CORROSION STUDIES OF MAGNETICALLY-ACTIVE ALLOYS

by

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To my mother, with love.
SUMMARY

The technology of magnetic recording, which is involved in most aspects of modern life from credit cards to video tapes, is evolving at an ever quickening pace. As the industry strives to produce greater recording capacity and increased information density the demands on the development of improved magnetic storage and recording head materials cannot always keep up with the pace of change. The materials being considered are not only required to have the desired magnetic properties but also to have the necessary corrosion resistance in the operating environment. It is often the latter which can limit the rate of development of new devices since many of the new materials considered for magnetic storage applications consist of very reactive metals with low corrosion resistances.

In establishing how research on the corrosion properties of new magnetic materials should be approached, two different experimental routes are explored in this thesis. These studies were a) a combined electrochemical and surface analysis study and b) a novel 'in-situ' SIMS study.

The electrochemical study proved to be a very valuable route in obtaining information on the corrosion properties of the magnetically-active alloy FeMn and such a study can be highly recommended for the application to other magnetic materials.

The complete electrochemical properties (anodic and cathodic) of FeMn were determined. A region of passivity was revealed through the application of the very sensitive solution analysis technique of ICPMS. The passive layer is associated with a manganese hydroxide
rich surface layer. Passivity in the alloy is very vulnerable to corrosion attack by sodium sulphate active ions. The influence of temperature and pH was investigated. Only under low values of pH with the conditions investigated was the corrosion attack increased compared to neutral conditions. The application of sodium chromate inhibitor was found to enhance the passive layer formed.

Using the second route the application of a novel 'in-situ' SIMS technique to look at the oxidation properties of magnetic metals and alloys was explored. The interpretation of the SIMS data for the oxidised and unoxidised components of cobalt was achieved and a model for the reaction of cobalt with oxygen at the initial stages of oxidation was successfully produced. At this present stage it is not possible to model the oxidation of more reactive metals than cobalt.
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CHAPTER 1

Introduction

Magnetic recording is the universal means of storing information, in audio and video tapes, credit cards, computer discs and in various types of instrumentation. The current worldwide business involved in the production of magnetic media, disc drives and other associated equipment is estimated at $100 billion, which is greater in money value than solid state silicon device technology.

The technology is advancing fast to produce greater recording capacity and increased information density. The demands on the development of improved magnetic storage materials and recording head materials are great and cannot always keep up with the pace of change. The new materials being considered are not only required to have the desired magnetic properties but also to possess the necessary corrosion resistance in the operating environment. It is often the latter which limits the rate of development of the new devices since many of the new materials considered for magnetic storage applications consist of very reactive metals whose corrosion resistances are low.

In this thesis, the aim is to establish how the research on the corrosion properties of new magnetic materials should be approached. Two magnetically active alloys are investigated, with great potential in two aspects of magnetic recording; the recording head for which Fe$_{50}$Mn$_{50}$ is being considered and a new mode of magnetic storage for which Co$_{80}$Cr$_{14}$ could dramatically increase the information storage density. These materials have the required magnetic properties but for their successful application, problems related to their chemical stability must be overcome.
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2.1. Magnetic Recording

2.1.1. Basic Principles

A magnetic recorder consists of a storage medium, a transducer to convert magnetic energy to electrical energy, a means of moving the medium and suitable electronics.
or is in contact, with the moving medium. The information is stored as a sequence of transitions in the magnetic microstructure, or magnetic domain structure, of the ferromagnetic medium. These transitions are induced by varying the magnetic field of the writing head. They have a finite linear separation and lie in a record track. Replay involves a reverse process in which the microfields above these transitions induce a varying signal voltage in the read head.

The materials used for the storage medium and the recording head have different magnetic properties. The magnetic properties of materials can be most easily represented by plotting the induced magnetisation in the material, $M$, versus the applied magnetic field, $H$. Examples of two such plots for a) a magnetically 'hard' material and b) a magnetically 'soft' material are given in Figure 2.1. The saturation magnetisation, $M_s$, is the maximum induced magnetisation in the material. The remanent magnetisation, $M_r$, is the residual magnetisation when the applied field is removed.

