivate the stainless steels but assists the formation of passive film. This is because of the formation of molybdenum compounds on the active surface sites during an active dissolution, will decrease the activity of the sites. The experimental results of Moriya and Ives [89] in which Mo was shown enriched in surface inside pit and of pit wall but not in unpitted surface of single phase Ni-13 wt% Mo alloy has further supported the suggestions.

Minor alloying elements other than Mo have also contributed some effects on the resistance of stainless steels towards pitting corrosion. Osozawa and Okato [90] have studied the effect of addition 0.02-0.2 wt% of nitrogen in austenitic stainless steels of varying amount of Cr(16-25 wt%). The stainless steels tested in 4% NaCl solution show a shifting in pitting potential towards more noble direction with the increasing amount of nitrogen. Its affect is more pronounce on the steels of higher Cr content. The addition of nitrogen also imparts a great effect on the size of pit in the steels.
Pits, if present, are small in size. It seems that the pit growth is suppressed by nitrogen. It has been speculated that this phenomenon is due to the consumption by nitrogen of a proton when it dissolves in the pit solution, thus opposing the lowering of the pH value in the early stage of pit formation.

In general, the effect of all elements which are possibly present in stainless steels have been summarized by Sedriks [85]: those which are beneficial, in an environment favourable to pitting, are V, Cr, Ni, Mo, Ag, Re, Si, and N. Those which are detrimental are Ti, Cb, Mn, Se, Te, S, Gd, and Ce. Cu, B, and C give variable effects depend on their quantity and the phase present. For example, lowering carbon content, improves pitting resistant, but it will be detrimental when present as precipitated carbide. Boron is beneficial when in solid solution, but detrimental when precipitated as intermetallic compound.
2.4 **Objective Of This Investigation**

The needs for surface analysis as portrayed in the literature survey lead to the following objectives for this investigation:

1. To provide a better understanding to the phenomena of the existence of active and inactive pits.
2. To develop a method for determining whether pits initiated in stainless steel after exposure to chloride containing media are still active.
3. To estimate potential variation around an active pit with respect to a standard reference electrode.
4. To develop simple models representing active and inactive pits for pits associated with inclusion and inclusion free pits.
5. To investigate the mechanism of pitting corrosion resistance of stainless steel by molybdenum.

It is the aim of this work to attain the objectives by means of a combination of the surface chemistry and electrochemistry. The concept of a local cell whereby accumulation of anions at anode and cations at cathode was chosen. The chloride to magnesium ratio which was shown significantly correlated to surface electropotential by Castle and Epler [91] in their work on aluminium brass has been used as a basis for the study of surface electrochemistry of a local cell (i.e pit). The XPS and AES are the main tools for the surface
chemistry work, along with other surface chemical analysis techniques i.e EDXA and, to a small extent SIMS. It is hoped that this work will be useful not only as an addition to the previous and current knowledge in pitting corrosion but also to offer a practical means for ascertaining the conditions in pitting attacks in real situations outside laboratories.
CHAPTER 3

3  Surface Analysis

3.1  X-Ray Photoelectron Spectroscopy (XPS)

3.1.1  Introduction

XPS is a relatively new technique for surface analysis, originating from a phenomenon in physics known as the photoelectric effect which has been well understood since the beginning of this century. Kai Siegbahn and his co-workers [92] were the people who first realised the usefulness of X-Ray induced photo-emission and made use of the phenomenon called photopeaks. They were also the first who found that XPS technique was able to determine the chemical state of most elements and that it was surface sensitive.

The development of XPS which has taken place since its discovery by Siegbahn's group in 1954, includes the selection of the X-Ray source, the high vacuum electrostatic analyser system, the detection system, and data handling systems. The X-Ray source is chosen to optimise the resolution and intensity. Mg and Al are the examples of the X-Ray anode elements which have been universally adopted. The characteristic X-Ray lines, Kα, of Mg and Al have natural line widths of 0.7 and 0.8 eV respectively. The low energy of Kα radiation of Mg(1253 eV) and Al(1486.6 eV), is ideal for electrostatic electron
energy analyzers. The cylindrical and hemispherical mirror analyzer are typical types of analyzer available in the present commercial XPS instruments [93].

3.1.2 Photoelectron Emission and Ion Decay

When a sample is irradiated with monochromatic photons of frequency $\nu$, electrons from all the orbitals of the atoms of the sample with binding energy $E_b$ (with respect to the Fermi level and for $E_b$ up to the value of the photon energy) are excited, and released with a kinetic energy, $E_k^p$, (Fig. 6a). The process follows the Einstein relation with a correction for the spectrometer work function, $\phi_a$. The relation is given by

$$h\nu = E_b + E_k^p + \phi_a$$  \hspace{1cm} (24)

where $h$ is a Planck constant; so the electrons emitted will have a specific kinetic energy characterizing the elements present in the sample surface.

The kinetic energy is generally measured only after the electron has emerged from the solid into vacuum. The mean free path of electrons with energies between 100 to 1000 eV is in the range of 5 to 25 Å in most solids [94]. This represents the thickness of sample surface from which informations can be provided by XPS.

The 'sampling depth' (the sample space from which all possible emergent electrons are collected) decreases as $-\sin \theta$, where $\theta$ is the
Fig. 6 Basic processes involved in photoelectron, X-Ray, and Auger spectroscopy.
electron take-off angle as measured with respect to sample surface [95]. The electrons excited deeper in the solid may also escape the solid but lose energy on their way to the surface and are detected in the background on the high binding energy side of the peaks [96]. The attenuation of electron energy due to inelastic scattering results in the intensity of electron escaping the solid being less than that which is originally excited.

The number of electrons detected, I, from a given quantum level of a species of the sample is given by the relation [97],

\[ I = J \sin \psi \int_0^\infty \exp(-x/\Lambda \sin \theta)dx \cdot \exp(-d/\Lambda \sin \theta)T \]  \hspace{1cm} (25)

\( J \) is the photon flux and \( \psi \) is its angle to the sample. \( z \) is the concentration of electrons of a given element in a defined valence state. \( \delta \) is the photo-emission cross section for the appropriate element and quantum number, where \( \delta \) is a function of photon energy and the incident angle relative to electron collection angle. The integrated part represents the 'sampling depth'. \( \Lambda \) is inelastic mean free path, which is a strong function of the electron kinetic energy and a weaker function of the crystal and the electronic structure of the sample. The term, \( \exp(-x/\Lambda \sin \theta) \), is an attenuation factor from depth \( x \) in the sample. For monolayer adsorption this factor \( \Lambda \sin \theta \) is unnecessary since all electrons from the monolayer may be assumed to escape without self attenuation. The term, \( \exp(-d/\Lambda \sin \theta) \), is related to the attenuation of the electron by a contaminant layer of thickness \( d \). \( T \) is the instrumental collection efficiency.
Ejection of electrons from an atom will take the atom to an excited state. An ion with an electron vacancy in a core level can decay in energy by any of these three processes: emission of an X-Ray photon (X-Ray fluorescence), emission of an electron in an Auger process and emission of an electron in a Coster-Kronig process. Electrons released by the Auger and Coster-Kronig processes will effect the photoelectron spectrum. For example, Coster-Kronig processes for a decay of L\textsubscript{1} and M\textsubscript{1} ions lead to broad lines for 2s and 3s photoelectrons while spectrum of Auger electrons will overlap with photoelectron spectrum in which only the stronger Auger lines will be able to be detected.

3.1.3 Chemical Shift

The systematic shift in photoelectron peak and Auger line positions resulting from changes in the chemical structure and oxidation state of chemical compounds has been under investigations since 1958 when Siegbahn, et al. [98] discovered that the chemical difference between copper and its oxide was clearly distinguishable by XPS. For most metals the shift is frequently in the order of 1eV per unit charge in oxidation state. There are cases where the chemical shift of oxidation state of certain metals are too small to be detected eg. silver and cadmium [98]. This problem has however been resolved by using the Auger chemical shift which in such cases happens to give a large shift.

It has been found that the chemical shifts in X-Ray excited
Auger lines are usually larger and very different from those in photoelectron lines [99]. The differences between the kinetic energy of photoelectron, $E_k^p$, and the kinetic energy of the X-Ray excited Auger electron, $E_k^a$, has been called Auger parameter, $\alpha$, and it has a unique value to each chemical state. It can be accurately determined because the static charge effect (charging effect) which normally present in chemical shift calculation of photoelectron and Auger lines, is cancelled [100].

$$\alpha = E_k^a - E_k^p$$  \hspace{1cm} (26)

### 3.1.4 Charging Effect

During X-Ray irradiation, nonconductive samples normally acquire a positive surface potential since, because of poor conductivity, charge lost from the surface by photo-emission is not replaced. This positive potential reduces the kinetic energy of the photoelectron and results in higher apparent binding energies than the true values. This problem can be solved with a high reliability that is by flooding the sample surface with low energy electrons to replace the photo-emitted electrons. The usual practice in Scanning Electron Microscopy (SEM) of forming a metallic overlayer on the surface, e.g. depositing with gold is impossible because the layer then obscures the surface chemistry of the sample.
3.1.5 XPS: Basic Instrumentation

The major parts in instrumentation for XPS are X-Ray source, electron energy analyzer, electron detector and data system for data acquisition and display. An X-Ray source consists of a heated filament and a target anode. Electrons emitted from the filament are accelerated toward the target anode by electrostatic potentials applied between the two, i.e. a positive potential is applied to the anode while the filament is maintained at, or close to ground. Electron bombardment of the target anode causes the emission of X-Rays, Bremstrahlung radiation and electrons. A foil window of suitable material (usually aluminium) filters the radiation so that X-Rays are the predominant component reaching the sample.

The electron energy analyzer has the function of measuring the energy distribution of electrons emitted from a sample. Electrostatic analyzers are commonly used in the commercial spectrometers now available because of the relative ease of stray field cancellation by using mu metal shielding. A variety of analyzer geometry has been adopted in XPS instruments, 180° or 150° hemispherical deflector and cylindrical mirror are the most common [93].

A resolution requirement for XPS is around 0.2 eV at kinetic energy of 1000 eV. This is difficult to achieve with adequate sensitivity. Thus electrons are normally pre-retarded to lower kinetic energies before entering the hemispherical analyser. The pass energy of the analyser is set, typically at 50 eV giving a resolution requirement of 50/0.2 or 250. This is easily attainable by modern spectrometers.
The detector widely used to collect electrons from analyzer is a channel electron multiplier (channeltron). The channeltron has a continuous dynode consisting of a tube of semiconducting glass for its inner surface of which has been processed to give a high secondary emission coefficient of electron. A gain as high as $10^8$ can be obtained. In general it has very good resistant to poisoning by contamination released from samples. The final output of detector, which is a series of pulses, is fed into a pulse amplifier/discriminator and interpreted via a data handling system i.e multichannel analyzer and computer.
3.2 Auger Electron Spectroscopy (AES)

3.2.1 Introduction

The Auger process was discovered by Pierre Auger [101] in 1925 and the use of electrons emitted from this process, Auger electrons, for surface study technique was pioneered by Lander [101] in 1953. The progress on the development of AES in experimental field is rather slow, only in the last 10 years the well equipped and high spacial resolution Auger electron spectrometers have been commercially available. Nowadays, Auger electron spectrometers are coupled with finely focused scanning electron microscopes and used in conjunction with inert gas ion sputtering for sample depth profiling.

In AES instruments, for the production of Auger electrons, an electron beam is used instead of X-Rays. There are advantages to using an electron beam, of which the most important are: a) it can be obtained with an intensity many orders in magnitude greater than is possible for an X-Ray source and b) it can be focused to a very fine spot. These two combined mean that practical analyses can be carried out on region as small as 0.1 μm. Although soft X-Rays can be focussed, it needs a high technology to produce a beam of reasonable intensity and the current limit of the analytical region is ~150 μm.
3.2.2 Auger Process

If a vacancy of a core level of an atom has been created by electron or photon bombardment, an immediate transition of electron from higher energy subshells will take place to fill the hole. The energy released during the transition will be transformed into X-Rays or transferred to another electron in the outer level which is then ejected from the atom as an Auger electron, (Fig. 6b) The electrons ejected are designated according to electronic orbital subshells associated with vacancy, transition and the level from which electron is ejected. The kinetic energy of an Auger electron, $E_{KL_1L_2}$, originating from a transition, say, $KL_1L_2$ can be estimated by a relation below [101],

$$E_{KL_1L_2} = E_K(z) - E_{L_1}(z) - E_{L_2}(z+\Delta) - \Phi_a$$  \hspace{1cm} (27)

The K state represents the band level in which the original vacancy occurred. The $L_1$ level is the level for an electron which filled the original vacancy, and the $L_2$ is the level from which the Auger electron was ejected. All the energy states are relative to the Fermi level. $\Phi_a$ is the work function of the analyzer. The term, $\Delta$ is a correction term introduced because the energy of the final doubly ionized state is somewhat larger than the sum of the energies for individual ionization of the same level. Experimental value for $\Delta$ lie between $1/2$ and $3/4$.

The Auger electron energies are characteristic of the target material and independent of the incident beam energy. The electron transitions in an atom which lead to the ejection of Auger electrons,
in fact have various transition probabilities \cite{102}. The inner shell vacancies created due to the electron transition or ejection, will soon be filled up by additional Auger processes and a series of repetitive Auger process is called a vacancy cascade. A spectrum derived from Auger electrons has a large background consisting mainly of backscattered primary electrons and inelastically scattered Auger electrons. The electrons contribute to the spectrum have come from a depth, 5 to 20 Å of a surface which corresponds to the mean free path of the electron. The mean free path of the electron is independent of the incident primary electron beam energy.

The total number of emitted Auger electrons is related to the electron mean free path, \( \lambda \), in a simple expression viz.

\[
N = N_e \int \exp(-x/\lambda) dx
\]

(28)

where \( N_e \) is the number of Auger electrons generated at a depth \( x \) from the surface.

The emitted Auger current (signal intensity) depends on many factors as shown by an expression below \cite{103}. It shows the emitted Auger current produced by a \( wxy \) Auger transition, \( I_{\alpha}^{(wxy)} \), from an element, \( \alpha \), of a sample, excited by an incident electron beam of diameter, \( d \), and energy, \( E_p \), as depicted in Fig.7.

\[
I_{\alpha}^{(wxy)} = \iint \int_{\Omega} I_p(E,E_w) \sigma_{\alpha}(E,E_w) N_{\alpha}(x) \gamma_{\alpha}(wxy) \left[ \exp(-x/\lambda) \right] dx\theta dE dx
\]

(29)
Fig. 7  Schematic representation of source volume of Auger electrons.
where $I_p(E, x)$ is the excitation flux density, $\sigma_\alpha(E, E_w)$ is the ionization cross section of core level $\alpha$, $N(x)$ is the atomic density of element $\alpha$ at a depth $x$ from the surface. The term, $\text{Exp}(-x/\lambda)$, is the Auger electron probability for escape, $\gamma_{\alpha}(wxy)$ is the $wxy$ Auger transition factor.

3.2.3 Charging Effect

Charging effects are a particularly severe problem in Auger spectroscopy. Instability of the surface potential due to charging will make an Auger spectrum distorted and meaningless. However, this problem can be overcome by choosing the proper angle of incidence and energy of the incoming primary electron beams. This method will affect the ratio of the number of secondary electrons leaving the target to the number impinging on the target. This ratio will determine whether the surface charge is stabilized or otherwise become negative or positive. It is not normally a problem with thin surface films.

3.2.4 AES: Basic Instrumentation

Most of the devices used in AES are similar to those in XPS except in the system for the production of the primary excitation beam and in secondary electron imaging, thus an AES instrument has an electron gun to produce a primary electron beam and other related facilities such as an electromagnetic lens system and scan coils. A modern AES system is combined with SEM in order to make the best use
of the high spacial resolution of AES. The position of an analytical point on the sample surface can be then precisely located by the help of the SEM image. High vacuum is also required in AES technique. This in practice is achieved in a bakeble system capable of better than $10^{-10}$ torr ultimate pressure. The presence of the electromagnetic lens and scan coils in the Auger electron spectrometer column, however, makes bakeout difficult. Baking temperatures are typically about 200°C sufficient to drive off the adsorbed water and carbon contaminant in the system. If the residual gas in the vacuum system is inert i.e argon or helium, a pressure of not higher than $10^{-5}$ torr is tolerable, eg. during simultaneous Auger analysis and ion beam profiling. Argon gas present in the analyzer chamber during ion beam profiling is constantly cleaned by a titanium sublimation pump. The sublimation pump is also used to reduce the number of active gases to a partial pressure of well below than $10^{-10}$ torr.
3.3 Energy Dispersive(X-Ray) Analysis (EDXA)

3.3.1 Introduction

The EDXA technique which employed a focussed electron beam for the production of X-Ray characteristic from target materials is a well established technique for bulk analysis. The use of this technique in microanalysis of organic and inorganic materials is also wide spread. It becomes more significant when combined with AES because a simultaneous surface and inner layer compositions of a sample can be obtained.

3.3.2 X-Ray Emission

When a beam of energetic electrons (~ one to tens of KeV) impinges a sample, core level electrons will be ejected. The vacancy in a core level will be reoccupied by electrons from the outer quantum levels. This will be followed by emission of photons (characteristic X-Rays) of energy corresponded to the difference between electron energy levels (states) involved. Auger electrons are also produced in this process (Fig.6c). The deceleration of the beam electron in the Coulombic field of tightly bound electrons and atom nucleus (if the electron energy in the order of MeV) will result in the emission of continuous X-Rays (Bremsstrahlung) of energy between zero to the value of those possessed by the incident electrons. Thus the spectrum resulting from the process consists of peaks of characteristic X-Rays with a continuum X-radiation (Bremsstrahlung) as its background.
The intensity of the X-Rays detected from a sample surface is less than the characteristic yield of the bulk due to backscatter loss and absorption [104]. If the attenuation of the X-Rays intensity is caused by absorption, the total intensity of characteristic X-Rays, \( I \), emerging at angle \( \theta \) relative to sample surface (Fig. 8a) is given by [104]

\[
I = \int_{0}^{\infty} \phi(\rho x) \exp\left(-\frac{\mu}{\rho \sin \theta}\right) d(\rho x)
\]

where \( \phi(\rho x) d(\rho x) \) is the intensity of X-Ray generated in an element \( d(\rho x) \) at depth \( X \) below the surface which has a density, \( \rho \) which is a function of mass thickness (\( \rho x \)). \( \mu/\rho \) is the X-Rays mass attenuation coefficient of the sample for a characteristic line of interest. \( \theta \) is the X-Rays take-off angle and \( \mu \) is absorption coefficient. The intensity of the emerging X-Ray radiation is dependent on sample composition (atomic number of elements present) and depth of penetration of the electron beam which is determined by its energy.

Kanaya and Okayama [105] have derived an expression for the maximum electron range in solid, as

\[
R = 0.0276E_0^{1.67}/(Z^{0.889}\rho) \text{ mm}
\]

where \( E_0 \) is the electron energy in KeV, \( \rho \) is the density of solid in g/cm\(^3\), \( Z \) is the atomic number and \( A \) is the atomic weight in g/mol. The depth range normal to the surface in a tilted sample (Fig. 8b), \( R(\beta) \), is given by

\[
R(\beta) = RCos \beta.
\]
Fig. 8 Interaction volume and geometrical arrangements with tilt angles, $0^\circ$, and $\beta$. $\theta$ is X-Ray take-off angle.
where $\beta$ is the tilt angle. The size of a region in which the beam electrons interact with the solid (interaction volume) depends linearly on the energy of beam electron and the atomic number of target material but inversely on the tilt angle of the sample. The results of Monte Carlo calculations by Goldstein, et.al [104,106] have clearly shown these relationships.

3.3.3 EDXA: Basic Instrumentations

The electron gun with a focusing system and an X-Ray detector are the main components of the EDXA system. The electron gun and focusing system are as described in section (3.2.4). The most common X-Ray detectors for EDXA are solid state detectors (e.g., the lithium-drifted silicon detector) with a detection capability (detector resolution) of better than 150 eV. The X-Ray signal from the sample passes through a thin beryllium window of the detector before reaching the lithium-drifted silicon in the detector. The interaction of X-Ray photon with Si atoms lead to the ejection of photo and Auger electrons which in turn lose energies by subsequent interactions. The electron-hole pairs formed in this process are swept apart to form charged pulses when a bias voltage is applied across the Si(Li) detector. The charge pulses are then converted into voltage pulses by a charge-sensitive pre-amplifier before amplified and fed into data system.
3.4 Surface Analysis Equipment:

The MA500 Auger Lab

MA500 Auger Lab is an Auger microprobe instrument built by VG Scientific Co., United Kingdom. The MA500 Auger Lab used in this work also has facilities for other surface study techniques, XPS, EDXA, and XRF (X-Ray Fluorescence Spectroscopy) as well as an argon ion gun for surface profiling of samples. It is a high resolution Auger electron microprobe where it is possible to attain a spatial resolution as small as 100 nanometers for analytical work using a very low beam current. It also functions as a scanning electron microscope with a secondary electron imaging resolution around 200 Å. The picture of the machine and its physical arrangement are shown in Fig.9, Fig.10, and Fig.11.

3.4.1 Electron Gun

The electron gun of MA500 machine operates at 1 KV to 30 KV. It has two electromagnetic condenser lenses for reducing the electron diameter and an electromagnetic objective lens for focusing. A beam spot of size about 130 nanometers is obtained when a beam current of around about 4 nA is used. The beam spot size, \( d \), and beam current, \( i \), has been found to follow a relation \([107]\),

\[
d = 66 \sqrt{i}
\]  

(33)
Fig. 10  The physical arrangement of the MA500 instrument.
Fig. 11 The arrangement of the MA500 instrument chambers. Samples are transferred into analyser chamber via past entry lock and preparation chamber.
where \( d \) in nanometer and \( i \) in nA.

An electromagnetic deflection system and electromagnetic stigmators have been mounted around the centre tube inside the objective lens. Extractor apertures are placed immediately in front of its filament to control the initial beam size (beam current). There is also an externally adjustable final aperture blade, positioned at the final lens centre for a final control of spot size. A choice of 3 apertures or wide open is obtained. Fig.12 schematically illustrates the position of the components of the electron gun.

3.4.2 The Electron Energy Analyser

The electron energy analyser of the MA500 machine is a \( 150^\circ \) spherical sector analyser with a mean radius of 10 cm fitted with a channeltron electron multiplier detector. A three different size slits are available which are externally selected to control the angular dispersion of electrons passing through the analyser and hence its resolution. The size of the slits are 2, 1, and 0.5 mm.

The analyser acts as a narrow pass filter letting through only electron with energy \( E \) (\( E = HV \), where \( V \) is the potential difference between inner and outer hemispheres (in Volts) and \( H \) is a constant determined by the physical dimensions of the analyser). The sample is at earth potential. Electrons emitted from the sample are transmitted to the analyser by the electrostatic lens. A retarding potential, \( R \),
Fig. 12   MA500 Electron gun.
is applied between the sample which is at earth potential and the electrical centre point of the 'hemispheres' of the analyser. Thus the electrons will be retarded in energy by an amount \( R \) (eV) immediately before entering the analyser. The kinetic energy of an electron emitted from the sample is therefore given by,

\[ K = R + E + \phi_a \]  

(34)

\( \phi_a \) is the work function of the analyser materials.

The analyser can be operated in two modes:

1. **Constant Analyser Energy (CAE)**

   In this mode, pass energy \( E \) is fixed and \( R \) is scanned accordingly, allowing only electrons with energy \( E \) (pass through the analyser. The spectrometer control unit of the MA500 machine has a facility for controlling pass energy either manually or by computer control. Under computer control, the choice for pass energies are 2, 5, 10, 20, 50, 100, and 200 eV.

2. **Constant Retard Ratio (CRR)**

   In this mode, the ratio of kinetic energy, \( K \), to pass energy, \( E \), is kept constant during spectrum. The retard ratio, \( k \), is defined by

\[ k = (K - \phi_a)/E = K/E, \quad \text{where } \phi_a \approx 4.2 \text{ eV}. \]  

(35)

Since \( E \) varies with \( K \) to maintain a constant \( k \), a second voltage
supply is used to ramp the hemispheres separately and with opposite polarity. The spectrometer control unit of the MA500 machine only allows retard ratios of 1, 2, 4, 10, 20, 50, and 100:1 to be selected either manually or via computer control.

3.4.3 X-Ray Source (for XPS)

A twin anode type X-Ray source is attached to the MA500 machine for XPS experiments. It has magnesium on one side and aluminium on the other (Fig.13). This gives two independent X-Ray lines i.e. Al Kα at 1486 eV and Mg Kα at 1253 eV. The X-Ray source is operated with its filament near earth potential and the anode at a positive potential from 0 to 15 KeV.

3.4.4 X-Ray detector (for EDXA)

A Si(Li) solid state X-Ray detector is utilised to enable X-Rays emitted from a sample due to electron beam excitation (EDXA) to be detected. It has an active area, of 10 sq. mm and sensitive depth of 3 mm. The resolution is 158 eV FWHM at 5.9 KeV. A 1 mm aperture is fitted in front of a beryllium window in order to reduce problems of detector saturation.

3.4.5 Argon Ion Source for Depth Profiling

An argon ion gun model A21 VG Scientific, UK, is mounted on the analyser vessel. Ion beam energy can be controlled between 0.5 KeV
Top, air view of filament and water connections

Fig. 13 X-Ray Source.
and 10 KeV. An electrostatic lens with a variable power supply from 0 to 10 KV is used to focus the ion beam. The ion beam current which can reach in the order of 100 uA is dependent on accelerating potential and gas pressure. At energy 6 KeV, focus 3 KV, and gas pressure about $2.0 \times 10^{-5}$ torr, the beam current obtained is about 30 uA. A very high purity of Argon gas is required in order to avoid any unwanted chemical reactions occurring on the sputtered sample surface and contamination of the analyser vacuum system. Argon gas of 99.999% purity has been used throughout this work. In order to get rid of any trace of oxygen, water, or hydrocarbon contamination the argon gas has been passed through a small furnace containing titanium powder before injecting into the MA500 analyser chamber.
3.5 Acquisition and Presentation of Data

3.5.1 Data Acquisition

The collection of spectra and processing of data of AES, XPS, and EDXA have been done through Link Computer Series 860. This computer has also been used to control retarding potential, ramp potential of analyser hemispheres and spectral collection time. All these have been acquired by means of a readily available software system from Link Computer Co., which is technically known as Multi-Spec Software system.

There is a variety of modes for data output namely, wide spectra (spectra covering a whole energies of interest), individual peak spectra, and maps (two dimensional data representation of the entire area of interest of the sample surface). Mapping can be carried out in AES and EDXA, not in XPS since the former allows spatial resolution while the later does not. The use of a computer enables the electron beam to be scanned automatically over a selected area in a 128X128 matrix. There are also facilities for transferring the spectral and maps data from the Link Computer storage to the Prime Computer of Surrey University for further data processing operations, such as representing maps of elemental concentration in contour or three dimensional form (Fig.14 and Fig.15). The software for the extra facilities of data manipulation have been prepared by Richardson [108] of The ESCA Users Group of Surrey University.
Fig. 14  Chlorine Auger map of an active pit in stainless steel.

Contours:

- 80% of maximum intensity.
- 50% of maximum intensity.
- 20% of maximum intensity.
Fig. 15  A three dimensional map of chlorine Auger of the same pit as Fig. 14.
The peak heights (\(\wedge\)) indicate the intensity of the chloride ions and the mesh (\(\wedge\)) indicates the zero offset level.
The AES spectra obtained are processed in normal (integral) mode, not in the conventional differential mode. The concentration of elements obtained from AES and XPS data have been calculated from the spectra of the individual peaks. The area of each peak has been corrected for a linear background.

3.5.2 Presentation of Data

AES Data

AES point analysis data are either presented qualitatively or semi-quantitatively, depending on the objective of the analysis. For an example of the presentation of qualitative data, a full spectrum (Fig. 16) is labelled according to the peak position of the elements concerned. The height of the peaks in the spectrum indicates the rough amount of elements present in the surface. It is possible to compare the elemental surface concentration of different samples by using this method of data presentation providing the condition for AES are held constant. Another qualitative presentation of AES data is in the form of maps. The level of concentration of the element present can be read from the contour lines of a contour map or visualised at the height levels of a three dimensional map. The data of the ratio of net peak height over background, \((P-B)/B\), have been used to construct the maps (Fig. 14, Fig. 15). The use of data \((P-B)/B\) will eliminate topographical effects [109], such as a defect or unsmoothed surface, which will affect the take-off angle and hence change in absorption of the emitted radiations.
Fig. 16 An example of a full Auger spectrum (wide scan) with all peaks are labelled accordingly.
For a semi-quantitative presentation of data, individual peak areas, corrected for a linear background have been used to calculate the relative concentration of elements in unit of percentage of total peak area, as follows:

\[ \text{Normalized Peak Area } 1 = \left( \frac{A_1}{\sum_{i=1}^{n} A_i} \right) \times 100 \]  

(36)

where \( A_i \) (i=1, 2, 3,......n) are the individual peak area of elements.

The normalized peak areas of elements in each set of data have been added up subsequently one another in order to construct a cumulative concentration diagram as shown in Fig.17. By this way the level of the elements present in the different points across an area of interest can be easily visualised. The width of the gap between the respective lines in the plot represents the relative amount of the element presents. Fully quantitative analysis requires knowledge of the relative sensitivities of the elements concerned. There is no agreed standard set of values, as there is in the case of XPS, and values have been determined concurrently with the corrosion work. The results are discussed in section 3.5.3 and quantitative comparison of XPS and Auger data are made in chapter 5. The semi-quantitative diagrams used in the thesis, ie. based on equation (36) over estimate magnesium and nickel by a factor of about 2.0 and molybdenum by a factor of about 3.5.

The elements which have been taken into account in this AES work
Fig. 17 Cumulative concentration diagram (top) and non-cumulative concentration plot (bottom) of an active pit in type 304 stainless steel.
are Fe, Cr, Ni, Mo, O, Mg, and Cl. Elements such as Si, Mn, S and Cu are in general neglected because of their very low concentration (below AES detection level) in the normal surface of steels. However, in the exceptional case of inclusions Mn, S, and Cu show very strong intensities and have been included in Auger maps of pitted surfaces. High signal intensity and non-overlapped peaks have been taken as the basis for the choice of appropriate Auger peaks for the quantitative work. The Auger peaks chosen are at 703 eV for iron, 848 eV for Ni, 529 eV for Cr, 186 eV for Mo, 1186 eV for Mg, 510 eV for O, 181 eV for Cl and 272 eV for C.

The Cl peak at 181 eV is very close to Mo peak at 186 eV and in all cases they overlap on each other. In order to have a correct peak area for both Cl and Mo, the Mo peak at 221 eV which signal intensity is lower than that at 186 eV, has been used. A factor which relates the peak areas of Mo at 186 eV and 221 eV has been calculated from high purity Mo metal (99.995%). The slope of a plot of peak areas at 181 eV against peak areas at 221 eV, represents the factor. From Fig. 18 the factor was found to be equal to 1.465. The different peak areas for the related peaks were obtained by changing the electron beam current while other experimental parameters were retained. This factor was then used to obtain the peak areas of Cl at 181 eV and Mo at 186 eV. The relations between the peak areas of Mo at 186 eV, Mo at 221 eV and Cl at 181 eV are as follows,

\[ Mo(186) = G_{Mo}(221) \]  \hspace{1cm} (37)
Fig. 18 The relationship between Auger signal intensities of Mo(186 eV) and that of Mo(221 eV).
\[
\text{Cl}(181) = A - \text{Mo}(186) \tag{38}
\]

\[ G = 1.465 \]

where \( \text{Mo}(186) \), \( \text{Mo}(221) \), and \( \text{Cl}(181) \) are the peak areas of Mo at 186 eV(calculated) and 221 eV(measured), and Cl at 181 eV(calculated) respectively. A is a measured area of a combined peaks of \( \text{Mo}(186) \) and \( \text{Cl}(181) \).

**EDXA Data**

The EDXA technique has only been used for qualitative analysis. Full X-Ray spectra for energies from 0 to 10 KeV (Fig.19) have been used for the qualitative representation of EDXA data. The peaks in the spectra have been labelled accordingly, where the height of the peaks indicating the amount of elements present deep below the surface of the sample. The X-Ray maps have also been produced using the same routine as used in Auger mapping.

**XPS Data**

The area of XPS spectra of individual peaks corrected for a linear background, have been used to calculate the concentration of elements in atomic percent. The sensitivity factors of elements used in this work, as listed in Table 1, are based on the work of Jorgensen and Berthou [110] and from the previous results of researches carried out by The ESCA Users Group of Surrey University [111,112].
Fig. 19 An example of an X-Ray spectrum with all peaks are labelled accordingly.
Table 1. Elemental sensitivity factors for XPS analysis and photoelectron peaks

<table>
<thead>
<tr>
<th>Element</th>
<th>photoelectron peak</th>
<th>binding energy (eV)</th>
<th>sensitivity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>1s1/2</td>
<td>284</td>
<td>0.27</td>
</tr>
<tr>
<td>O</td>
<td>1s1/2</td>
<td>532</td>
<td>0.60</td>
</tr>
<tr>
<td>Fe</td>
<td>2P3/2</td>
<td>710</td>
<td>1.80</td>
</tr>
<tr>
<td>Cr</td>
<td>2P3/2</td>
<td>575</td>
<td>1.10</td>
</tr>
<tr>
<td>Ni</td>
<td>2P3/2</td>
<td>855</td>
<td>1.70</td>
</tr>
<tr>
<td>Mo</td>
<td>3d5/2</td>
<td>230</td>
<td>1.30</td>
</tr>
<tr>
<td>Cl</td>
<td>2P1/2,3/2</td>
<td>202</td>
<td>0.42</td>
</tr>
<tr>
<td>Mg</td>
<td>1s1/2</td>
<td>1305</td>
<td>2.24</td>
</tr>
</tbody>
</table>

Table 2. Elemental Sensitivity factors for AES analysis (determined in this work) and Auger peaks.

<table>
<thead>
<tr>
<th>Element</th>
<th>Auger Peak (eV)</th>
<th>sensitivity factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>181</td>
<td>0.72</td>
</tr>
<tr>
<td>Mg</td>
<td>1186</td>
<td>1.54</td>
</tr>
<tr>
<td>Cr</td>
<td>529</td>
<td>0.73</td>
</tr>
<tr>
<td>Ni</td>
<td>848</td>
<td>1.21</td>
</tr>
<tr>
<td>Fe</td>
<td>703</td>
<td>0.63</td>
</tr>
<tr>
<td>Mo</td>
<td>186</td>
<td>2.54</td>
</tr>
<tr>
<td>O</td>
<td>510</td>
<td>0.71</td>
</tr>
</tbody>
</table>
Atomic % of element 1 = \( \left\{ \frac{A_i}{S_i} \right\} \times 100 \) \( i=n \)

(39)

where \( A_i (i = 1, 2, 3, ..., n) \) are peak areas of elements, \( 1, 2, 3, ..., n \), and \( S_i (i = 1, 2, 3, ..., n) \) are sensitivity factors of elements, \( 1, 2, 3, ..., n \).

The XPS peaks used in this work are shown in Table 1. Peak area of \( Mg_{1s} \) has been corrected for \( Cl_{KLL} \) Auger peak by means of a simple peak area ratio calibration. A thin layer of pure sodium chloride was analysed for the spectra of \( Cl_{KLL} \) and \( Cl_{2p} \). The ratio of the peak areas of \( Cl_{KLL} \) to of \( Cl_{2p} \) calculated is about 0.424. The ratio was then used to estimate the peak area of \( Mg_{1s} \) by using the following relations,

\[
Cl_{KLL} = R Cl_{2p} \tag{40}
\]

\[
Mg_{1s} = T - Cl_{KLL} \tag{41}
\]

\( R = 0.424 \)

where \( T \) is a measured area of the combined peaks \( Mg_{1s} \) and \( Cl_{KLL} \). \( Cl_{KLL} \), \( Cl_{2p} \), and \( Mg_{1s} \) are the peak area of Auger peak, \( Cl_{KLL} \)(calculated), and XPS peaks, \( Cl_{2p} \)(measured) and \( Mg_{1s} \)(calculated) respectively. \( R \) is the ratio of \( Cl_{KLL} \) to \( Cl_{2p} \) calculated from sodium chloride spectra.

The correction using peak area ratio has also been made for the peak area of \( Mo(3d_{5/2}) \) because in \( Mo \) spectra, \( Mo(3d_{5/2}) \) and \( Mo(3d_{3/2}) \) are very close with energy separation of only \(-5 \) eV. Pure
Mo metal (99.995\%) has been used to obtain Mo spectrum from which areas of the individual peak of Mo(3d\(_{5/2}\)) and Mo(3d\(_{3/2}\)) were calculated using peak separation routine available in the Prime Computer. The peak area ratio of Mo(3d\(_{5/2}\)) to of the combined peaks of Mo(3d\(_{5/2}\)) and Mo(3d\(_{3/2}\)), was found to be about 0.56. The area of the combined peak was corrected for a linear background before applying the following relationship for obtaining the peak area of Mo(3d\(_{5/2}\)).

\[
\text{Mo}(3d_{5/2}) = 0.56P
\]  

(42)

where \(\text{Mo}(3d_{5/2})\) is the area of \(\text{Mo}(3d_{5/2})\) peak(calculated), and \(P\) is the area of combined peaks, Mo(3d\(_{5/2}\)) and Mo(3d\(_{3/2}\)) (measured).

### 3.5.3 Comparability of AES and XPS Data of Cl/Mg Ions Ratio

Some of the sensitivity factors for XPS determined by Berthou and Jorgensen [110], (using a Varian Spectrometer) were similar to those used for the ESCA3 Spectrometer [111,112]. The sensitivity factors in Table 1 are the ones used for ESCA3 which have also been the basis for the treatment of XPS data obtained from MA500 instrument because the specific sensitivity factors for MA500 have not been fully determined yet. Even though the ESCA3 and MA500 both have semi-hemispherical electron energy analysers, the latter has a lens in front of its analyser whereas the former has not. This difference results in each of them having a different transmission function. Since the transmission function is one of the parameters which
determines the value of a sensitivity factor, as shown in equation (44) [113], the two instruments are likely to have different values of the elemental sensitivity factors.

\[
n = \frac{I}{A_\text{focylTC} \cdot S} = \frac{I}{S} \quad \text{(43)}
\]

\[
S = A_\text{focylTC} \quad \text{(44)}
\]

where,

- \(n\) = the number of atoms of element per cm\(^3\) of sample.
- \(I\) = the number of photoelectrons detected.
- \(S\) = the sensitivity factor of an element.
- \(A\) = area from which photoelectrons can be detected.
- \(f\) = flux in photons/cm\(^2\).sec.
- \(\sigma\) = photoelectric cross section in cm\(^2\) per atom.
- \(\Phi\) = angular efficiency factor for the instrumental arrangement (angle between photon path and detected photoelectron).
- \(y\) = the fraction of photoelectric transitions from the given level that results in an ion in the ground state and a photoelectron of the appropriate kinetic energy.
- \(\lambda\) = mean free path for the photoelectron in the sample medium.
- \(T\) = transmission function, ie. efficiency of detection of the electrons entering the spectrometer.
- \(C\) = attenuation factor due to the hydrocarbon (contaminant) layer.

The most important ratio and that which shows greatest uncertainty in the MA500 is magnesium relative to chlorine, because
the peaks are at either end of the spectrum. A ratio of the sensitivity factor of Cl to that of Mg for the MA500 instrument however has been calculated by analysing several samples containing Cl and Mg in their surface using both the MA500 and ESCA3 instruments (equations (45) and (46)). A constant, $K$, has been determined relating the relative sensitivity factors of Cl/Mg for the MA500 to the ESCA3 value which is known (equation 49). The relative value obtained by this way has automatically included the affects of all the parameters as in equation (44).

\[
\left( \frac{\text{Cl}}{\text{Mg}} \right)_m = \frac{I_{\text{Cl}}^m}{I_{\text{Mg}}^m} \cdot \frac{S_{\text{Cl}}^m}{S_{\text{Mg}}^m}
\]

(45)

\[
\left( \frac{\text{Cl}}{\text{Mg}} \right)_e = \frac{I_{\text{Cl}}^e}{I_{\text{Mg}}^e} \cdot \frac{S_{\text{Cl}}^e}{S_{\text{Mg}}^e}
\]

(46)

where $\frac{\text{Cl}}{\text{Mg}}$ is the atomic ratio of Cl to Mg. $I_{\text{Cl}}$ is the peak area of Cl and $I_{\text{Mg}}$ is the peak area of Mg. $S_{\text{Cl}}$ and $S_{\text{Mg}}$ are the atomic sensitivity factors of Cl and Mg respectively. Indices $e$ and $m$ denote the data obtained using ESCA3 and MA500 respectively.