![Figure 2.1 Hysteresis loops of magnetisation plotted against applied magnetic field, for a) a magnetically 'hard' material, and b) a magnetically 'soft' material.](image)

For a magnetic storage material, the required property is that it should be a magnetically
a magnetically 'hard' material, and b) a magnetically 'soft' material.

For a magnetic storage material, the required property is that it should be a magnetically 'hard' material. The squareness ratio of $M_r/M_s$ of a magnetically hard material is near unity which means that any stored pattern of domains or bits is retained in zero magnetic field. A high value of the magnetic coercivity, $H_c$, the applied magnetic field required to demagnetise the material, ensures that the recorded information is stable with time and against any stray magnetic fields. A large $M_s$ is also helpful in providing strong replay signals.

The magnetic core material in the transducer head must be a magnetically 'soft'. A concentrated magnetic field must be provided at the head gap above the medium and therefore $M_s$ must be large but $M_r$ must be small so that the field is zero when the head is not energised. To avoid energy losses in the alternating cycle $H_c$ must be small and to provide large induced signals the material must be easily magnetised by the microfields above the magnetic transitions; ie the slope of the magnetising curve or the material's permeability must be large.

2.1.2 Magnetic Storage Media

There are two types of magnetic storage media, particulate or thin film. The thin film materials can be further characterised into longitudinal or perpendicular recording storage and compact disk storage.

The particulate magnetic storage recording media which is approximately half a century old, uses longitudinal recording, the traditional means in which the magnetisation direction lies
higher recording output amplitudes. They do have the problem, however, of a high tendency to oxidise since they are in the elemental state and have the high specific area of small particles. Attempts to stabilise the particles by use of alloying elements, by organic coatings or controlled oxidation tend to reduce the effective magnetization intensity. The trend for development in this area lies in producing smaller particles with higher coercivities to achieve higher magnetic storage density tapes. The main application of particulate storage media is in audio and video recording.

Thin film media are alloys of cobalt, with their composition optimised to maximise the magnetic properties. For longitudinal storage, magnetic films are usually plated CoP or CoNiP alloys, or sputtered or evaporated films of CoNi, CoNiCr, CoCrTa and CoCrPt.

CoCr is the main material of interest in a new and potentially important mode of magnetic recording, that of perpendicular or vertical storage which can produce ultra high storage densities. Yamamoto et al. (1987) were able to demonstrate a magnetic storage density of 680,000 bits per inch (bpi) using a disk of CoCr/NiFe (1000Å/5000Å thick films). This compares very favourably with a typical longitudinal recording media of up to 80,000bpi with a 500Å CoCrM/Cr film. It may be noted that these values are from research laboratories and commercially available systems tend to be of much lower magnetic storage densities, typically 4,000bpi. In perpendicular recording, the magnetisation in the storage film is aligned perpendicular to the film plane and the film is magnetically uniaxial. The magnetisation in the storage film is aligned perpendicular to the film plane by the magnetic and crystallographic properties of the film and the particular texture. It can be shown that the width of transitions in such a medium is in the order of 5% of the thickness of the film.
Here, there is a trend to develop thinner films so as to maximise storage densities.

Reducing the thickness of the thin film both in the longitudinal and perpendicular recording modes increases the storage density available but also reduces their corrosion resistance and a protecting layer has to be coated onto the thin films.

Compact disk erasable magnetic storage media have only recently appeared on the market. Previously read only memory (CD-ROM) compact disks were available which once supplied by the manufacturer did not allow any alteration by the user to rewrite to disk. CD-ROM disks were then followed by write-once media which allowed the user to write data to disk once. Thermo-magneto-optic (TMO) storage materials are used in the erasable CD recording. They consist of amorphous alloys formed from rare earth metals such as terbium, gadolinium and the transition metals iron or cobalt. A laser is used to nucleate a domain on the storage material. When reading, the laser is reflected and rotated by the domain by the phenomenon of the Kerr effect. The advantage of this system is that the head can be placed a greater distance from the tape compared to the traditional methods and reduces wear of the head. Instabilities in the disk can occur from the reactivity of the rare earth metals; magnetic rare earth elements react strongly with oxygen in the air or moisture to form non-magnetic oxides.