From equations (45) and (46) and since Cl and Mg originate from the same samples, thus

\[
\frac{S_{\text{mg}}^m}{S_{\text{Cl}}^m} = \left( \frac{I_{\text{mg}}^m}{I_{\text{Cl}}^m} \right) \cdot \frac{S_{\text{mg}}^e}{S_{\text{Cl}}^e}
\]

(47)

\[
\frac{S_{\text{mg}}^m}{S_{\text{Cl}}^m} = K \cdot \frac{S_{\text{mg}}^e}{S_{\text{Cl}}^e}
\]

(48)

\[
K = \left( \frac{I_{\text{mg}}^m}{I_{\text{Cl}}^m} \right) \cdot \frac{I_{\text{mg}}^e}{I_{\text{Cl}}^e}
\]

(49)
where $K$ is the factor relating the relative sensitivity factor of Cl/Mg for MA500 and for ESCA3. The average value of $K$ determined was 0.334. As all the XPS experiments in the work now reported have been carried out using the MA500 instrument, so the value of $K (=0.334)$ together with equation (50) have been used throughout to calculate the actual ionic ratio of Cl to Mg.

$$\left( \frac{\text{Cl}}{\text{Mg}} \right)_{\text{XPS}} = 0.334 \cdot \frac{I_{\text{Cl}}}{I_{\text{Mg}}} \cdot \frac{S_{\text{Mg}}}{S_{\text{Cl}}}$$

(50)

where $I_{\text{Cl}}$ and $I_{\text{Mg}}$ are the peak areas of Cl$_2p$ and Mg$_1s$, respectively obtained from each sample using the MA500.

In order to be able to compare Cl/Mg ions ratio of XPS results to those of the AES results, the sensitivity factors for the conversion of Auger peak areas of Cl and Mg into atomic percent have to be determined. The Auger sensitivity factors for Cl, Mg, Fe, Cr, Mo, Ni, Mo, and O have been determined using silver peak, 3d$_{5/2}$ as a standard. Pure materials used in determining the Auger sensitivity factors are magnesium, iron, chromium, nickel, and molybdenum metals, silver chloride, and iron oxide, Fe$_3$O$_4$. Fig.20 shows a typical Auger spectrum of a pure Fe$_3$O$_4$. The Auger sensitivity factors were estimated by using the following relations after taking the Auger sensitivity factor for silver as unity.

For pure metals and pure AgCl,

$$\frac{A_i/f_i}{A_{\text{Ag}}/f_{\text{Ag}}} = 1$$

(51)
Fig. 20 Auger and X-Ray spectra of pure magnetite (Fe₃O₄)
and for pure Fe$_3$O$_4$,

$$\frac{A_o/f_o}{A_{Fe}/f_{Fe}} = \frac{4}{3}$$  \hspace{1cm} (52)

where $A$ is a peak area of the respective elements. $f$ is the Auger sensitivity factor. The subscript $i$ can be Fe, Cr, Ni, Mo, Mg, and Cl. $A_o$ and $f_o$ are the peak area and Auger sensitivity factor for oxygen. The Auger sensitivity factor for silver, $f_{Ag}$, is assumed to be equal to 1. The Auger sensitivity factors determined are listed in Table 2. The atomic ratio of Cl/Mg from AES results is given by

$$\left(\frac{Cl}{Mg}\right)_{AES} = \frac{f_{mg}}{f_{Cl}} \cdot \frac{A_{Cl}}{A_{mg}}$$  \hspace{1cm} (53)

$$\left(\frac{Cl}{Mg}\right)_{AES} = 2.14 \cdot \frac{A_{Cl}}{A_{mg}}$$  \hspace{1cm} (54)

$A_{Cl}$ and $A_{mg}$ are the peak areas of Cl and of Mg obtained in each AES analysis.
4 Electrochemical Investigation

4.1 Introduction

The corrosion behaviour of metals can be easily recognised from their polarisation test curves. Information such as corrosion potential, critical current density, passive current density, passivation potential, and pitting potential given by this curves enable the corrosion property of different metals to be compared. In the present work, five type of stainless steels namely type 304, type 316, cronifer 2328, cronifer 1925LC, and cronifer 1925hMo have been investigated. Potentiostatic polarisation tests have been carried out in sulphuric acid and magnesium chloride solution. The surface chemistry of electrochemically exposed samples of 316 stainless steel were also extensively investigated by means of the XPS technique. The electrochemical history of the steels in this high chloride concentration aqueous environment will be deduced from this investigation including the role of Mo and Cr in corrosion resistant of the steels.
4.2 Experimental

4.2.1 Materials

Five types of commercial stainless steel of different molybdenum content have been investigated. The chemical composition of the steels are listed in Table 3. Only type 316 stainless steel has been investigated extensively. Experiments on other type of steels were conducted in order to obtain some evidence in support of the results of the experiments on type 316 stainless steel.

4.2.2 Sample Preparation

The samples were prepared from the commercial stainless steels (Table 3) after milling to a final thickness of about 1.0 mm from the original thickness of the steel plates of between 1 mm to 6 mm. The milling operation was carried out in the departmental workshop. The thinned plate were then cut with a die to give circular test samples of 10 mm in diameter. This dimension is suitable for the MA500 spectrometer chamber for XPS analysis. The samples were ultrasonically cleaned in acetone to remove particles and machine oil which might stick on their surface during production. No heat treatment was performed on the samples. The samples were wet ground using 240, 400, 600, and 1200 grit silicon carbide papers and followed by polishing with diamond paste to a one micron finish. The polished samples were rinsed in acetone, cleaned in tefol and thoroughly rinsed in tap water before a final rinse in acetone. The samples were then
Table 3. Compositions of the materials used (wt.%)  

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Ti</th>
<th>N</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS304</td>
<td>&lt;0.08</td>
<td>18.50</td>
<td>9.60</td>
<td>-</td>
<td>&lt;0.40</td>
<td>1.80</td>
<td>&lt;1.00</td>
<td>&lt;0.04</td>
<td>&lt;0.03</td>
<td>-</td>
<td>-</td>
<td>balance</td>
</tr>
<tr>
<td>SS316</td>
<td>&lt;0.08</td>
<td>18.60</td>
<td>11.70</td>
<td>2.20</td>
<td>&lt;0.40</td>
<td>2.00</td>
<td>&lt;1.00</td>
<td>&lt;0.04</td>
<td>&lt;0.03</td>
<td>-</td>
<td>-</td>
<td>balance</td>
</tr>
<tr>
<td>Cronifer 2328</td>
<td>&lt;0.04</td>
<td>24.10</td>
<td>27.50</td>
<td>2.60</td>
<td>2.70</td>
<td>0.69</td>
<td>&lt;0.75</td>
<td>-</td>
<td>-</td>
<td>0.60</td>
<td>-</td>
<td>balance</td>
</tr>
<tr>
<td>Cronifer 1925LC</td>
<td>&lt;0.02</td>
<td>22.50</td>
<td>24.70</td>
<td>4.90</td>
<td>1.80</td>
<td>1.50</td>
<td>&lt;0.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.04-0.08</td>
<td>balance</td>
</tr>
<tr>
<td>Cronifer</td>
<td>&lt;0.02</td>
<td>20.60</td>
<td>24.70</td>
<td>6.30</td>
<td>1.60</td>
<td>1.70</td>
<td>&lt;0.50</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.12-0.20</td>
<td>balance</td>
</tr>
</tbody>
</table>
dried in a stream of cold air. The samples were kept in a desiccator for at least one day to stabilise the surface and used within one week.

4.2.3 Test Environment

The test environments for potentiodynamic polarisation experiments were 1N $H_2SO_4$ (deaerated) and 1M $MgCl_2$ solution (freely exposed to air). Sulphuric acid was chosen because of it has widely been used in polarisation studies, therefore it is considered as a standard solution for comparative corrosion data of many materials. While the use of magnesium chloride solution in this investigation is because of its ability in characterizing the electrochemistry of the surface of the materials [91]. Magnesium chloride solution of two molar concentration of chloride ion is supposed to be able to initiate a rapid corrosion attack especially pitting. Magnesium hydroxide and basic chlorides have a much lower solubility product than those of the singly charged cations. The element thus has a strong tendency to precipitate at the cathode.

1M $MgCl_2$ solution was prepared from $MgCl_2.6H_2O$ (analytical grade), while 99.98% concentrated sulphuric acid (analytical grade) was used for the preparation of 1N $H_2SO_4$. High purity distilled water of solution conductance 0.2 $\mu$siemens, was used in the solution preparation. The distilled water was obtained from a cyclic still of The Surface Chemistry Laboratory of Surrey University which was developed by Richardson [114]. A picture of a full assembly of the
Fig. 21 Cyclic Water Purification Apparatus.
still is shown in Fig.21.

The sulphuric acid solution used in polarization experiments was fully deaerated by bubbling with high purity nitrogen gas for at least 16 hours and continuous throughout until the experiment complete. The solution of 1M MgCl₂ was not deaerated but freely exposed to air before and during the experiment. In the experiments where the pH value of MgCl₂ solution was taken as a variable, a few drops of 1M hydrochloric acid or 1M sodium hydroxide (analytical reagent) were utilised to bring the solution to a starting pH as required. The original pH value of 1M MgCl₂ solution is about 5. The pH value was changed within a range 1.8 to 8.6. PH 8.6 was the maximum pH value has been able to be established without the precipitation of Mg(OH)₂. All experiments were carried out at room temperature between 20° to 23°C. The solutions (1N H₂SO₄ or 1M MgCl₂) were consumed within 1 week after preparation.

4.2.4 Electrochemical Cell

A glass electrochemical cell was specifically manufactured and provided facilities for a Luggin probe of reference electrode, an auxiliary electrode, and a gas inlet and outlet. The stopper of the cell was also made of glass, and had a facility to support a sample holder. A pair of holes on the stopper served as the gas/air outlet. The cell can accommodate more than 200 ml solution. A schematic diagram and a picture of the cell are shown in Fig.22 and Fig.26.
Fig. 22 Schematic diagram of electrochemical cell.
Fig. 26: Electrochemical Cell
4.2.5 Sample Holder

A lack of experimental reproducibility in electrochemical study is frequently due to the effects of sample mounting procedures. Anodic polarization behaviour is distorted if crevices exist between the metal sample and mounting materials. In view of this problem a special sample holder has been designed for use in the present electrochemical investigation (Fig. 23). Other requirements have also been referred in this design, namely: a) It will be able to take a sample of size suitable for the surface analysis works, and b) It has a facility for a rapid and effective sample mounting and dismounting, which will minimize the time of handling the sample in open air before and after a test. Thus any contamination on the sample will be avoided which is especially important in the study of the surface electrochemistry of the sample.

Polytetrafluoroethylene (PTFE) has been used in making the holder. The PTFE was chosen because of its easy machinability which means an intricate design with accurate dimensions may be obtained. It is also known to be inert in many corrosion environments and has good insulating properties. Basically the holder was designed according to design of France [115] but its specification was changed to suit the needs of this present work. Some modifications have also been made especially on its front portion (Fig. 23). The front portion has been made detachable from the main body of the holder via a screw thread. This, therefore, enables the sample to be loaded in or removed from the holder with ease. The holder can accommodate a
Fig. 23 Sample holder (actual dimensions).
circular sample of 10 mm in diameter and of about 1.2 mm in thickness. A well defined exposed area, 0.5 cm$^2$ is obtained by the utilisation of a replaceable PTFE gasket with internal diameter 7.98 mm.

An excellent electrical contact between a sample and the working electrode terminal of a potentiostat has been attained by the use of a flattened end copper wire coupled with a stainless steel backplate (Fig. 23). The copper wire was insulated from the electrolyte by passing it through the handle of the holder which was also made of PTFE. When the threaded PTFE bolt is tightened up from the rear of the holder with sufficient torque, the backplate together with the sample will be pushed forwards compressing the gasket. By this way, only the well defined area of the sample will be left exposed to the electrolyte. The corrosion products and evolved gas are prevented from accumulating at the sample surface by an oblique entrance angle.

All screw threads on the male and female parts of the holder have been cut with precision to prevent leakage. Neither leakage nor crevice effects was observed throughout the period of this research so long as the gasket was in good condition. The picture in Fig. 24B exhibits a typical exposed sample using this holder. The distinct demarcation between corroded and protected areas, demonstrates the effectiveness of the seal. It also has no mark of crevice effects. When a sample from the same steel (type 304) whose unexposed area was masked with organic lacquer (lacomit) was exposed in the same test condition as for the sample in Fig. 24B (polarisation test from rest potential to +500 mV(SCE)), a deep crevice occured at the area under...
Fig. 24  The appearance of sample surface of type 304 stainless steel after polarization test.
A) Masking unexposed area with lacomit.
B) Using the sample holder.
the edges of the lacomit mask (Fig. 24b). This feature clearly demonstrates the superiority of mounting by the holder against for example, the simple lacquer masking technique.

4.2.6 Reference Electrode

Reference electrode used in this electrochemical investigation was a calomel electrode (Type SR1, Russel pH, Ltd.). It was placed in a separate compartment containing saturated KCl solution and connected to the electrochemical cell via a Luggin probe (Fig. 26). The Luggin probe tip was positioned 2 mm from the working electrode (sample) surface. The distance from the tip of Luggin probe to the working electrode surface was within the range of which no apparent effects of electrode screening or resistance error [116]. If the probe tip is too close to the working electrode, it tends to screen current from electrode, and if it is placed too far away, appreciable resistance or Ohmic error will be introduced into the potential measurement.

4.2.7 Auxiliary Electrode

A one centimeter square platinum sheet was used as auxiliary electrode. It was always kept in its glass container or in distilled water when was not in use to prevent atmospheric dust contaminant. The auxiliary electrode was connected to the electrochemical cell by means of a male-female glass joint and separated from the bulk solution in the cell by a glass frits at the joint. This will prevent electrochemical reaction products in auxiliary electrode compartment
from mixing with the bulk solution.

4.2.8 Polarization Experiment

The potentiodynamic polarization experiments were conducted on all steels as listed in Table 3, to obtain their potential versus current density curves in both 1N H₂SO₄ and 1M MgCl₂ solutions. The samples were mounted in the sample holder as described in section 4.2.5. A potentiostat, Wenking Model LT78, Bank Elektronik was used to control potential and the potentials applied to a working electrode were swept by using Linear Sweep Generator, Chemical Instrument (UK). The changes of current as applied potentials were increased, were recorded by a chart recorder. The picture in Fig.25 shows the equipments used in the polarization experiments.

a) Anodic Polarization In 1N H₂SO₄ Solution

The anodic polarization experiments were carried out in fully deaerated 1N H₂SO₄ (see Section 4.2.3). Samples were pre-polarized at -600 mV(SCE) in the same solution for at least 5 minutes until a steady rest potential was achieved in another two minutes of checking. This treatment was to ensure that all the samples have the same surface state. Pre-polarization was continued until a steady rest potential was achieved and then the scanning of potential was started immediately. The polarization was begun from the rest potential, and the applied potential was swept towards the anodic direction with a scanning rate of 80 mV/min.
b) **Polarization In 1M MgCl₂ Solution**

The sample was held at open circuit potential for about two minutes in the test solution (1M MgCl₂ solution) before applying external potentials. The polarization was carried out from -600 mV(SCE) and the potential was swept towards the anodic direction at a scanning rate of 10 mV/min. The solution was freely exposed to air and remained stagnant throughout the experiment.

4.2.9 **Exposure At Different Potentials**

The steels used in this experiment were type 316, type 304, and cronifer 1925hMo. The samples were mounted in the sample holder as described in section 4.2.5 and coupled to a Wenking Model LT78 potentiostat and a Wenking Model EVI80 long term voltage integrator (Fig.25): the former to provide external potentials control while the latter measured the net charge. After holding the sample at its open circuit potential for not more than two minutes, a potential then applied and held in position until 0.5 Coulomb.cm⁻² of charge transfer occurred. The test solution, 1M MgCl₂, was unstirred and freely exposed to air during exposure. Samples were exposed at different potentials between -1000 mV to +800 mV(SCE) for type 316 and type 304 stainless steel, and from -1000 mV to +1300 mV(SCE) for cronifer 1925hMo.

When the amount of charge reached the required value, the sample
(together with the holder) was immediately removed from the cell with the potential 'on'. The sample was then separated from the holder and immediately dipped, in turn, into two beaker of distilled water from the cyclic still. The dipping process was carried out gently but quickly in order to remove residual test solution without destroying or sweeping away a corrosion reaction film formed on the surface of the sample. The samples were dried in a vacuum desiccator and kept in a nitrogen atmosphere until transferred into analyzer chamber of the MA500 machine.

4.2.10 Exposure At Different pH Values

The steels used in this test were cronifer 1925hMo and type 316 stainless steel. The same equipments as in section 4.2.9 were used. The test environment was 1M MgCl₂ solution with different pH values (see section 4.2.3). Only selected potentials have been applied to the samples. Cronifer 1925hMo samples were held at +1000 mV(SCE) (Pitting potential of cronifer 1925hMo) and also at -1000 mV(SCE), while type 316 stainless steel samples were held at +500 mV(SCE). The samples were exposed at the potentials until a net charge transfer of 0.5 Coulomb.cm⁻² occurred and then removed from the test solution with the potential was still 'on'. The current decay characteristics for cronifer 1925hMo samples were also recorded during the exposure. The washing and drying procedure for the exposed samples are similar to those as described in section 4.2.9.
4.2.11 Surface Analysis: XPS

i) Sample Preparation

The surface of all the electrochemically polarized samples (section 4.2.9 and section 4.2.10) have been analysed by means of XPS. Each of the samples was firmly stuck onto a stub by means of a small piece of double sticky tape before inserting into the MA500 analyzer chamber. A good electrical contact between the stub and the sample was achieved by painting part of the stub and the sample side with silver dag.

ii) Experimental Conditions

The X-Rays used for XPS analysis was Al Kα excited using a gun potential of 12.5 KV. The Constant-Analyzer-Energy (CAE) mode of the electron energy analyser was used. The pass energy selected was 50 eV. The sample was tilted such that an exit angle (the angle of electron exit relative to the sample surface) of about 60° was obtained. The vacuum of analyzer chamber during analysis was about 1x10⁻⁹ torr.

The type 316 stainless steel samples which were exposed at different potentials have also been ion etched for 20 seconds after first XPS analysis. The etched surface then again analyzed by XPS. The ion etching was performed at base pressure of 2x10⁻⁵ torr, ion beam energy of 6 KeV and with a focusing potential of 3 KV. This gave
a landing current of about 30 uA. The 20 seconds etching period was selected based on a preliminary experiment which was done to investigate the relative removal of surface contaminants on a stainless steel sample after a week of immersion in 1M MgCl₂ solution. The AES technique was used in the preliminary experiment. Result of the experiment, Fig. 27, shows that at about 20 seconds etch carbon removed was between 50% to 70% while oxygen remains at high level. This indicates that the ion etching procedure adopted was sufficient to remove carbon contaminant (from ambient or test solution) without altering the surface composition below the contaminant layer. The amount of carbon on the surface has recovered after about 250 seconds etch, presumably due to the formation of carbide in the sample during a long etching.
Fig. 27 Etch profile of carbon and oxygen for stainless steel samples exposed to 1M MgCl₂ solution for 7 days.
4.3 Results

4.3.1 Polarization

The results of the anodic polarization test in 1N H₂SO₄ (deaerated) for stainless steels type 304, type 316, cronifer 2328, cronifer1925LC, and cronifer 1925hMo are presented in Fig.28 while Fig.29 presents the results of the polarization tests in 1M MgCl₂ solution. As seen in the figures, the polarization curves can be divided into two groups, one consists of the polarization curves of type 304 and type 316 stainless steels and the another consists of the polarization curves of cronifer 2328, 1925LC, and 1925hMo. The distinction between the two groups is very clear in 1N sulphuric acid: the two are remarkably different in Flade potential and in the transpassive regions (Table 4). However, all the steels shown have about the same passive current density ( ~6.0 uA.cm⁻²) at a potential ( ~400 mV(SCE)) in the mid-point of the passive range. Cronifer 2328, 1925LC, and 1925hMo have a range of passivity between -50 mV(SCE) to 920 mV(SCE) whereas SS304 and SS316 have a slightly greater range of passivation, i.e -230 mV(SCE) to 930 mV(SCE).

In 1M MgCl₂ solution, the rest potentials within each group are close to each other (Table 5) although there is again a difference between the groups themselves. A similar trend is observed in their pitting potential. The passive currents of 1925LC and 1925hMo in 1M MgCl₂ are in the order of about ten fold of those of the SS304 and SS316, but cronifer 2328 does not show a clear passivation. Table 5
Fig. 28 Anodic polarization behaviour of commercial stainless steels of different Mo content in 1N H$_2$SO$_4$ (deaerated by nitrogen)

Temperature: 20 - 23°C
Sweep Rate: 80 mV/min.

- Type 304SS
- Type 316SS
- Cronifer 2328
- Cronifer 1925LC
- Cronifer 1925hMo
Fig. 29 Polarization behaviour of commercial stainless steels of different Mo content in 1M MgCl₂ solution (freely exposed to air)
Table 4. Polarization data* for stainless steels in deaerated 1N H₂SO₄.

<table>
<thead>
<tr>
<th></th>
<th>Potential (mV)</th>
<th>Current Density μA/cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Rest Flade Passive Trans-passive</td>
<td>Critical Passive Trans-passive</td>
</tr>
<tr>
<td>SS304</td>
<td>-336 -235 +400 930</td>
<td>≈93.0 6.6 6×10³</td>
</tr>
<tr>
<td>SS316</td>
<td>-310 -230 +350 930</td>
<td>≈25.0 5.9 5×10³</td>
</tr>
<tr>
<td>2328</td>
<td>-252 - 40 +400 920</td>
<td>≈28.0 5.8 160×10³</td>
</tr>
<tr>
<td>1925LC</td>
<td>-249 - 55 +400 920</td>
<td>≈20.0 5.7 165×10³</td>
</tr>
<tr>
<td>125hMo</td>
<td>-242 - 50 +400 920</td>
<td>≈17.0 5.5 135×10³</td>
</tr>
</tbody>
</table>

Table 5. Polarization data* for stainless steels in 1M MgCl₂ solution

<table>
<thead>
<tr>
<th></th>
<th>Rest potential mV(SCE)</th>
<th>Passive current μA.cm⁻²</th>
<th>Pitting potential mV(SCE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SS304</td>
<td>+ 60</td>
<td>≈0.2</td>
<td>320</td>
</tr>
<tr>
<td>SS316</td>
<td>+120</td>
<td>≈0.2</td>
<td>330</td>
</tr>
<tr>
<td>2328</td>
<td>+400</td>
<td>-</td>
<td>980</td>
</tr>
<tr>
<td>1925LC</td>
<td>+410</td>
<td>≈2.0</td>
<td>985</td>
</tr>
<tr>
<td>1925hMo</td>
<td>+500</td>
<td>≈1.2</td>
<td>1000</td>
</tr>
</tbody>
</table>

* average of two tests
summarizes the polarization data for the steels in 1M MgCl₂ solution. The passive range in 1M MgCl₂ of both SS304 and SS316 are small (about 200 mV wide) compared to a wider range of those of the cronifers (about 480 mV wide). There is no significant difference in current density at high cathodic potentials. However the drop of current density as the cathodic potential decreases towards the rest potential is remarkable in SS304. The Mo containing-steels shown have a cathodic region in which current density is independent of applied potential. No Flade region has been found for all the steels tested in 1M MgCl₂ solution, but on the other hand current blips did occur during the polarization test on SS316 and cronifer 2328, in a region before the pitting potential.

4.3.2 Surface Chemistry At Different Potentials

The results of XPS analysis on the samples which were exposed in the test solution at various potentials are presented here. Carbon is excluded from the calculation of percent composition because of its consistent presence on the surface of the samples at an almost constant level regardless of types of steel used and exposure condition. The carbon level present on the test surface was 42.17 ± 8.00 at.% (Appendix 2, using sensitivity factors in Table 1) and arises in the main from trace organic levels in the solutions used and in the spectrometer. The 20 seconds etch as in the case of type 316 stainless steel samples has reduced carbon to about 70 % of its original. The thickness of the surface layer removed was about 4.7 Å. This was estimated using a relation (equation 55) as used by Castle
and Epler [91],

$$\frac{R_j}{R_k} = \exp \left[ \frac{-d}{\sin \theta} \left( \frac{1}{\lambda_j} - \frac{1}{\lambda_k} \right) \right]$$  \hspace{1cm} (55)

where $R_j$ and $R_k$ are the relative enhancement of an electron of energy $j$ and $k$ respectively, caused by removal of a layer of thickness $d$ in which the respective escape depths are $\lambda_j$ and $\lambda_k$. The value of $d$ is then calculated after taking escape depths values for magnesium Auger (kinetic energy 1186 eV) and of magnesium photoelectron (kinetic energy 181 eV) similar as those used by the above authors [91], i.e $\lambda_{181} = 5$ Å and $\lambda_{1186} = 18$ Å and the experimental value obtained in the present work $R_{1186} = 1.475$ and $R_{181} = 3.91$. The removal of about two monolayers of surface contaminant by 20 seconds argon ion etching has increased the signal intensity of all cations to more than double their previous values (Appendix 3). The signal intensity of Cl increased about 30% while the oxygen signal almost unchanged.

The surface compositions presented are in atomic percent based on intensities normalised by the sensitivity factors in Table 1 (section 3.5.2). The application of these laboratory standard sensitivity factors in Table 1 to the intensities of oxygen and the transition elements which lie in the middle of the spectrum (between Mg and Cl) is not thought to cause a great deviation from the values obtained had the actual sensitivity factors for the MA500 been available. However the ratio of the sensitivity factors for elements at either ends of spectrum i.e. Mg and Cl for the MA500 and the ESCA3, standard instrument, is significant (3:1). Therefore the data for the
chlorine to magnesium ratio was corrected for the particular sensitivity factor associated with the MA500 instrument.

The normalised intensities of all the elements detected excluding carbon which is considered to be a non-participating impurity, have been normalised to 100% and, in addition the intensities of the alloying elements only (Fe, Cr, Ni, and Mo) have been normalised to 100% in order to see the interdependence between them in characterisation of the corrosion behaviour of the steels and to remove the influence of the large change in chloride ion concentration near to the rest potential. Figures 34 and 35 show the surface composition of SS316 samples before and after etching, for all elements whilst Fig.36 shows the surface compositions for alloying elements only. Figures 37 and 38 show the surface composition of SS304 samples without etching.

The chlorine to magnesium ratio was plotted against applied potential in order to see the inter-relation between the accumulation of chlorine ions and deposition of magnesium on anodic surfaces, passive surfaces, and cathodic surfaces. Hence it will then be possible to extend this ratio to the situation which occurs on a micro-pit and which will be discussed later in chapter 5. The smooth curves in the figures 30 and 31 are the mean curves drawn between the scattered experimental points which lie between two broken curves. The ratio shows a series of maxima and minima which clearly divide the potential range into four regions. These are marked I to IV on Fig. 32. These regions are used to describe the surface and
Fig. 30  Cl/Mg ions ratio as a function of applied potential for type 316 stainless steel samples. The continuous curve is for the main values. The area between the two broken curves represents the range in which the experimental points scattered.
* - experimental points

Fig. 31  Cl/Mg ions ratio as a function of applied potential for type 304 stainless steel samples. The continuous curve is for the main values. The area between the two broken curves represents the range in which the experimental points scattered.
Fig. 32  The mean curves of Cl/Mg ions ratio as a function of applied potential for SS316 and SS304. The exposure potentials were divided into regions I, II, III, and IV. The small arrows show the positions of the rest potential and the pitting potential of the steels.
Fig. 33(a) Typical XPS spectra (before etching) for SS316 samples exposed at potentials in Region I to IV.
Fig. 33(b) Typical XPS spectra (after etching) for SS316 samples exposed at potentials in Region I to IV.
Fig. 34 Concentration of elements in the surface of SS316 samples exposed at different potentials in 1M MgCl₂ solution. The exposed samples were not etched.
Fig. 35 Concentration of elements in the surface of SS316 samples exposed at different potentials in 1M MgCl₂ solution. The exposed samples were etched for 20 seconds.
Fig. 36 Concentration of alloying elements (before and after 20 second etch) in the surface of SS316 samples as for figures 34 and 35. Fe, Cr, Ni, and Mo are normalised to 100 at.%. Horizontal lines indicate the concentration of elements in the samples surface before exposure.
Fig. 37 Concentration of elements in the surface of SS304 samples exposed at different potentials in 1M MgCl$_2$ solution. The exposed samples were not etched.
Fig. 38 Concentration of alloying elements in the surface of SS304 samples as for figure 37. Fe, Cr, and Ni are normalised to 100 at.%.
Horizontal lines indicate the concentration of elements in the samples surface before exposure.
electrochemical results in the following section. A comparison between Fig. 32 and the polarisation plots for SS304 and SS316 (Fig. 29) show that regions I and II lie entirely in the cathodic part of the curve and IV is in the anodic part. Both the rest potential and the pitting potential are contained within Region III. Figures 33a and 33b show the typical XPS spectra (before and after ion etching) for the surface of samples exposed at the potentials in Region I to IV.

Region I

During exposure in this region hydrogen evolution occurred and the chlorine to magnesium ratio was at an almost constant value of 2:1 while surfaces were covered with a uniform white deposit. By taking the percentage for only alloying elements in SS316, it was found that iron, chromium, nickel, and molybdenum present in the surfaces (deposit) were at about the same concentration as in the surface before test (Table 6) which are shown by lines drawn across the plot in Fig. 36. In SS304, the average value of the composition of iron, chromium, and nickel after the exposure in this region were also close to the value of before test (Fig. 38). The high chlorine concentration comparable to the oxygen, found in the surface indicates that the white deposit was not hydroxide but was more likely an insoluble basic chloride.
Table 6. Surface composition of samples before electrochemical test. (Data obtained by XPS analysis.)

<table>
<thead>
<tr>
<th>Stainless steel</th>
<th>Element (At.%)</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
<td>O</td>
</tr>
<tr>
<td>SS316</td>
<td>36.66</td>
<td>46.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SS304</td>
<td>38.40</td>
<td>44.23</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cronifer 1925hMo</td>
<td>37.27</td>
<td>42.88</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Region II

This region is that in which the Cl/Mg ratio changes from the high value of Region I to the minimum value found for both steels. At this minimum the evidence supports surface films of oxides or oxy-hydroxides rather than chlorides. When samples were exposed in region II, their surfaces were found enriched in chromium and deficient in iron. Chromium began to increase from the beginning of the region (~-370 mV(SCE)) and reached maximum at about -100 mV(SCE). The increase of chromium was accompanied by a loss in iron which went to a minimum also at about -100 mV(SCE). At this potential the percentage of iron and chromium was about equal ie. ~45 at.% in both SS316 and SS304. The composition plot shown by Fig. 36 was able to show the nickel metal content in the surface analysis of the samples exposed in this region gradually decreased across the region whereas molybdenum has a slightly higher mean value than those of the surfaces exposed at the potential in Region I (mean value of Mo: Region I 2.2 at.% and Region II 3.1 at.%). When related to the polarisation curves of both steels, SS316 and SS304, the -100 mV(SCE) value was found almost exactly equivalent to the mid-point of the 'plateau' current range in the cathodic curve (Fig. 29).

Oxygen linearly increased and chlorine linearly decreased across the entire Region II, showing a considerable change from the constant levels of both oxygen and chlorine found in Region I. Beyond -100 mV(SCE) the compound containing iron starts to increase again relative to chromium but oxygen continues to increase and is
accompanied by a further drop in chlorine as well as magnesium.

Region III

The main feature shown from the samples exposed in Region III are the peaks in the concentration of iron and oxygen, and the minima in chromium and chlorine. This peak occurs at +200 mV(SCE) for SS316 and +100 mV(SCE) for SS304. The low intensities of magnesium and chlorine throughout this region and the high intensity of oxygen indicates that for the surfaces exposed in this region iron oxide is the main surface species. Even though chromium was still relatively enriched in the surfaces (original concentration of Cr before test was 26 at.% for SS316 and 29 at.% for SS304). Further anodic dissolution (potential greater than +200 mV(SCE) for SS316 and +100 mV(SCE) for SS304) result in chromium composition slowly recovering and iron composition dropping. Nickel and molybdenum remain at the same level throughout the region. The chlorine to magnesium ratio increases dramatically towards the pitting potential which occurs at about the end of this region.

Region IV

The change in surface chemistry between Region III and Region IV is quite abrupt. The high rate of anodic transpassive dissolution which dissolves iron selectively leads to the enrichment of chromium in the surface. All the surfaces of samples exposed in this region seem to have iron, chromium, and oxygen concentration independent of
the exposure potential. An increasing concentration of molybdenum and a decreasing concentration of nickel were observed as samples were exposed at higher potentials in this region. The soluble chlorides of Mg, Cr, Mo, and Fe present in the surfaces are indicated by the existence of high chlorine and magnesium in the surface film. The chlorine to magnesium ratio fell remarkably (especially in the case of type 316 stainless steel) from the beginning of this region and indicates that complexes containing chlorides as formed in Region III, gradually diminished in this region replaced instead by a different form of complex which possibly contains more magnesium and molybdenum.

The unexpected drop in Cl/Mg ratio in the surfaces of the highly anodic samples and a high value of Cl/Mg on cathodic surfaces were suspected to be due to the existence of different complexes or basic chlorides. An attempt has been made to clarify the existence of the complexes by investigating the Auger parameter of magnesium in the surface of each sample. Mg\(_{1s}\) photopeak and Mg\(_{KLL}\) Auger line were used. The result for type 304 stainless steel samples, Appendix 4, shows that the Auger parameters for Mg in the surface of samples are virtually the same regardless the potential applied. Therefore no positive interpretation can be made regarding the type of magnesium compound present in the sample surface.

4.3.3 Surface Chemistry Of Cronifer 1925hMo At Different Potentials

Cronifer 1925hMo samples during the exposure in the range of hydrogen evolution potentials, ie. -400 mV(SCE) to -1000 mV(SCE),
have a surface chemistry very similar to those of the samples of type 316 stainless steel in that all the elements found in the surface were at about the same amount, approximately equal to the bulk composition, regardless of the potential applied (Fig. 39a and Fig. 40a). The chlorine to magnesium ratio was approximately at a constant value of 2:1. A smooth curve drawn between the experimental points (Fig. 41) indicates the general variation of Cl/Mg ratios. The exposures between the rest potential and the pitting potential, which is equivalent to the Region III for SS316, shows the surface chemistry of cronifer 1925hMo (Fig. 39b and Fig. 40b) to be slightly different than that of SS316 in that it has an enrichment of Mo in the surface, whereas SS316 does not. Chlorine was also high and dropped towards the end of this region. It is also enriched in chromium and deficient in iron. High chloride and oxygen coupled with high molybdenum in the surface of cronifer exposed at this region suggests that they have a similar form of chloride complex to that formed on the SS316 for a region between Region III and Region IV.

A slight drop in molybdenum content was observed when cronifer 1925hMo samples were exposed at potentials greater than the pitting potential which is equivalent to the Region IV in SS316. However the level of molybdenum was still not less than that in the surface of the cronifer before test. Chlorine was found less in the surface compared to the ones exposed in the region before it. The chlorine to magnesium ratios drop at potentials 1100 mV (SCE) and 1200 mV(SCE) and increases at 1300 mV(SCE).
Fig. 39 Concentration of elements in the surface of cronifer 1925hMo samples exposed at different potentials in 1M MgCl₂ solution. The exposed samples were not etched.
Fig. 40 Concentration of alloying elements in the surface of cronifer 1925hMo samples as for figure 39. Fe, Cr, Ni, and Mo are normalised to 100 at.%. Horizontal lines indicate the concentration of elements in the samples surface before exposure.
Fig. 41 Cl/Mg ions ratio as a function of applied potential for cronifer 1925hMo samples exposed at different potentials in 1M MgCl₂ solution.
4.3.4 Electrochemistry At different pH values

During the exposure of cronifer 1925hMo samples at -1000 mV and +1000 mV (pitting potential of cronifer 1925hMo), in 1M MgCl$_2$ solution of different pH values, the current decay characteristics of each exposures was also recorded. Fig. 42 and Fig. 43 show the current decay characteristics for the exposures at -1000 mV(SCE) and +1000 mV(SCE) respectively. The areas below the curves (log-linear plot) are equivalent to 0.5 Coulomb.cm$^{-2}$, charge density acquired during the exposure. At both exposed potentials, the current density increased as the acidity of the test solution increases. The exposure at -1000 mV shows the current density was high in the early period of exposure and dropped to a constant value, and the exposure at +1000 mV(SCE) shows current increased in the early period of the exposure for all pH values of the solution, and gradually decreased towards the same value except for pH 8.6 where the current gradually increased after a slight decrease in the early period of the exposure.

4.3.5 Surface Chemistry At Different pH Values

The surface of samples which were exposed at fixed potentials in 1M MgCl$_2$ solution of different pH values (section 4.2.10) were analysed by means of XPS. Only the surface as "after exposure" were analysed (ie. no ion etching was performed). Figures 44 - 49, are the results of XPS analysis of the samples exposed at -1000 mV(SCE) and +1000 mV (SCE) for cronifer 1925hMo, and +500 mV(SCE) for SS316.
Fig. 42 Current decay characteristics at -1000 mV(SCE) for cronifer 1925hMo as a function of pH values. Time shown in each case indicates the period required to achieve a charge transfer of 0.5 Coulomb.cm$^{-2}$. 

Applied Potential : -1000 mV

Temperature : 20 - 23°C
Fig. 43. Current decay characteristics at +1000 mV(SCE) for cronifer 1925hMo as a function of pH values. Time shown in each case indicates the period required to achieve a charge transfer of 0.5 Coulomb.cm⁻². Curve f is a common locus for the decay currents in which pitting took place.
Fig. 44 Concentration of elements in the surface of cronifer 1925hMo exposed at -1000 mV(SCE) as a function of pH values of the solution.
Fig. 45 Concentration of alloying elements in the surface of cronifer 1925hMo samples as for Fig. 44. Fe, Cr, Ni, and Mo are normalised to 100 at.%. Horizontal lines indicate the concentration of elements in the samples surface before exposure.
Fig. 50 shows the Cl/Mg ratios of the samples exposed at the potentials. The smooth curves in Fig. 50 are the mean curves for the experimental data. The results of XPS analysis for the exposure at +1000 mV, Fig. 46, show that the chlorine and oxygen concentrations were constant between pH values 3 and 7. At pH values less than 3 or greater than 7.8, the oxygen concentration drops whilst chlorine increases. Molybdenum and nickel were almost constant throughout the range of pH used. Iron and chromium also showed no significant different for the low and the high pH values. However, all the surfaces of samples exposed at this potential were enriched in chromium and molybdenum but deficient in iron and nickel regardless of pH values. The Cl/Mg ratio was also at an almost constant value throughout the range of pH values concerned.