2.1.3. Recording Heads

There are two main types of recording head; inductive and magnetoresistive heads. MnZn and NiZn ferrites, $(Mn,Ni)_1-xZnO_xFe_2O_3$ are most widely used for inductive recording heads. In these heads, the magnetic transitions cause a changing magnetic field which
induces an electrical current.

Magnetoresistive (MR) heads are capable of reading transitions through a phenomenon of magnetoresistance in which the electrical resistance of a ferromagnetic material changes in an applied field.

As the technology progresses and higher density and greater recording potentials are required it is necessary to miniaturise the transducer head so that it is capable of reading and writing on the high density information storage medium. FeMn has a great potential of being used in miniaturised MR heads.

By reducing the size of the heads we see anomalies in the electrical output due to the changes in the domain structure as the magnetic fields vary in strengths. Troublesome discontinuous changes in sensitivity and linearity are termed 'Barkhausen noise' (Klaassen, 1990) although the original meaning of the phrase was restricted to induced voltage spikes.

Magnetic domain effects result from changes in position of the domain walls hence conceptually the effects can be eliminated by removing the domain walls or by making them immobile. This must be accomplished without destroying the high permeability which is required in all thin film transducer designs and without destroying other properties such as magnetoresistance or corrosion resistance which are required for particular designs.

Removal of the domain walls has the effect of making each film a single domain. One way to bias and stabilise the domain structure in this way is to use the phenomenon of exchange
coupling (Yelon, 1971) which occurs between a ferromagnetic and antiferromagnetic materials. This is what occurs between the antiferromagnetic FeMn and the magnetoresistive NiFe, permalloy. By exchange coupling, magnetic anisotropy is induced in the NiFe such that the magnetisation curve of the material along its easy axis (the crystallographic axis in which magnetization occurs most favourably) is displaced (Russak, 1989) and a relative high applied magnetic field would have to be applied for the permalloy to overcome the torque produced from the exchange coupling. This torque and resulting displacement of the magnetisation curve is greatest at the 50/50 FeMn composition (Hempstead, 1978). The hard axis which is the axis most sensitive to the magnetoresistance, remains unaffected by the coupling and retains its high permeability. The hard axis and easy axis for an exchanged coupled NiFe/FeMn bilayer (Cohen, 1988) is shown in Figure 2.2.

![Figure 2.2. The magnetic hysteresis loop of an exchanged coupled NiFe/FeMn bilayer (Cohen, 1988).](image-url)
This principle is behind IBM's recent experimental magnetoresistive NiFe/FeMn head (Tsang, 1989) which coupled with an inductive-write head and a CoCrPt thin film disk produced the ultra-high gigabit/in² density recording (Tsang, 1990) which was a major breakthrough in magnetic recording.

Since the magnetic signal during reading falls off exponentially with the spacing between the head and the tape or disk (the 'flying' height), to achieve strong replay signals this distance has to be as small as possible. For example the flying height in IBM's dual head is 0.6µm (Tsang, 1990). Such small flying heights create difficulties in manufacturing. The head has to be lapped to produce a uniform flat head which involves exposing the head to lapping solutions which could cause corrosion problems. In addition since the flying height is so critical there is no room for coating the head with a protective film. This renders the device very vulnerable in service particularly with the possibility of 'dew' forming, condensation of water vapour in the atmosphere on the unprotected recording head.

2.2. Corrosion

As discussed above it is of great importance for the future development of new alloys for the application in service that their oxidation characteristics be determined.

The corrosion resistance of the alloys being considered for these novel applications; such as FeMn, CoCr, FeTb, CoGd are generally not well known unless the alloys are found in other applications. There has been very little work done on FeMn. The only study of any significance was by Cohen (1988) who performed controlled oxidation studies with in-situ XPS. Iron terbium has received a little more attention and the study by Dover (198..)
illustrated the problem of having a reactive component of a rare earth (terbium) in the material.