During the exposure at +500 mV(SCE) for a various pH values, the surface of type 316 stainless samples shown have a different chlorine and magnesium uptake between low and high pH values (Fig. 48). At pH value 1.8 the Cl/Mg ratio has a value twice of that the mean value for pH values between 3 and 8.6 (Fig. 50). The concentration of Cl and Mg at pH 1.8, however, is far lower than those for pH values greater than 5 (Fig. 48). The oxygen concentration varies with the solution pH value, as a mirror image to the chlorine. The concentration of Fe, Cr, Ni, and Mo were almost independent of pH values (Fig. 49). As in the case of cronifer 1925hMo exposed at +1000 mV(SCE), SS316 steel samples exposed at +500 mV(SCE) were also enriched in Cr and Mo and deficient in Fe throughout the pH range used. Nickel remained at an approximately similar concentration level as that before test.
Fig. 46. Concentration of elements in the surface of cronifer 1925hMo exposed at +1000 mV(SCE) as a function of pH values of the solution.
Fig. 47 Concentration of alloying elements in the surface of cronifer 1925hMo samples as for Fig. 46. Fe, Cr, Ni, and Mo are normalised to 100 at.%. Horizontal lines indicate the concentration of elements in the samples' surface before exposure.
Fig. 48 Concentration of elements in the surface of SS316 samples exposed at +500 mV(SCE) as a function of pH values of the solution.
Fig. 49 Concentration of alloying elements in the surface of SS316 samples as for Fig. 48. Fe, Cr, Ni, and Mo are normalised to 100 at.%. Horizontal lines indicate the concentration of elements in the samples surface before exposure.
Fig. 50  Cl/Mg ions ratio for SS316 and cronifer 1925hMo for different exposure potentials as a function of pH values. All curves shown are the mean curves for the experimental data.
All the surfaces of the cronifer 1925hMo samples exposed at -1000 mV(SCE) in solution of different pH values, were found covered with white deposit. The XPS analysis show that the surface composition of the deposit was not affected by the pH value of the solution (Fig. 44 and Fig. 45). The surface remained high in oxygen and chlorine for all pH values. Iron, chromium, nickel, and molybdenum were at approximately the same composition as that in the surface of sample before test.
4.4 Discussion

4.4.1 Electrochemistry

It is clear from the result of the potentiodynamic polarization experiments in sulphuric acid that molybdenum strongly influences the pitting behaviour of the stainless steels. As Mo content increases the tendency for the stainless steels to exhibit passivity become more significant. The rate of the cathodic reduction should be greater or equal to that of anodic dissolution for spontaneous passivation to occur [126]. Fig. 28 shows a remarkable drop of critical current density as the molybdenum content in steel increases which makes it increasingly possible for this requirement to be met.

By comparing the polarization curves of the steels (Fig. 28), it was found that the addition of Cu, or the presence of high content of Cr and Ni in the steels did not result in a large drop in critical current density. The drop in the critical current densities in the present case seems to be mainly due to the presence of molybdenum. For example, type 316 stainless steel and cronifer 2328 which have about the same amount of Mo have about the same value in critical current density whilst cronifer 1925hMo which has a highest Mo content in the series of stainless steel used shows having the lowest value of the critical current density.

A clear effect of the high Cr and Ni content in steels is in the size of the active–passive transition region. This region becomes
smaller as the Cr and Ni content increases (Fig. 28). Other corrosion parameters which are affected by the addition of Cu and high Cr and Mo are the rest potential and the primary passivation potential (in 1N H$_2$SO$_4$ solution) which shifted to a more noble value compared to those lower in Cu, Cr, and Ni, i.e. type 304 and 316 stainless steels. Although the combination of Cu, Ni, Cr, and Mo in the steels did not greatly reduce the passivation current, the effect of Mo on the passivation current can still be seen. The addition of about 2.2 at.% Mo lowered the passivation current (although not substantially). The addition of Mo of a greater value does not result in further drop in the passivation current.

The potentiodynamic polarisation curves in 1M MgCl$_2$ solution of natural pH value (pH5), have no active-passive transition region, Fig. 29 [127]. The high chloride concentration is apparently responsible for the disappearance of the region which had pushed the rest potential to a more noble value.

Fig. 29 also shows the effect of Mo, Cr, Ni, and Cu on pitting potential. The general trend of the effect of Mo is that the pitting potential shifted towards more noble value as Mo content increased. The different value of pitting potential of SS316 and cronifer 2328 suggests that the increase in Cr content from about 18 at.% to 20-24 at.%, Ni from about 12 at.% to 20-27 at.%, and also the addition of Cu of 1.6-2.7 at.% will improve the pitting resistance of the stainless steels to even better. The larger range of passivation region with a low passivation current as shown by curves D and E in Fig. 29 is the indicative of a better corrosion resistance of
the high Mo-bearing steels, cronifer 1925LC and cronifer 1925hMo in a severe corrosion condition. SS316 and cronifer 2328 which have 2.2 at.% and 2.6 at.% molybdenum respectively have a relatively higher passivation current (Fig. 29) compared to others steels. This is probably because of the appearance of current blips especially in the region near to pitting potential. The occurrence of the current blips was suggested to be due to the alternate formation and repassivation of very tiny pits or depressions in the sample surface [50,81]. The repassivation of a bare surface (after passive film was removed) at a potential below its pitting potential as shown in a "scratching experiment" by Galvele, et al [128] is also a match to the present observation. The ability to repassivate small pits by the steels may be due to the ease of the formation of a passive film by chromium compounds with the assistance of molybdenum [81]. Type 304 stainless steel used in this investigation, which does not contain molybdenum, shows a sudden jump of current at its pitting potential without any clear indication of current blips. This illustrates the fact that without Mo, the ability of steels to repassivate small pits (if formed) is poor.

The current decay characteristics at +1000mV(SCE) in 1M MgCl₂ solution for cronifer 1925hMo, the highest Mo alloy studied, illustrates the effects of pH values of the solution on metal dissolution at the pitting potential of the steel, Fig. 43. The current-time curves for pH values 1.8 to 6.5 shows a series of common features. These are i) an initial delay before the inception of pitting, during which the current decreases; ii) a period of
increasing current as active dissolution at the pits builds up,

iii) a decline in current to a value which may be independent of pH value. The initial delay increases with pH value and, in fact, pitting does not occur at pH 8.6. The rate of current increase after pitting increases towards the more acid solutions and the final decline match a common locus (curve f in Fig. 43). It is probable that the final current at all pH values is determined by diffusion through a salt film within the pit.

The exposure at -1000 mV shows the steady state cathodic reaction rate increases as the acidity of the solution increased (Fig. 42). This is obviously because the higher concentration of hydrogen ion present in the solution will lead to a cathodic reduction reaction on the hydrogen ion becomes predominant. Since a steady state reaction occurred (shown by a constant current for a period of time) the critical diffusion layer thickness which is necessary to account for the observed precipitation of basic magnesium compounds can be calculated as a function of pH using a relation which has been derived from Fick's Law by Castle and Tremaine [122]. The approximate thickness of the diffusion layer for the present case can be estimated as follows (equation 56), after firstly assumed that the critical current density for precipitation, $i_{cp}$, is equal to the steady state current density, $i_{ss}$ in every exposure.

$$\delta = \frac{FA}{i_{cp}} \left[ D_{OH^-} \left( \frac{K_s}{[Mg^{2+}]} - \frac{K_w}{[H^+]} \right) + D_{H^+} \left( [H^+] - K_w \left( \frac{[Mg^{2+}]}{K_s} \right) \right) \right]$$

where $i_{cp}$ is the critical current for precipitation, A is the sample area, F is Faraday's constant, $D_{OH^-}$ and $D_{H^+}$ are the diffusion
coefficient of OH\(^-\) and H\(^+\) ions respectively, K\(_s\) is the solubility product of Mg(OH)\(_2\), K\(_w\) is the ionic product of water, and [H\(^+\)] and [Mg\(^{2+}\)] both represent the concentration of H\(^+\) and Mg\(^{2+}\) in bulk solution. By assuming [Mg\(^{2+}\)] remains unchanged up to the metal surface and taking D\(_{H^+}\) = 9.3 \times 10^{-9}, D\(_{OH^-}\) = 5.2 \times 10^{-8} m^2 s\(^{-1}\) and K\(_s\) = 5 \times 10^{-11} (see Ref. 122), the value of \(\delta\) now obtained as shown in Table.7.

The value of \(\delta\) decreases as the pH value of the solution increases. However even the largest value, at pH 1.8, is less than diffusion layer thickness frequently found in inquiescent conditions [122]. Thus the high reduction rate can result in the concentration of [OH\(^-\)] and [Mg\(^{2+}\)] in the boundary layer region reaching the solubility product of Mg(OH)\(_2\) in even acid conditions. Probably the different reduction reaction rate at highly cathodic potential will lead to the diffusion layer regions having similar alkalinity even though the bulk solutions have different pH values. The chloride ions present in the solution in the diffusion layer will be adsorbed in the sample surface with its precipitate of magnesium hydroxide which then forms basic hydroxy-chloride compound. This, is probably, the reason why the surfaces of cronifer 1925hMo samples exposed at -1000 mV for all pH values of the bulk solution are covered with a deposit of a similar appearance and composition.

4.4.2 Surface Chemistry

The exposure at various potentials in Region I (Fig. 36) i.e
Table 7. The dependence of steady state current density ($i_{ss}$) and critical diffusion layer thickness ($\delta$) on pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>$i_{ss}$ $\mu$A.cm$^{-2}$</th>
<th>$\delta$ $\mu$m</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.8</td>
<td>269</td>
<td>5.29</td>
</tr>
<tr>
<td>3.0</td>
<td>203</td>
<td>$4.43 \times 10^{-1}$</td>
</tr>
<tr>
<td>6.0</td>
<td>112</td>
<td>$3.96 \times 10^{-2}$</td>
</tr>
<tr>
<td>7.8</td>
<td>103</td>
<td>$3.15 \times 10^{-3}$</td>
</tr>
<tr>
<td>8.6</td>
<td>87</td>
<td>$1.79 \times 10^{-3}$</td>
</tr>
</tbody>
</table>
between -370 mV(SCE) and -1000 mV(SCE) shows no difference between the concentration of iron, chromium, nickel, and molybdenum in the surface of samples before and after the exposure but high concentration of chlorine, oxygen, and magnesium were observed. This suggests that the surface contained mainly basic hydroxy-chloride of magnesium ($\text{Mg}_x\text{(OH)}_y\text{Cl}_z$). The exposure at -1000 mV(SCE) of cronifer 1925hMo indicates that the basic chloride will be formed at any pH values, probably, because of at high cathodic potential eg. -1000 mV(SCE) the reduction reaction rate is very high thus resulting in the concentration of $[\text{OH}^-]$ and $[\text{Mg}^{+2}]$ in the diffusion layer region reaching the solubility product of $\text{Mg(OH)}_2$. An ion exchange between chloride ions and magnesium hydroxide will then take place at metal-solution interface to form the basic chloride.

The exposure at potentials between -370 mV(SCE) and -100 mV(SCE), Region II, results in a decreasing rate of cathodic reaction from the high value in Region I (cathodic current in Region I was greater than 7 uA.cm$^{-2}$) and hence in a decreasing amount of basic hydroxy-chloride formed on the surface. Instead the oxy-hydroxide increases. The anodic reaction which is also becoming important in this region dissolved iron selectively leaving behind chromium enriched in the surface in the form of oxide or oxy-hydroxide and also attached by bound water [117]. The samples exposed at the potential in this region began to develop passive film as indicated by the enrichment in chromium and the deficiency in iron. There was no enrichment in molybdenum. The trends of chromium and molybdenum present in the surface agreed well with the observation by the
previous authors [79,80] even though they used different test environments. At exposure potentials greater than -100 mV(SCE) the effect of anodic dissolution becomes more significant thus more iron ions are present in the solution-metal interface and appear to exceed the critical concentration level to precipitate compounds of iron (e.g. FeOOH and Fe$_2$O$_3$).

The reactions governing the formation of FeOOH and Fe$_2$O$_3$ are as follows [118],

\[
\begin{align*}
\text{Fe} & \rightarrow \text{Fe}^{+2} + 2e^- \\
2\text{Fe}^{+2} + \text{O}_2 + 2\text{H}_2\text{O} & \rightarrow 2\text{FeOOH} + 2\text{H}^+ \\
\text{FeOH}^+ + \text{H}_2\text{O} & \rightarrow \text{FeOOH} + 2\text{H}^+ + e^- \\
2\text{Fe} + 3\text{H}_2\text{O} & \rightarrow \text{Fe}_2\text{O}_3 + 6\text{H}^+ + 6e^-
\end{align*}
\]

The increasing anodic dissolution of Fe will dissolve more iron (equation 57) thus the concentration of Fe$^{+2}$ ions will increase until the solubility product of FeOOH (equation 58) is exceeded which precipitates on the sample. The precipitation of FeOOH, result in high intensities of iron and oxygen being detected by XPS (Figures 34, 36, 37, and 38). The alternative precipitation of Fe$_2$O$_3$ is less likely. FeOOH (or Fe$_2$O$_3$) becomes a dominant constituent of surface film in Region III especially between the rest potential and +200 mV(SCE) for SS316, and +100 mV(SCE) for SS304. At potentials greater than +200 mV(SCE) for SS316 and +100 mV(SCE) for SS304 at which the anodic reaction becomes more intense, the dissolution of
Iron becomes more rapid than before and is accompanied by higher degrees of hydrolysis and results in increasingly high acidity of the solution-metal interface. This will oppose the precipitation of FeOOH (equation 58) and account for the decrease in surface iron at high potentials.

The potentials in Region III are within the passivation range of chromium in 1N HCl [77] so Cr$_2$O$_3$ is also likely to be formed through the reaction of chromium with water,

$$2\text{Cr} + 3\text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_3 + 6\text{H}^+ + 6\text{e}^- \quad (61)$$

The surface of samples exposed at potentials of greater than +200 mV(SCE) (in Region III) may contain chromium oxide and a film of soluble oxy-chlorides of iron and chromium. This is shown in figures 34 and 37 in which chlorine concentration begins to increase at exposure potentials +200 mV(SCE) for SS316 and +100 mV(SCE) for SS304.

In the anodic region (Region IV) there is again a relative enrichment of chromium. The compounds precipitated here are those which are stable in the presence of strongly acidic chloride media. Chloride ions are again important in this region of surface chemistry. The dissolution rate when the samples are exposed at a potential greater than +380 mV(SCE) (Region IV) was at a saturation level (saturation of current Fig.29) and accompanied by the evolution of oxygen and the increase of hydrogen ion concentration. The breakdown of the air-formed protective film during the exposure will expose bare metal to a rapid anodic dissolution which selectively dissolves iron,
leaving behind chromium enriched in the surface. Iron is more readily dissolved in acid solution than chromium as shown by their polarisation tests in 1N HCl in which chromium has a wide passive range but iron has none[77].

Based on the potential-pH diagram in Fig. 51, at the range of potential in Region IV for type 316 and type 304 stainless steels, at pH values less than 5 (pH value of bulk solution was 5), MoO$_2$ and MoO$_3$ may be formed of which MoO$_2$ is more likely. MoO$_2$ may be formed by a reaction as follows [119]

\[
\text{Mo}^{3+} + 2\text{H}_2\text{O} \rightarrow \text{MoO}_2 + 4\text{H}^+ + \varepsilon^{-} \] (62)

Although MoO$_2$ film is very protective [56], it is possible to hydrolyse [120]

\[
\text{MoO}_2 + 2\text{H}_2\text{O} \rightarrow \text{H}_2\text{MoO}_4 + 2\text{H}^+ + 2\varepsilon^{-} \] (63)

Molybdate ions may form iron molybdate (probably FeMoO$_4$) and be adsorbed in defects in the surface films and act as an anodic inhibitor as suggested by Sugimoto and Sawada [121]. Thus molybdenum will act as repairing element particularly when the Mo-bearing stainless steels undergo high anodic dissolution. High oxygen and molybdenum observed in the surface of sample in the present investigation may be attributed to the above reactions of molybdenum. The high chlorine observed in the surface probably due to the formation of soluble oxy-chloride of iron and chromium.

The samples of chronifer 1925hMo exposed at a potential range
Fig. 51 Potential-pH equilibrium diagram at 25°C for the system Mo-H₂O (After reference 56)
between +600 mV(SCE) and +1000 mV(SCE) showed molybdenum being enriched in the surface in the presence of a high concentration of oxygen. This would be in accord with the formation of MoO$_2$ and MoO$_3$ as suggested by the potential-pH equilibrium diagram in Fig. 51. The decrease of molybdenum in the surface towards higher potentials may be due to the formation of MoO$_3$ which is less protective [56] than MoO$_2$. This phenomena can be seen as a further drop of molybdenum concentration in the surface of cronifer 1925hMo samples exposed at +1300 mV(SCE) to the level of Mo in the surface before exposure. Exposures at +1000 mV(SCE) for cronifer 1925hMo and at +500 mV(SCE) show that the molybdenum level remained unaffected by the different pH values of the solution. This is probably because the rate of formation of MoO$_4^{2-}$ at high pH values (pH>6) and MoO$_3$ or MoO$_2$ at low pH values (pH<6), does not depend on H$^+$ ions.
5 Investigation On Pitting Site

5.1 Introduction

A highly corrosion resistant alloy is unlikely to pit when it is exposed naturally to a chloride-containing aqueous medium for a short time, but if the exposure period is extended sufficiently it will finally pit. Nevertheless the exposure period can be cut short to be able to conduct experiments at laboratory scale by introducing more powerful corrosion conditions such as increasing chloride ion concentration, applying external potential, or creating a very stable stagnant condition of the environment.

By creating an artificial crevice (involving the alloy), a stable stagnant environment will be obtained. If the environment contains chloride ions, a very high chloride concentration will be developed inside the crevice. The existence of ionic concentration gradients of Cl⁻ and oxygen [20,22,23] will help to generate pitting attack. This method of generating pits has been used in the present work. It has the advantage that externally applied potentials are not used and hence the distribution of adsorbed or electrodeposited species in and around the pit will reflect the local electropotentials more strongly. This distribution has been examined for the surfaces of type 316 and to a small extent of type
304 stainless steels using a high resolution scanning Auger microscope.

5.2 Experimental

5.2.1 Test Environment

The test environment was 1M MgCl₂ solution prepared from MgCl₂·6H₂O (analytical grade) and distilled water from the cyclic still of solution conductance 0.2 \( \text{usiem} \) (see section 4.2.3). Only fresh solution was used in each run. During sample exposure, the solution was freely exposed to the air.

5.2.2 Sample Preparation Before Exposure

Samples were prepared from type 316 and type 304 commercial stainless steels. The chemical composition of the steels are as in Table 3. The stainless steel plates of about 1 mm thick were cut with a die to produce oval-shape samples of dimensions 15 mm x 10 mm, Fig. 52(a). The cleaning and polishing procedures applied to these samples were similar to those as mentioned in section 4.2.2.

5.2.3 Pit Production

In order to develop pits naturally, a metal to metal crevice was simulated by clamping two samples across one another by means of a PTFE clamp, figures 53(a) and 53(b). The bolt on the clamp was
Fig. 52  Top view: a) Sample  b) A special stainless steel stub for holding the sample in the MA500 chamber  c) Sample on the stub.
Fig. 53(a) Side view: a pair of samples clamped in a PTFE holder.

53(b) Top view: a pair of samples in a cross formation.

Fig. 54 A large crater formed in a crevice after one month exposure in 1M MgCl₂ solution.
tightened just enough to hold the two samples together. Because the samples were made very flat and have a one micron surface finish the crevice gap obtained was in the order of a micron. The clamping was done in the test solution in order to avoid air bubbles trapped between the samples.

The whole assembly was kept seven days in the solution in a large shallow petri-dish. About 100 ml solution was used in each single exposure. 1 ml of distilled water from the cyclic still was added everyday during the exposure to compensate the water lost due to evaporation, thus maintaining the solution concentration, and also supplying oxygen to the solution. An exposure for seven days was found to be sufficient to develop pits in the sample surface. A variety of exposure periods were also tried. Two day and four day exposures failed to develop pits but when the exposure period was prolonged to about one month, a severe pitting attack occurred and large craters due to coalescence of pits were observed, Fig. 54. The seven day exposure, however, produced a very comprehensive crevice morphology including a good distribution of pit sizes (figures 58(a-f)).

5.2.4 Washing Procedure

To maintain the element distributions which arise from pit activity is a difficult problem once the sample has been removed from the solution. Thus, only by trial and error, was a correct washing method achieved. The main trial and error efforts to find out the
right washing method were as follows:

a) After seven days exposure the whole test assembly was removed from the solution. The samples were separated from the clamp, and washed in a distilled water jet. After drying in a vacuum desiccator, the exposed surface of the sample was analysed by AES technique. From AES spectra, Fig. 55(a), no trace of Mg or Cl was found. Thus it was concluded that this washing method was not suitable because it seems to wash away the surface film formed during the exposure.

b) After the exposure, the whole test assembly was removed from the solution, then excess solution which has still remained on the assembly surface was shaken off, followed by drying in a stream of hot air. The clamped was dismantled after the drying and the samples were again kept in the stream of hot air to ensure their surface were properly dried. The surface seemed to be covered with a layer of magnesium chloride salt. This was confirmed by AES analysis, Fig. 55(b).

c) After the exposure, the whole test assembly was dipped into distilled water from the cyclic still to remove the excess test solution from it. It was then reimmersed into distilled water (fresh) for about 10 minutes. After the immersion, the excess water on the assembly was removed by absorbing with a filter paper. The clamp then dismantled, the top and the bottom samples were separated and finally dried in a vacuum desiccator. They were kept in a nitrogen atmosphere.
Fig. 55(a) Auger spectrum of the crevice surface (SS304), the sample was washed in distilled water jet.
Fig. 55(b) Auger spectrum of the crevice surface (SS304), the sample was not washed.
Fig. 55(c) Auger spectrum of an area between crevice mouth and central part of the crevice. The sample was washed by immersion the whole crevice assembly in distilled water for about 10 minutes.
before transferring into MA500 analyzer chamber for AES analysis. This washing method has produced a reliable result in which AES spectra, Fig. 55(c), taken at a region between crevice mouth and crevice centre shows that chlorine and magnesium have still been preserved. The revelation of sharp iron peaks in the AES spectra, (Fig. 55(c)), indicates that the surface was not covered with a salt layer of magnesium chloride. As far as pitting is concerned, the maintenance of the crevice during washing means there is no breakdown of the electropotentials of individual pits in the crevice. Instead ionic diffusion only takes place. The other advantage is that the surface film remains as it was because no mechanical force, eg. jet of water, has been applied to it.

5.2.5 Sample Preparation For AES Analysis

Because of the serious charging which can occur in AES analysis, especially on a surface covered with a thick oxide layer or on a material which is not very well conducting, the sample must have a very good electrical contact to its holder (earthed). In this work a special stainless stub has been made, which has a pair of metal spring clamp, Fig. 52(b) and Fig. 52(c). The springs firmly hold the sample and also provide a good electrical contact.

5.2.6 AES and EDXA: Experimental Conditions

The sample was positioned in the analyzer chamber of the MA500 machine, 45° relative to the electron beam. A 10 KeV electron beam
was used for all the AES work whilst a 4 nA beam current was used in point analysis and a 7.5 nA beam in most of Auger electron mapping. The low beam currents have been adopted because they:

a) minimize charging effects when the sample surface is subjected to a long exposure in electron beam; and

b) give a small analytical beam spot but with a reasonable counting statistic (Beam spot size, \(d = 66 \sqrt{i}\), \(d\) in nm and \(i\) in nA).

A Constant Retard Ratio (CRR) of 10:1 was used when a high energy resolution was required, such as in collecting individual peak spectra, but where a high energy resolution was not so important, such as in wide spectra, a CRR of 2:1 was used. However, in order to compromise between energy resolution, Auger electron signal and time for mapping, a CRR of 4:1 was used in all Auger mapping. The relationship between CRR, energy resolution, and Auger electron signal intensity can be seen in Fig. 56. In these surface analysis works, AES and EDXA were carried out simultaneously. The X-Ray mappings were done at 10 KeV electron energy and 7.5 nA beam current.

5.2.7 SIMS Mapping

Mapping by SIMS technique for chlorine and magnesium in pit and its vicinity was carried out at a laboratory of VG Scientific, UK. The ion beam source was metallic gallium. A 10 KeV ion beam and 0.5 nA beam current were used in the mapping. This conditions gave a sputtering rate of about 1/10 monolayer per second. Since the time used in mapping was 60 seconds then the amount of surface removed in each mapping was about 6 monolayer (~12 Å).
Silver spectra at 352 eV, showing the effect of CRR on peak resolution and Auger intensity.

Fig. 56(b) A relationship between CRR and spectral resolution for silver peak at 352 eV.
5.3 Results

5.3.1 Sample Surface After The Exposure

After seven day exposure the appearance of the surface of sample was as shown in the picture in Fig. 57(a). The brownish surface at the both ends of the sample was the surface just outside the crevice which was covered with corrosion products. The square section between the two ends represents one face of the crevice and contained a highly etched area in the middle (circular section in the middle of the sample). The different appearances of the surface seem to suggest that different kinds of chemistry have occurred in different regions. Thus the surface of the exposed sample was divided into four zones for further investigation as illustrated in Fig. 57(b), namely

i) Outside crevice

ii) Crevice mouth zone.

iii) Intermediate zone.

iv) Central zone.

The crevice mouth zone is a region which is inside the crevice but adjacent to the crevice mouth. The intermediate zone is the surface between the defined crevice mouth zone and the central zone (a circular region in the middle of the crevice).

All surfaces and pits developed in these zones were investigated. The zone outside crevice, which was caked with corrosion product, was examined separately. A series of scanning electron micrographs, figures 58(a-f) shows the crevice morphology
Fig. 57(a) The appearance of the surface of sample after the exposure.

Fig. 57(b) Schematic diagram of an exposed sample illustrates the zones of crevice.
across the entire zone of the crevice. Fig. 58(a) shows the crevice edge at which a corrosion product layer broke down due to dehydration during drying in vacuum. The surface which was on the left of the broken corrosion product layer was on the exterior of the crevice and the one which was on the right was in the interior of the crevice. Fig. 58(b) is a magnified picture (X2000) of the white surface which was on the right of the picture in Fig. 58(a) which is shown to be still heavily covered with corrosion product deposit. Fig. 58(c) is the typical surface of the crevice mouth zone lightly covered with corrosion product deposit with pits being rarely found. Note the increased density of precipitate associated with the pits. Fig. 58(d) is a picture of the intermediate zone, at 2000 magnification, taken at a group of small pits of less than one micron in size. The biggest pits found in this zone were about two and half microns in diameter (Fig. 59). The area of the central zone next to the intermediate zone was shown in Fig. 58(e). The grain structures shown in this figure is the indicative that the area has been electrochemically etched and the oxide has been lost. This is the beginning of the central zone. Next to this area, the central zone (Fig. 58(f)) seems to have been engulfed in a general corrosion in which the surface was very heavily etched. The coalescence of pits made the zone appears rough and there are some remaining pits left.

AES and EDXA analyses on the corrosion product formed just outside and just inside the crevice of type 304 stainless samples show a differing contents of chromium on either side of the boundary. Corrosion products on the outside of the crevice have more chromium
Fig. 58(a)  SEM picture of crevice edge (X200)
Corrosion product layer broke down due to dehydration in vacuum.

Fig. 58(b)  SEM picture of the white area on the right of the picture of Fig. 58(a)  (X2000)
Fig. 58(c) A typical surface of crevice mouth zone (X2000)

Fig. 58(d) SEM picture of the intermediate zone (X2000). Intensity of pits increases as compared with the crevice mouth zone.
Fig. 58(e) SEM picture of an area in the central zone near to the intermediate zone. Grain structures were revealed by corrosion process. (X2000)

Fig. 58(f) SEM picture of the central zone. Its surface was heavily etched (X2000).
Fig. 59  SEM picture of one of the biggest pits found in the intermediate zone of the crevice. (X10000)
than those on the inside (Fig. 60). The corrosion products also contained a high concentration of magnesium and chlorine. Iron, as expected, is also found in the corrosion products. The sample surface under the corrosion products (eg. surface in between the broken corrosion products layer) was high in chlorine but without any trace of magnesium (Fig. 60(b) and Fig. 61(b)).

The general surface of different zones of the crevice were also investigated using AES. The AES spectra obtained, Fig. 62(c), show magnesium to be higher in concentration in the mouth region than in the precipitation at the actual mouth (Fig. 61). The level of magnesium present in the surface then decreases from crevice mouth zone towards the central zone in which magnesium was below detection limit of the spectrometer used. Chromium, by contrast increases from the mouth towards the central zone. The AES spectrum for the central zone of type 316 stainless steel (Fig. 63) shows that a high concentration of molybdenum was also present in the surface in addition to chlorine, iron, chromium, and oxygen. Chlorine levels relative to oxygen were lower in the crevice than in the thick precipitate at the mouth itself.

5.3.2 Surface Chemistry Across Pits

AES point analysis were carried out across individual pits in the crevice mouth zone, the intermediate zone, and the central zone of the crevice. An analytical resolution of about 130 nm was obtained from the 4 nA electron beam current was used in this analysis, and is
Fig. 60 The X-Ray spectra showing the bulk composition of corrosion products layer adjacent to the crevice edge: a) just outside crevice b) sample surface in between the broken corrosion products layer. c) just inside crevice (SS304 sample).
The AES spectra showing the bulk composition of corrosion products layer adjacent to the crevice edge: a) just outside crevice b) sample surface in between the broken corrosion products layer c) just inside crevice. (SS304 sample).
Fig. 62 The AES spectra showing the surface composition of different regions of the crevice: a) central region  b) intermediate region  c) crevice mouth region - region inside the crevice near to mouth of the crevice (SS304 sample).
Fig. 63 A typical AES spectrum of the central region of a crevice for SS316 sample.
shown relative to the size of pit investigated, by means of a bar on the micron marker on the SEM micrograph of a typical pit (Fig. 59). The concentration of elements across the pits are presented in cumulative concentration diagrams as described in section 3.5.2 (chapter 3). Carbon was not included for the same reasons as mentioned in section 4.3.2 (chapter 4). The typical cumulative concentration diagrams for pits in different zones of a crevice are shown in figures 64, 65, and 66.

Fig. 64 shows the relative concentration of elements for pit in the crevice mouth zone. The entire surface of the pit and its vicinity are high in magnesium, oxygen, and iron. A very low chlorine concentration was detected. In some pits the chlorine presence was even below the detection limit of the Auger spectrometer used. For example pit shown in Fig. 67(a) has no chlorine peak in its spectra for inside and outside pit (Fig. 68). A high magnesium intensity particularly at the edge of pit was observed. The Auger Map (refer sections 3.5.2 and 6.3 for details) acquired for this pit (Fig. 67(b)) shows a high magnesium intensity (>80 % of the maximum magnesium intensity) surrounding the pit. A chlorine map was not available for this pit because of a very low intensity of chlorine present. The small pits at the bottom right of the pit had also been covered with magnesium deposit. Based on the contour level for 20 % of the maximum intensity, it was found that the entire surface of the mapped region was covered with magnesium along with oxygen.

The pit at the intermediate zone has a clear different in
Fig. 64 Cumulative concentration diagram for a pit in the crevice mouth zone for SS316 sample.
Fig. 65(a) Cumulative concentration diagram for a pit in the intermediate zone for SS316 sample.
Fig. 65(b) Cumulative concentration diagram in atomic percent for a pit in the intermediate zone for SS316 sample (as for Fig. 65(a)). The concentration of all elements was normalised using sensitivity factors in Table 2.
Fig. 66 Cumulative concentration diagram for a pit in the central region of a crevice for SS316 sample.
Fig. 67  (a) Pit in the crevice mouth zone (X10000) for SS316 sample.
(b) Magnesium Auger map

Contours:  
- □ 80% of maximum intensity.
- □ 20% of maximum intensity.
Fig. 68 The AES spectra for pit in Fig. 67(a).
concentration of chlorine inside and outside pit. As can be seen in Fig. 65, more chlorine is present in the pit than on the surface outside the pit. The surface in pit was high in chromium and iron but relatively low in oxygen and magnesium as compared to the area at the edge of the pit. While the surface outside pit was high in magnesium relative to chlorine and high in iron and chromium but slightly low in oxygen. There was almost no different in molybdenum concentration for both areas inside and outside pit. A similar result for chlorine, magnesium, iron, chromium, and oxygen were observed for the pits in SS304 (Fig. 69). A chlorine Auger map for a pit of 1.5 microns in diameter, situated in the intermediate zone is shown in Fig. 70(b) in which chlorine was again very intense inside the pit as indicated by 80 % contour line encircling the pit. SIMS mapping which has also been carried out on a pit in the intermediate zone, Fig. 71(a-d) show an annulus of a high intensity magnesium of two to three microns in width surrounding the pit of two microns in diameter. By comparing Fig. 71(b) and Fig. 71(c), the surface inside the pit seems to be high in chlorine but less in magnesium. Chlorine was also present in the area in near vicinity to the pit. The second SIMS map for magnesium (i.e after about 12 monolayers of surface was removed during the first magnesium map and chlorine map), Fig. 71(d), showed magnesium was still present in the area surrounding the pit.

A sample of SS316 was ion etched in order to obtain an oxygen etch profile for a pit in the intermediate zone. A landing current of 30 uA with beam energy and focus potential of 6 KeV and 3 KV respectively were used. The AES analysis result across the pit for a
Fig. 69 Cumulative concentration diagram for a pit in the intermediate zone for SS304 sample.
Fig. 70 (a) Pit in the intermediate zone of the crevice (X20000) for SS316 sample.
(b) Chlorine Auger map

Contours:  
- 80% of maximum intensity.
- 20% of maximum intensity.
Fig. 71 a) SEM picture of pits in the intermediate zone. b) First Mg SIMS map.  
c) First Cl SIMS map. d) Second Mg SIMS map.
various etching interval up to 376 seconds was presented in Fig. 72. After 20 seconds ion etching in which about 70% of carbon impurities on the surface was removed (see section 4.2.11(ii)), higher oxygen concentration at pit edge than at pit centre was revealed. The oxygen concentration inside pit dropped substantially during etching as compared to the outside pit. After 376 seconds etching about 95% of the original level of oxygen in the surface of inside pit was removed comparable to only about 65% for the surface at pit edge. These indicate vividly the greater thickness of oxide on the pit edge relative to that in the centre.

A typical cumulative concentration diagram for a pit in the central zone of a crevice for SS316 sample is presented in Fig. 66. The surface of the inside and outside pit contained a similar concentration of chlorine, iron, chromium, nickel, and oxygen. Magnesium was hardly detected and in most cases were below detection limit of the spectrometer used. Pits existing in this region had a higher molybdenum concentration in the surface of pit than just outside the pit.

It was shown above that the pits in different zones of crevice have different chemical composition particularly chlorine and magnesium. The average concentration of elements in the surface of pits and their surrounding area from the above results were summarized in Table 8. The data in the table for pits in the crevice mouth zone and the central zone were the average values of all data obtained in the point analysis across the pits, for these two zones the
Fig. 72 Relative concentration of oxygen in the surface of a pit and in its immediate vicinity as a function of etch time for SS316 sample. 
Etch time: a) 0 sec. (original), b) 20 secs., c) 115 secs. and d) 376 secs.
Table 8. Average concentration of elements in the surface of pits at different zones of crevice for type 316 stainless steel sample.

<table>
<thead>
<tr>
<th>Position of pit in crevice</th>
<th>Element (at.%)</th>
<th>Mo</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>Cl</th>
<th>Mg</th>
<th>O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pit in crevice mouth zone</td>
<td></td>
<td>0.71</td>
<td>5.26</td>
<td>6.13</td>
<td>33.10</td>
<td>2.69</td>
<td>6.84</td>
<td>45.26</td>
</tr>
<tr>
<td>Pit in intermediate zone</td>
<td>Pit edge</td>
<td>1.88</td>
<td>7.86</td>
<td>N.D*</td>
<td>36.57</td>
<td>8.56</td>
<td>7.53</td>
<td>37.55</td>
</tr>
<tr>
<td></td>
<td>Pit centre</td>
<td>1.65</td>
<td>12.11</td>
<td>N.D</td>
<td>43.57</td>
<td>10.21</td>
<td>4.73</td>
<td>27.73</td>
</tr>
<tr>
<td></td>
<td>1 pit radius from pit edge</td>
<td>1.51</td>
<td>12.37</td>
<td>N.D</td>
<td>42.91</td>
<td>5.50</td>
<td>4.82</td>
<td>32.90</td>
</tr>
<tr>
<td>Surface before test</td>
<td>B.D*</td>
<td>1.87</td>
<td>6.27</td>
<td>45.11</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>46.76</td>
</tr>
</tbody>
</table>

*B.D - below detection limit
*N.D - not detected
distribution of elements in the surface seems to be independence of
position. For the pit in the intermediate zone has different
concentration of elements in its surface and in the surface of its
immediate vicinity the average values of three nearby points for
concentration of elements at pit centre, pit edge, and one pit radius
from pit edge are listed. The concentration of chromium, chlorine,
magnesium, and oxygen do show a consistent trend whether in a large
scale (crevice mouth and central zones) or in a microscale (centre of
the pit and pit edge). The pits in the crevice mouth zone are
uniformly high in oxygen and magnesium whilst those in the central
zone are high in chromium and chlorine. Similar changes in surface
compositions were also observed in the anodic (inside pit) and the
cathodic (pit edge) areas of the individual pit in the intermediate
zone. In the cathodic area further away from the pit edge (e.g one
pit radius from the edge) all elements detected were decreased in
their concentration compared with those at pit edge but chromium and
iron did show an increment in their concentration. In general, all
surfaces examined were enriched in chromium but deficient in iron
compared with the initial surfaces.

In order to relate the localised surface analyses at individual
pits to the detailed surface chemical variations with electropotential
discussed in chapter 4 the chlorine to magnesium ratio was used. For
several pits in the intermediate zone atomic ratios of chlorine to
magnesium were plotted as a function of distance from the pit centre
relative to the pit radius (Fig. 73). The Cl/Mg ratios have a highest
value at the centre of pits, gradually decreasing and reaching a
Fig. 73 Cl/Mg ratios as a function of relative distance from centre of the pit.
minimum value approximately at a distance 1/4 pit radius from the pit edge before recovering again to reach another maximum value at about one pit radius from the edge. The Cl/Mg ratios then gradually decrease again (Fig. 73) at greater distances from the centre. Fig. 73 also shows that there is not much different in the trends in this variation of Cl/Mg ratio across the pits between type 316 and type 304 stainless steels.
5.4 Discussions

5.4.1 Sample Surface After The Exposure

At the very beginning of the crevice attack, micropits are developed [20,36]. A highly acid solution and high concentration of chloride ions will be developed inside the crevice due to metal dissolution and hydrolysis of the metal ions and the diffusion of chloride ions inward into and corrosion reaction products outward from the crevice. The gradient of acidity and chloride concentration fall to lower values at the exterior of the crevice has resulted in the development of different stages of morphology across the crevice (Fig 58(a-f)). The different concentration of chloride ions also lead to a different level of chloride ions adsorbed into the surface of samples (figures 64, 65, and 66). The higher the acidity in the crevice solution and the higher the concentration of chloride ions the more will the interior part of the crevice be driven to anodic potentials while the exterior part becomes the more cathodic. This difference in electrochemistry forces magnesium to leave the crevice. In part, the magnesium will be deposited on a microscale in that area, in the immediate vicinity of a pit, which is acting as the cathode for the pit. This occurs in particular at the pits in the intermediate zone of the crevice.

The bulk of the corrosion products which results from corrosion reactions inside the crevice will be deposited at the exterior part of the crevice. The chlorine present in the corrosion products and in
the surface of pit in the crevice mouth region is probably in the form of basic chloride (probably Mg₂(OH)Cl₃ and FeOHCl), as suggested for stainless samples exposed at cathodic potentials (Chapter 4). Iron and chromium in the corrosion products may be in the form of oxy-hydroxide or iron oxide as indicated by a high intensity of oxygen peak in the spectrum of the corrosion products (Fig. 61(a) and Fig. 61(c)) and brownish in colour of the deposit on the exterior part of the crevice. The presence of chlorine in the surface of sample under the loose corrosion products suggests only some of FeOHCl was left on the surface as the corrosion products layer peeled off (Fig. 61(b)).
5.4.2 **Surface Chemistry of Individual Pits**

Pit-like features are seen in the SEM in each zone of the crevice i.e. in the highly etched centre (anodic) zone, in the crevice mouth (cathodic) zone and in the intermediate zone between them. It is probable that at some time during the development of the crevice chemistry these have all been active pits but that those in the centre have been engulfed in the general anodic corrosion whereas those in the mouth have become repassivated by the extension of cathodic activity. An examination of the magnesium and chloride ions concentrations associated with each of those classes of pit supports this view. The significant results are as follows:

a) **Anodic, Central Zone**

This entire zone including the remaining pits was rich in chlorine and magnesium was hardly detected. There was no different in the magnesium to chloride ratio between the pit centre and its periphery showing that the residual pits in the zone do not have individual anodic and cathodic parts. The high concentration of chromium and molybdenum but low concentration of iron in the surface of this area, including the pits, agreed well to the result of the exposure of the samples at high anodic potentials (potentials greater than the pitting potential - see chapter 4) which suggests that the zone was under uniformly a high anodic corrosion reaction. The chromium and molybdenum concentrations in this area arise from the high selective dissolution of iron and the formation of chromium
oxy-chloride and MoO₂ as discussed in the previous chapter. The formation of MoO₂ is possible because the solution inside a crevice has a low pH value, i.e. less than 4 [24, 129]. The hydrolysis of metal ions (equation 10) will be responsible for lowering the pH value of the crevice solution, in which the hydrolysis of Mo⁺³ will result in the formation of MoO₂ (equation 62).

b) Cathodic, Crevice Mouth Zone

Pits in the crevice mouth zone have high magnesium concentrations all over their surfaces and in their immediate vicinity. The presence of the high concentration of magnesium and low concentration of chlorine with no change of ratio inside or outside the pits (Fig. 64) means that the pits were no longer active. The cathodic reactions seem to have increased to counterbalance the increasing rate of the anodic reactions in the centre of the crevice. The iron detected in the surface of the passive pits was at the highest concentration, relative to chromium found in any part of the crevice or at any potential. The entire surface was clearly covered with magnesium compounds, probably the basic chloride and hydroxide, but also seems to have received a precipitate of iron as oxide or hydroxy-oxide as indicated by the high oxygen and iron detected on the surface.

In contrast to the above classes of pits those in the intermediate zone (Fig. 65) do show a variation from excess chloride over magnesium at the centre to excess magnesium over chlorine beyond
their edge. Thus the pits possess the mixed characteristic of the central zone and the crevice mouth zone, i.e. inside pit is anodic and the area in the immediate vicinity of the pit is cathodic. The individual activity of the pit can also be demonstrated by the plot of chlorine to magnesium ratio against the distance from centre of the pit and can thus be compared to the chlorine to magnesium ratio of anodic and cathodic surfaces obtained in the earlier work (chapter 4) as a function of potential. The theoretical calculation of Melville [44] on the potential variation around a pit can be used to relate potential to a distance scale. This correlation is made in the next section.

5.4.3 Potential Variation Around Active Pits

According to the Melville's calculation [44] (chapter 2 - section 2.1.2.1), the potential is high at the centre of the pit (r<a, Fig. 74) but falls away rapidly for greater distances from the centre of the pit. The potential variation of the pits under investigation is assumed to be similar to that predicted by Melville but the calculation provides only a scale of relative potential variation. To make a comparison to the electropotentials used for the XPS experiments a scale of actual potential must be provided. To be able to do this the potential of pit surface and its vicinity has to be estimated.

Rosenfeld et.al [39] did measure the potential inside pits in stainless steel for a test environment of 0.04M FeNH₄(SO₄)₂·H₂O + 0.56M NH₄Cl. They found the potential
Fig. 74 Potential variation around a pit (After Melville, reference 44)

$a =$ pit radius, $r =$ distance from pit centre.
inside the pit was more active than the outside of the pit. However, the potential-current curve of SS316 in 1M MgCl₂ solution (Fig. 29) shows no active-passive transition region, thus the pit in the steel developed in 1M MgCl₂ solution is very unlikely to have an active potential. The only possibility is that the potential in the pit will be around the pitting potential. Since the pits observed were in the order of a micron and have high concentration of chlorine that implies that the pits had just initiated and were ready for further propagation when the potential reached greater values [50]. The potential at the pit edge should not be less than the rest potential of the steel electrode in the present environment. The potential of the surrounding cathode surface in the present case should not exceed the hydrogen evolution potential since the formation of hydrogen gas bubbles was not observed in the natural crevice. Hydrogen evolution was observed at about -400 mV(SCE) for both steels, SS304 and SS316.

Basing on these arguments, the potential at the centre of the pit was then assumed to be equal to the pitting potential of the steels i.e. +330 mV(SCE) for SS316 and +320 mV(SCE) for SS304 and the edge of pits were assumed to be at the rest potential of the steels, i.e. +120 mV(SCE) and +60 mV(SCE) for SS316 and SS304 respectively. The potential axis of the Melville's plot was then re-scaled to suit the requirement of the values adopted for each stainless steels (SS304 and SS316) to obtained the plots in Fig 75 and Fig. 78. By matching the potentials in Fig 75 and Fig. 78 to Cl/Mg ratios of the whole electrodes exposed at different potentials (Fig. 32) the values of Cl/Mg ratios from Fig. 32 could be replotted against r/a (distance
Fig. 75 Potential variation around a pit for SS316 sample. Y-axis of Fig. 74 was re-scaled to obtain potential values with respect to saturated Calomel electrode (SCE).
Fig. 76 Cl/Mg ratio as a function of relative distance from pit centre for SS316 sample, estimated using Cl/Mg ratio of whole electrodes (XPS data) and variation of potential around a pit.
Fig. 77  Cl/Mg ratios as a function of relative distance from pit centre

i) Obtained from direct measurement (AES data).

ii) Estimated from Cl/Mg ratio of whole electrodes (XPS data).
from centre of the pit relative to pit radius) to obtain figures 76 and 79. The variation of Cl/Mg ratio predicted by this method for the pits using the XPS data seems to be in a reasonable accord to the results of Cl/Mg ratios directly measured from the pits by AES (Fig. 73). In particular the shape of the distribution, (Fig. 77 and Fig. 80) is in very close agreement. In view of the present difficulties in making quantitative comparison of Auger and photoelectron intensities this is as good as can be expected. Therefore the assumption for the variation of potentials around a pit (figures 75 and 78) seems to be a good match to the real situation for a newly initiated pit.

5.4.4 Surface Composition of The Steel Elements

Having shown in the preceding section that the potential variation around the pits can be modelled using the Cl/Mg ratio as a guide it is appropriate to examine the composition of the other elements as a function of this potential. Table 9 shows the mean AES data for the steel elements obtained from the crevice regions discussed in the preceding sections. The data for the steel elements (Fe, Cr, Ni, and Mo) were normalised to 100 % and are plotted as a function of estimated potential as 'red points' (Fig. 81) on a reproduction of the XPS data of section 4.3.2 (Fig. 36) for type 316 stainless steel. The equivalent potential for the pits in the central zone and in the crevice mouth zone shown in Fig. 81, i.e. at +500 mV(SCE) and -300 mV(SCE) respectively are only estimated values. Nevertheless the potentials seems to be reasonable compared to the
Fig. 78 Potential variation around a pit for SS304 sample. Y-axis of Fig. 74 was re-scaled to obtain potential values with respect to saturated Calomel electrodes.
Fig. 79  Cl/Mg ratio as a function of relative distance from pit centre for SS316 sample, estimated using Cl/Mg ratio of whole electrodes (XPS data) and variation of potential around a pit.
Fig. 80  Cl/Mg ratios as a function of relative distance from pit centre

i) Obtained from direct measurement (AES data).

ii) Estimated from Cl/Mg ratio of whole electrodes (XPS data).
Table 9. The mean AES data for concentration of steel elements in the surface of the pits in different crevice zones for SS316 sample.

<table>
<thead>
<tr>
<th>Position of pit in crevice</th>
<th>Element (at %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mo</td>
</tr>
<tr>
<td>Pit in crevice mouth zone</td>
<td>1.57</td>
</tr>
<tr>
<td>Pit in central zone</td>
<td>6.21</td>
</tr>
<tr>
<td>Pit in the intermediate zone</td>
<td></td>
</tr>
<tr>
<td>Pit centre*</td>
<td>2.48</td>
</tr>
<tr>
<td>Pit edge*</td>
<td>3.50</td>
</tr>
<tr>
<td>1 pit* radius from pit edge</td>
<td>2.27</td>
</tr>
</tbody>
</table>

* average of three points

^a derived from wide scan spectra
Fig. 81 The concentration of the steel elements in the surface of pits (Table 9) are plotted as a function of estimated potential on a reproduction of the XPS data. The concentration of the steel elements are shown as 'red point' in the plot.

- a - pit in crevice mouth zone.
- b - one pit radius from edge
- c - edge of pit
- d - centre of pit
- e - pit in central zone
value of potentials at various points at the pit in the intermediate zone, i.e. +330 mV(SCE), +120 mV(SCE) and -70 mV(SCE) for the pit centre, the pit edge and one pit radius from the pit edge respectively.

The concentration of iron, chromium, and molybdenum in the surface of the pit in the central zone of crevice is in a good match to the XPS data for the whole electrodes exposed at potentials in Region IV of the surface electrochemical behaviour plot of type 316 stainless steel (Fig. 36), thus strongly supports the suggestion that high anodic dissolution in which iron was selectively dissolved has taken place in the centre of the crevice. A high concentration of molybdenum presents in this zone implies that MoO$_2$ was formed [56] in order to counter the high rate of the anodic reaction. The exposure of molybdenum during the selective dissolution of iron has also helped in slowing the rate of anodic reaction because of the low solubility of molybdenum in highly acidic solutions [77]. At lower rates of anodic reaction it is the exposure of molybdenum which probably results in repassivation of the pit as suggested by Newman [130], as can be seen in the case of pits in the crevice mouth zone, the pits were repassivated with only a low concentration of molybdenum being found.

The concentration of iron and chromium at the potentials associated with the pits in the intermediate zone are very different to those expected from the XPS data. However the XPS values were obtained from whole electrodes exposed at a single potential. The
solution in this case contains only a very low concentration of iron ions derived from the samples. In the case of the crevice a near saturation concentration of iron ions develops at the crevice centre and, although only seen as visible stain at the crevice centre, must be expected to greatly influence the formation of salt films and precipitate throughout the intermediate zone. It is thus this iron rich precipitate that masks changes in the concentrations of the other elements in all but the active central zone.
5.4.5 The Precipitation of Magnesium Compounds Around Pits In A Crevice.

In the previous section some experimental evidence was presented showing the present of high concentration of magnesium around the pits together with other elements such as chlorine, oxygen, iron, and chromium. By estimating the potentials of a pit (Fig. 75), the surrounding area of the pit could be lied within a cathodic range of potential between +120 mV(SCE) and -110 mV(SCE) (for SS316). The XPS data showed that within this range insoluble basic chlorides (eg. $\text{M(II)}_2(\text{OH})_3\text{Cl}$) and oxy-hydroxide of iron, chromium and magnesium are formed. By Cl/Mg ratio plot (Fig. 73) it is shown that at the edge of the pit the value of Cl/Mg ratios are at the lowest value. Further, the presence of a high concentration of oxygen at the edge of the pit suggests that the magnesium was present as a mixed compound of magnesium hydroxy-chloride and magnesium hydroxide.

It is surprising to have magnesium hydroxide or magnesium hydroxy-chloride formed surrounding tiny pits in a crevice within which there is expected to be a highly acid solution whilst the precipitation of iron hydroxide or iron hydroxy-chloride in that kind of solution poses no problem. Magnesium hydroxide precipitates at pH value greater than 8.6 from 1M $\text{MgCl}_2$ solution or at pH 9.54 in 0.01M $\text{MgCl}_2$ solution as pointed out by Castle and Tanner Tremaine [122]. The cathodic areas around the pits show that it is possible for oxygen to diffuse into the crevice and undergo reduction to form $\text{OH}^-$ ion at the solution-metal interface. Whether this makes a significant
impact on local pH values depends on the critical thickness of the diffusion layer, \( \delta \), which is responsible for holding the OH\(^-\) ion in place until the solubility product of Mg(OH)\(_2\) is reached. The larger the diffusion layer thickness the larger amount of OH\(^-\) ion required to reach the solubility product of Mg(OH)\(_2\) [122] and the less likely is this thickness to be found. Thus would reduce the chance of precipitation especially in a highly acid solution.

To enable the critical diffusion layer thickness around the pit to be calculated a few assumptions have to be made to obtain relevant data i.e the pH value of the solution-metal interface, the critical current density for precipitation and concentration of magnesium ions in the solution-metal interface. The pH value in the bulk crevice solution where Mg(OH)\(_2\) was formed was assumed to be 4 after considering: i) Original bulk solution was 5. ii) The pH value of the pit solution as reported by previous workers [129] was about 3. iii)) pH values of less than 4 were the typical pH values for crevice solution [24]. The pH value of the solution-metal interface should be therefore less than the original pH value of the bulk solution but greater than the pH value of the pit solution adjacent to it. The potentials of the area outside pit in which magnesium compound was precipitated i.e about 2.5 pit radii from pit edge (SIMS maps in section 5.3.2) were estimated to be between +120 mV(SCE) and -155 mV(SCE) (see section 5.4.3); thus the mean cathodic current density at the region could be measured from the curve of Fig. 29 as 0.45 uA.cm\(^-2\) if the pH value of the crevice solution was 5. However, the pH value of the solution in the crevice is assumed to be
4 and thus the mean cathodic current density should be slightly higher than for pH 5. By referring to the set of data at differing pH values (Fig. 42) obtained for cronifer 1925hMo exposed at high cathodic potential, a value can be obtained by interpolation. This suggests that the current at pH 4 will be greater than that at pH 5 by a factor of 1.2 i.e 0.54 uA.cm\(^{-2}\) (Fig. 82).

![Fig. 82 Steady state current density as a function of pH values.](image)

By assuming the critical current density for precipitation, \(i_{cp}\), is equal to this mean cathodic current density (0.54 uA.cm\(^{-2}\)), and the concentration of magnesium ions in the solution remained at 1M, then by inserting these values, together with other values (\(K_s\), \(D_{OH}^+\) and \(D_{H}^+\)) as used in section 4.4.1 into equation 53, the critical diffusion layer obtained was 17 \(\mu\)m. The cathodic dimension of the pit within the crevice is less than the value of \(\delta\) but \(\delta\) is still very small compared to the overall dimensions of the crevice (1 cm). Thus it seems possible for local variations in pH to arise from local cathodic activity.
5.4.6 The Formation of Open Pits

All pits found during the investigation seem to be pits formed by undercutting the oxide. For example pits shown in Fig. 59 and Fig. 70(a). They did not have a polished bottom. Inside the pits, high concentration of chloride ions was found (Fig. 70(b)). These pits were probably generated from smaller pits i.e. pits with size of less than 1 μm (Fig. 58(d)). The smaller pits were probably not real pits but some kind of surface defects. This implies that the initiation of the pits began at these defects. The adsorption of chloride ions in the surface film through the defects then caused a further breakdown of the film. The accumulation of chloride ions in the defective points of the surface will accelerate the dissolution of metal matrix under the surface film which will then result in the collapse of the residual surface film into the pit. The collapsed surface film probably caused the roughening of the pit bottom. Moreover the oxygen etch profile for one of the pits (Fig. 72) revealed that the inside of the pit had a relatively thin oxygen-containing film compared with the pit edge.

The open pit like the ones shown in Fig. 70(a) was actually still holding close cell conditions in which the debris of the surface film serves as a semi-closed trap for the concentrated anolyte [45]. Under this conditions pitting attack will continue autocatalytically. From the experimental observations, thus, the nucleation of an open pit which is not associated with inclusions could be summarised in a simple model as shown in Fig. 83.
Fig. 83 The formation of an open pit.

a) Defective passive film

b) Metal matrix exposed to the electrolyte

c) Pit was formed, followed by the collapse of surface film, closed cell conditions maintained.

d) Pit established, precipitation of $M^+_{2}2(OH)_{3}Cl$, $Mg(OH)_2$
6 Pitting At Sulphide Inclusions

6.1 Introduction

Sulphide inclusions are well known pitting sites in stainless steels (see chapter 2 section 2.2). However the mechanism of this type of pitting attack is still one of the current topics in research and modelling of pitting attack. The association of pitting attack at inclusion with chloride ions has been also pointed out by many workers [69,76]. The opportunity was taken in the course of this study to investigate the pitting attack at sulphide inclusions. The technique is more refined than that of previous workers and uses combined Auger Electron Spectroscopy (AES) and Energy Dispersive (X-Ray) Analysis (EDXA). Incorporation of elements of the inclusion such as manganese and copper in the pitting solutions was investigated through their presence in the surface (AES) or deep below the surface of the inclusions (EDXA).

6.2 Experimental

The sulphide inclusions in type 316 stainless steel which were investigated were those found naturally in the samples which were exposed as simulated crevices as discussed in chapter 5. Most of the data presented for this investigation were in the form of both AES and
EDXA maps using 80% and 20% of the maximum intensity of elements as contours (details will be discussed in the next section). AES and EDXA maps of chlorine, sulphur, manganese, copper, oxygen, iron, and chromium were produced. A beam current of 7.5 nA which gave a spatial resolution of about 0.18 μm was used in all Auger mapping. The electron beam energy of 10 KeV was used in most Auger and X-Ray mapping except in the investigation on the depth concentration of sulphur, and copper in the inclusions in which beam energy was varied from 10 KeV to 15 KeV.

6.3 Auger and X-Ray Mapping

The shaded peaks in the AES spectra of Fig. 84 indicate the peak of the appropriate elements used in obtaining AES maps whilst the shaded peaks in the X-Ray spectrum of Fig. 85 were used for EDXA maps. During the acquisition of data for AES maps the peak intensity was substracted from background intensity and this data, (P-B), were collected. However such data do not eliminate topographical effects. To correct for this the net peak intensity was divided by background intensity, (P - B)/B, (see insert of Fig. 84) [109] and this value used for the AES mapping procedure. To do this the background of each appropriate peak was collected simultaneously. The manipulation of data to obtain the (P - B)/B maps was done on the pre-collected data by means of a computer software available from the Link Computer Company. It is also worth to note that manganese AES map was produced after correction by substraction of the iron map, since as shown in Fig. 84 Auger peak of iron at 651 eV overlapped with Auger peak of
Fig. 84 AES spectra at sulphide inclusions.

The shaded peaks are the Auger peaks used in mapping.
Fig. 85  An X-Ray spectrum at sulphide inclusions. The shaded peak are the X-Ray peaks used in the X-Ray mapping.
manganese at 636 eV whilst iron peak at 598 eV overlapped with manganese peak at 589 eV. The correction was done by subtraction the raw map data of net peak intensity, \((P - B)\) of iron from the raw map data of net peak intensity of manganese, before being divided with background data.

In EDXA map, a whole peak intensity (area of each peak) was collected. In the case of manganese map a correction to remove the chromium map has to be done because \(\text{Mn}_{K\alpha}\) (the only appropriate manganese peak available) overlapped with \(\text{Cr}_{K\beta}\) line. A map acquired at the \((\text{Mn}_{K\alpha} + \text{Cr}_{K\beta})\) peak was corrected by subtraction of the data of the \(\text{Cr}_{K\alpha}\) map to obtain \(\text{Mn}_{K\alpha}\) map. This map has to be multiplied by a factor (eg. 20) to enhance its intensity because the combined \((\text{Mn}_{K\alpha} + \text{Cr}_{K\beta})\) signal is lower than the signal of \(\text{Cr}_{K\alpha}\) which was used in obtaining the chromium map.

Both AES and EDXA maps presented, using 80 % and 20 % of the maximum intensity of elements as contours. It is a normal practice to use 80 % and 20 % contour levels since it will give a well defined edge between the highest and the lowest concentration of element present assuming the apparent distribution of element in the mapped area satisfies the Gaussian distribution.
6.4 Results

The seven day exposure of stainless steel samples in the form of a tight crevice in 1M MgCl₂ solution was found to be sufficient to remove weak layer on the surface of inclusions. The inclusions of size up to 6 microns were revealed as shallow flattened depressions (eg. Fig. 87(a)). Some of them had already been attacked at their edges (Fig. 87(a)) or had their top uniformly corroded (Fig. 90(a)). Only four inclusion sites which were typical of those observed in the investigation are presented in this section. They are named as inclusion I (Fig. 87(a)), inclusion II (Fig. 88(a)), inclusion III (Fig. 90(a)), and inclusion IV (Fig. 91(a)). The inclusions I, II, and III were used to show a different form and degree of attack, while inclusion IV was used to illustrate the concentration of sulphur, and copper at different depths by varying beam potential.

The initial pitting attack on an inclusion was shown by inclusion I in which part of its top was slightly removed and small crevices were found at its edges. AES point analysis of the surface of the inclusion (Fig. 86(a)) shows manganese and chlorine were present on the surface of inclusion I whilst in the surface further away from the inclusion iron is the major surface component and no chlorine was detected (Fig. 86(b)). Auger maps (Fig. 87(b) and Fig. 87(c)) show that manganese and chlorine present almost the same contour within the outline of the inclusion as revealed by the sulphur X-Ray (Fig. 87(g)). The Auger spectrum of the surface at the middle of the inclusion also shows sulphur was present but was much less
Fig. 86 Auger spectra of the inclusion I (see Fig. 87(a))

a) The surface of the inclusion.
b) The steel surface at 1 \( \mu \)m away from inclusion.

KINETIC ENERGY
Fig. 87 (a)

Fig. 87 (a) SEM picture of inclusion I (X10000).

(b) Manganese Auger map

Contours: □ □ 80% of maximum intensity.
□ □ 20% of maximum intensity.

Fig. 87 (b)
Fig. 87(c) Chlorine Auger map of Inclusion I.

Contours:
- □ 80% of maximum intensity.
- □ 20% of maximum intensity.
Fig. 3/(e) Iron Auger map of Inclusion I.

Contours:

- □ 80% of maximum intensity
- □ 20% of maximum intensity.

Fig. 37/(f) Chromium Auger map of Inclusion I.
Fig. 87(g) Sulphur X-Ray map of Inclusion I.

Contours:  
- 80% of maximum intensity.
- 20% of maximum intensity.

Fig. 87(h) Titanium X-Ray map of Inclusion I.
Fig. 87(i) Iron X-Ray map of Inclusion I.

Contours:

- 80% of maximum intensity.
- 20% of maximum intensity.
extensive than chlorine and manganese (Fig. 86(a)). The complete loop of a 20% contour line for iron (Fig. 87(e) and Fig. 87(i)) indicates that iron was at a minimum in both AES and EDXA modes within the contour for which chlorine was at a maximum. There was little difference in chromium concentration between outermost surface of the inclusion and the rest of the steel (Fig. 87(f)).

The SEM picture of inclusion II (Fig. 88(a)) shows a higher stage of pitting attack than of the inclusion I. The edges of the inclusion II apparently underwent a preferential pitting attack which resulted in the formation of the deep and sharp micro-crevice at the edge of the inclusion. The distribution of sulphur in the surface of the inclusion was uniform (Fig. 88(b)). There was no indication of any oxide inclusions present as shown by Fig. 88(d) in which oxygen was at a low uniform concentration of less than 20% of maximum intensity. The possible presence of iron sulphide inclusions is also very unlikely since only a low intensity of iron exists in the inclusion area (Fig. 88(g)). Chlorine was again very intense both on the surface of the inclusion as well as in the deep micro-crevice at the edge of the inclusion (Fig. 88(e)). These sulphide inclusions exist deep below the surface with part of their edges lost due to electrochemical reaction in the micro-crevice. This can be seen in Fig. 88(f) in which a smaller area is occupied by sulphur X-Ray map than is the "hole" unoccupied by the iron X-ray (Fig. 88(g)). The sulphur Auger map matches the iron X-Ray map quite well. The presence of chromium in inclusion II as chromium sulphide could be possible but chromium would have to be at a lower concentration than that in the
Fig. 88 (a) SEM picture of Inclusion II (X10000).
(b) Sulphur Auger map

Contours: □ 80% of maximum intensity.
□ 20% of maximum intensity.

Fig. 88(b)
Fig. 88(c) Copper Auger map of Inclusion II.

Contours:
- □ 80% of maximum intensity.
- □ 20% of maximum intensity.

map of Inclusion II.
Fig. 88(e) Chlorine Auger map of Inclusion II.

Contours:
- 80% of maximum intensity.
- 20% of maximum intensity.

Fig. 88(f) Sulphur X-Ray map of Inclusion II.
Contours: □ 80% of maximum intensity.
□ 20% of maximum intensity.

Fig. 3(a) Iron X-ray map of Inclusion II.

Fig. 3(b) Chromium X-ray map of Inclusion II.
bulk alloy as is shown by chromium X-Ray map, Fig. 88(h).

Not all the inclusions which have been observed in the investigation have undergone initial pitting attack at the sulphide phase - metallic matrix boundary as reported earlier, but some have been attacked almost uniformly over the entire surface of the inclusion, eg. inclusion III. The ones in Fig. 90(a), inclusion III, were revealed by AES point analysis not to be a pure MnS but contained copper (Fig. 89). Manganese Auger map, Fig. 90(f), shows manganese to be only present in small inclusions. Sulphur and copper Auger maps show copper and sulphur to be present on virtually the same areas of the surface (Fig. 90(b) and Fig. 90(e)). It was not able to obtain an X-Ray map for manganese because of the low manganese X-Ray signal. The X-Ray and Auger maps of iron and chromium (figures 90(g), 90(h), 90(k), and 90(l)) again vividly show that the inclusions did not contain iron or chromium neither as sulphide nor oxide or chloride.

An attempt was made to probe the depth distribution of the inclusions by varying the electron beam potential. This was unsuccessful because of the differing X-Ray efficiencies of copper and sulphur at low potential (10 KV). However the relevant Auger and X-Ray maps are given in figures 91(b – g).
**Fig. 89** AES spectra of inclusion III at two different areas. (see Fig. 90(a))
Fig. 90(a)

Fig. 90 (a) SEM picture of Inclusion III (X10000).
(b) Sulphur Auger map

Contours: 
- 80% of maximum intensity.
- 20% of maximum intensity.
Fig. 90(c) Chlorine Auger map of Inclusion III.

Contours: 80% of maximum intensity.
          20% of maximum intensity.
Fig. 90(e) Copper Auger map of Inclusion III.

Contours:  
- 80% of maximum intensity.
- 20% of maximum intensity.

Fig. 90(f) Monoparam Auger map of Inclusion III.
Fig. 90(g) Chromium Auger map of inclusion III.

Contours:

- 80% of maximum intensity.
- 20% of maximum intensity.

Fig. 90(h) Iron Auger map of Inclusion III.
Fig. 90(1) Sulphur X-Ray map of Inclusion III

Contours:
- □ 80% of maximum intensity.
- ■ 20% of maximum intensity.

Fig. 92(1) Copper X-Ray map of Inclusion III.
Fig. 90(k) Chromium X-Ray map of Inclusion III.

Contours:
- 80% of maximum intensity.
- 20% of maximum intensity.
Fig. 91(a) SEM picture of Inclusion IV (X10000)
Fig. 91(b) Sulphur Auger map of Inclusion IV

Contour: ☐ 80% of maximum intensity.

Fig. 91(c) Copper Auger map of Inclusion IV.
Fig. 91(d) Sulphur X-Ray map of Inclusion IV at 10 KeV.

Contour: □ 80% of maximum intensity.
Fig. 71: (1) Sulphur X-Ray map of Inclusion IV at 15 KeV.

Contour: □ 80% of maximum intensity.

Ray map of Inclusion IV at 15 KeV.
6.5 Discussions

Of the three inclusion features reported in the previous section, inclusion I and inclusion II seem to be under a similar mechanism of corrosion attack in which inclusion II was at a more advanced stage of attack than was inclusion I. This can be judged from the deep crevice at the sulphide-matrix boundary and the nearly complete pit formed at the smaller inclusion nearby the big inclusion, (inclusion II). By contrast, only very shallow crevices existed at the sulphide-matrix boundary of the inclusion I.

In the early stage of attack both inclusion I and inclusion II had their weak surface film dissolved via metal dissolution processes or broken down by the adsorption of chloride ions. Two points have been pointed out by Wranglen [69] reasoning on the activating effect and the preferential adsorption of chloride ions in the surface of sulphide inclusions. One was based on the Hofmeister Series (Table 10) which shows that chloride ions have strong tendency towards contact adsorption. The second point was based on electrostatic theory, namely that, because of the relatively high electron conductivity of sulphide inclusions, as compared to the surrounding oxide film, stronger electrostatic image forces are developed on the sulphide inclusions than on the oxide film. This effect preferentially attracts more chloride ions to the inclusions. These points both help explain the result of the present work in which the agglomeration of chloride ions at sulphide inclusions was observed in all cases without exception.
The exposure of manganese sulphide inclusion (after the breakdown of its weak surface layer) to aqueous environment will result in the oxidation of MnS to elementary sulphur according to the reaction [69]

\[
\text{MnS} \rightarrow S + \text{Mn}^{+2} + 2e^- \quad (64)
\]

and, as pointed out by Wranglen [69,131], the oxidation of MnS may proceed to \( \text{H}_2\text{SO}_3 \) and \( \text{H}_2\text{SO}_4 \). One of the routes leading to the formation of \( \text{H}_2\text{SO}_3 \) and \( \text{H}_2\text{SO}_4 \) is as follows,

\[
\text{S} + 3\text{H}_2\text{O} \rightarrow \text{HSO}_3^- + 5\text{H}^+ + 4e^- \quad (65)
\]

\[
\text{HSO}_3^- + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 3\text{H}^+ + 2e^- \quad (66)
\]
The total reaction is similar to that suggested by Eklund [74],

\[ \text{MnS} + 4\text{H}_2\text{O} \rightarrow \text{Mn}^{+2} + \text{SO}_4^{2-} + 8\text{H}^+ + 8\text{e}^- \]  

(67)

The acid anolyte formed due the reaction (65) and (66) exerts a dissolving action on the remaining MnS according to the reaction (68) namely,

\[ \text{MnS} + 2\text{H}^{+2} \rightarrow \text{H}_2\text{S} + \text{Mn}^{+2} \]  

(68)

and sulphur is possible to be formed in acid solution from the oxidation of \( \text{H}_2\text{S} \) [74],

\[ \text{H}_2\text{S} \rightarrow \text{S} + 2\text{H}^+ + 2\text{e}^- \]  

(69)

The dissolution of MnS will lead to a formation of a micro-crevice exposing the bare metal which subsequently undergoes dissolution under a favourable condition for pitting provided by the micro-crevice. The complete features of pitting attack on pure manganese sulphide inclusions can be consulted a model by Wranglen [69] in Fig. 5 (chapter 2). His model seems to suit to the type of inclusions as inclusion I, i.e. pure manganese sulphide inclusion. Only a small area containing sulphur was found on the surface of the inclusion I whereas manganese was very intense over the whole area of attack. This suggests that probably the elemental sulphur formed during the early stage of attack was dissolved (equations 65). Thus Eklund's overall reaction may be a better description (equation 67). The increase of acidity in the crevice, formed according to equation (67), at the attacked inclusions results
in the generation of manganese ions but the final aggressive medium appears to be manganese chloride solution, not the sulphate. The localised nature of this attack is shown by the almost complete absence of iron and chromium ions from these pits.

The 10 KeV X-Ray maps of sulphur and manganese for inclusion I (Fig. 87) show high intensity of sulphur and manganese compared with inclusion II (Fig. 88) which has almost undetectable level of manganese. This again strongly suggests that the inclusion I was at an earlier stage of pitting attack than inclusion II. For the case of the inclusion II probably nearly all MnS situated within at least 4000 A from the surface was dissolved (equation 68). The depth, 4000 Å, is an approximate analytical depth for EDXA in iron at 10 KeV electron energy, estimated using equations 31 and 32. The \( \text{H}_2\text{S} \) gas released then oxidized to form non-metallic sulphur (equation 69) and deposited on the surface of pit.

The surface of the corroded inclusion II was found to contain copper probably as copper sulphide as a high intensity of sulphur was also found on the surface of the inclusion. Manganese which was also found was probably as manganese chloride salt not as manganese sulphide since the later is not stable in highly acidic solution. Comparing the position of copper in AES map (Fig. 88(c)) with the SEM picture of the inclusion II (Fig. 88(a)), it is found that part of the intense copper area was situated in the micro-crevice at the boundary of the inclusion. This suggests that the copper sulphide was formed on the surface of the inclusion as well as in the micro-crevice at the
inclusion-matrix boundary. The copper sulphide formed probably by the reaction of the metallic copper in the inclusion with $H_2S$ (reaction 70) [35],

$$2Cu + H_2S \rightarrow Cu_2S + 2H^+ + 2e^-$$

Note that the formation of $Cu_2S$ as a separate phase in steel is very improbable because of free energy of formation of $Cu_2S$ is practically the same as for FeS and the low activity of Cu [68]. However, some enrichment of copper in the sulphide inclusions does take place as reported by Salmon Cox and Charles [124] who occasionally found 2 - 4 % Cu in the sulphide inclusions in a steel containing 0.24 % Cu.

Referring to the results of inclusion III, it is found that there is no micro-crevice such as existed in inclusion I and II. The SEM picture of inclusion III (Fig. 90(a)) also shows that only a thin layer of its top surface was uniformly removed. AES maps then reveal that the entire surface of the inclusion III contained copper, sulphur and chlorine. Manganese was also observed at the smaller inclusions. The copper and sulphur present in this inclusion may be also be present as copper sulphide or as temporary non-metallic sulphur. The presence of copper sulphide on the surface of the inclusion seems to reduce the corrosion attack especially pitting. There is no contradiction whatsoever on the assumed role of copper sulphide as applied to the case of inclusion II, since inclusion II shows little enrichment in copper whereas the sulphide inclusions in inclusion III were very enriched in copper. The beneficial effect of copper
sulphides is understood to be due to its insolubility in highly acidic solutions. The solubility product of copper sulphide is $10^{-48}$ and manganese sulphide is $10^{-13}$\[125\]. Therefore the formation of copper sulphide will reduce the detrimental effect of sulphur since sulphur is known to greatly increase the acidity of the solution (equations 65 and 66).

It was seen that in inclusion III in which copper was enriched that the corrosion attack was uniform on the entire surface, and the attack will be replaced by pitting corrosion if the geometry of the inclusions in favour of the pitting attack. From the results on the corrosion attack on the sulphide inclusions which are discussed above, it is possible to generalise the attacks into two types, depending upon the manganese and copper composition in the inclusions. The route of attacks for a pure MnS or MnS lacking in Cu are similar to those documented by Wranglen [69]. The initial stage of the both type of attacks are similar. The two types of attack are summarized in Fig. 92.
Fig. 92 Pitting at MnS inclusion

**a) Inclusion in stainless steel**

- Pure MnS
- Cu enriched MnS

**I(b) First stage of pitting attack,**
- the formation of micro-crevice
- the exposure of active steel

**I(c) Second stage of attack**
- pit propagates

**II(b) First stage of attack,**
- attack is uniform
- CuS is formed

**II(c) Second stage of attack,**
- the occurrence of pitting depends on inclusion geometry.
Chapter 7

7 Conclusions

The results from two main different areas of the present investigation namely i) Investigation on the surface chemistry of whole electrodes exposed at preset single potentials. ii) Investigation on the surface chemistry of the individual pits developed in a simulated crevice, show a very close similarity. Supporting by a theoretical model of variation of potential around a pit by Melville [44] the results obtained in the latter were convincingly explained by the results of the former. In addition the XPS technique which gives an average value of surface composition (used in the former) and the AES technique which gives a local surface concentration of an area as small as 0.1 \( \mu \)m in diameter (used in the latter) are proved possible to be used in complement to each other, at least in the area of surface electrochemistry.

Another important area investigated in this work viz. the association of pits with a micrometer size sulphide inclusions which has been demonstrated using combined X-Ray/Auger mapping reaffirmed the observations of previous workers particularly on the association of chloride, sulphur, and copper in the pitting attack on copper-containing manganese sulphide inclusions.

The results of the investigation as discussed in chapters four,
five, and six lead to general conclusions as follows,

The presence of magnesium ions in chloride-containing solution enables the chlorine to magnesium ratio to be used to classify the surface potential of the electrodes into different regions of corrosion behaviour viz. cathodic, passive (cathodic and anodic), and transpassive regions. The surface chemistry of the electrodes can then be generalised according to the regions.

Similarly, in the case of individual pits chlorine to magnesium ratio can be used as an indicator to determine the activity of pits. Pits which are still active show significantly high value of chlorine to magnesium ratio for the surface of inside the pit than that of outside the pit. Repassivated pit will constantly have small value of chlorine to magnesium ratio (large value of Mg/Cl ratio) for the entire surface of the pit and its surroundings.

A precipitate of basic chloride of magnesium probably $\text{Mg}_2(\text{OH})\text{Cl}_3$ will be formed on the surface of stainless steels exposed at high cathodic potential (i.e. potential of greater than hydrogen evolution potential) in magnesium chloride solution. The passive film formed in 1M $\text{MgCl}_2$ solution is enriched in chromium but not enriched in molybdenum. Iron which is also present in the passive surface is suggested to be mainly as oxy-hydroxide ($\text{FeOOH}$). Chromium and molybdenum are highly enriched in the surface of molybdenum-bearing stainless steel which has undergone high anodic-transpassive metal dissolution. Their presence probably in the form of a stable $\text{MoO}_2$.
and oxy-chloride of chromium is likely to slow down the rate of the attack.

Pits developed within the intermediate zone (area between the centre and the mouth) of a crevice do show individual activity. Old pits in the pit mouth region may become fully cathodic and hence passivated whilst old pits in the central region of the crevice may be fully enveloped by general corrosion.

Melville's calculation on potential variation around a pit [44] is applicable in predicting the true potential variation across a newly formed pit in stainless steel when exposed in 1M MgCl₂ solution. The potentials of the surface of the inside pit lie between the rest potential and the pitting potential of the steel whilst the cathodic region surrounding the pit has cathodic potentials of not more negative than -200 mV(SCE) (for type 316 and type 304 stainless steels).

An active pit has high chromium content in its surface and in the surface outside it, but not at its edge. Molybdenum remains low in concentration over the entire surface area. Molybdenum probably acts as a supporting element for the formation of a protective layer by chromium that is by its presence in the pit surface the pitting attack will be slowed down.

The pure manganese sulphide inclusions will be the most favoured site for pitting attack in which chloride ions are locally agglomerated on
its surface and results in an initial stage of attack at a micro-crevice at the sulphide and metallic matrix boundary. In contrast copper enriched-manganese sulphide inclusions show no sign of micro-crevice and then surface was uniformly corroded. The possible formation of copper sulphide on the corroded surface of the inclusions will reduce the presence of active sulphur species in the corroded area and consequently reduce the rate of attack on the metallic matrix adjacent to the inclusions.

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Appendix 1

The exposure period required for 0.5 Coulomb.cm\(^{-2}\) charge transfer for type 316 and type 304 stainless steels samples exposed at different potentials.

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>SS 304 Exposure Period (seconds)</th>
<th>SS 316 Exposure Period (seconds)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>7100</td>
<td>6870</td>
</tr>
<tr>
<td>-900</td>
<td>29240</td>
<td>25230</td>
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<td>-800</td>
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<td>76550</td>
</tr>
<tr>
<td>-700</td>
<td>85510</td>
<td>94110</td>
</tr>
<tr>
<td>-600</td>
<td>103400</td>
<td>134570</td>
</tr>
<tr>
<td>-500</td>
<td>164200</td>
<td>250450</td>
</tr>
<tr>
<td>-400</td>
<td>258300</td>
<td>278810</td>
</tr>
<tr>
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<td>333960</td>
<td>315620</td>
</tr>
<tr>
<td>-200</td>
<td>-</td>
<td>431250</td>
</tr>
<tr>
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<td>435860</td>
</tr>
<tr>
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<td>499560</td>
<td>467730</td>
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</tr>
<tr>
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<td>35470</td>
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<td>+700</td>
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<td>610</td>
</tr>
<tr>
<td>+800</td>
<td>-</td>
<td>560</td>
</tr>
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Appendix 2

Concentration of carbon before and after 20 seconds etching for type 316 stainless steel samples exposed at different potentials.

<table>
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<th>Potential (mV)</th>
<th>Carbon (at.%) before etching</th>
<th>Carbon (at.%) after etching</th>
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<td>28.49</td>
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<tr>
<td>(\bar{X})</td>
<td>(42.17 \pm 7.99)</td>
<td>(12.60 \pm 4.14)</td>
</tr>
</tbody>
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Appendix 3

Enhancement factors (atomic ratio of elements after and before etching) after 20 seconds etching for type 316 stainless steel samples.

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<th>Potential mV(sec)</th>
<th>Enhancement Factor (atomic ratios)</th>
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Appendix 4

Auger Parameter of Magnesium compound on the surface of type 304 stainless steel samples after exposure at different potentials

<table>
<thead>
<tr>
<th>Potential (mV)</th>
<th>Photoelectron Kinetic Energy (eV)</th>
<th>Auger electron Kinetic Energy (eV)</th>
<th>Auger Parameter ΔE (eV)</th>
</tr>
</thead>
<tbody>
<tr>
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