In contrast to FeMn, CoCr alloys have been researched to a far greater extent. This is due to the wider applications of CoCr alloys as implant and dental materials (Brune 1984) and as temperature and creep resistant materials (Kofstad 1969a). More recently, the commercial interest in the application of CoCr thin films as high density magnetic storage media has been reflected in an increase in the publications on the alloy.

As mentioned in the previous section there is a trend to develop thinner films of magnetic materials such as CoCr to maximise storage densities. In the thin film state it is very important to have a strict control on the saturation magnetisation of the material. One method of controlling this value is by controlling the amount of chromium in the alloy. If there is too low a concentration of chromium the saturation magnetisation is too high for the thin film. The saturation magnetisation falls off linearly (Haines 1984) with chromium content, vanishing at a chromium composition of approximately 25%.

The problem is that to ensure good corrosion protection of the alloy, a composition of greater than 25% chromium is preferable (Preece 1956). This is supported by Hagi’s (1990) study on various compositions of CoCr alloys. He observed thin passive oxide layers on CoCr alloys with 30% and above chromium compositions while thicker and therefore less effective oxide layers were observed with CoCr with 20% or less chromium content. Hence there is a discrepancy in compositional requirements for the desired magnetic and corrosion resistant properties.
There are various ways of achieving improved corrosion properties of the materials; these include alloying, use of overcoats or protective layers and enhancing the natural passivity of the material for example by heat treatment.

Alloying can often improve the corrosion properties but at the sacrifice of the magnetic or optomagnetic storage potential. This has been observed with many alloying additions to FeTb (Niihara 1988, Kobayashi 1985). Chromium additions to magnetic alloys appears to be one of the least harmful and is associated with improved corrosion properties (Kobayashi 1990, Rice 1976, Phipps 1984). This, nonetheless, does not help with the CoCr alloys where too much chromium is detrimental.

The use of overcoat materials is widespread in the magnetic recording industry as it can improve corrosion resistance and wear properties of the disk. Materials such as carbon, silica and aluminum nitride can be used if the distance between the recording head and the storage media is not crucial. The limitation of the overcoat appears to be the adsorption and subsequent transfer of water through the overcoat (Novotny 1988, Smallen 1985) which is often necessarily thin and even porous. The formation of corrosion products in this way reduces the magnetisation potential and at worst destroys the film media. Dubin (1982) found that relative humidity was the most important factor on the corrosion of his CoCr alloys.

Protection of higher chromium composition CoCr alloys appears to be associated with formation of a chromium oxide layer rather than a mixed cobalt oxide and chromium layer observed with lower chromium composition CoCr alloys (Phalnikar 1956). Several authors have observed a multilayered oxide structure in CoCr alloys with chromium contents less
than 25% (Hagi, 1990, Fowler 1988, Smits 1984, Kofstad 1969a). This layer structure consists of a cobalt rich outer layer which Kofstad suggested was cobalt chromite spinel and an inner Cr$_2$O$_3$ layer. Fowler (1988) suggested that once this layer structure has formed the oxidation of the material is controlled by the diffusion of cobalt through the chromium oxide layer. If, then, this protective chromium oxide layer could be improved or extended corrosion of lower chromium content CoCr alloys could be retarded. The mechanism of the formation of the oxide is still speculative and discrepancies exist. For example Swami (1985) found a chromium enrichment with his Co$_{80}$Cr$_{20}$ alloys but no cobalt rich layer on top.

### 2.2.1. Relative Reactivity of Metal Components

As mentioned above little may be known of some of the alloys being considered for the magnetic recording industry. An initial idea of the relative reactivity of the metal components of the alloys in solution can be determined from their standard electrode potentials. Table 2.1. shows some of the standard electrode potentials of some of the components of the magnetic alloys of interest and a few common metals in order of decreasing reactivity.

**Table 2.1.** Electrode potentials of some of the components of the magnetic alloys in order of reactivity.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Standard Electrode Potential (V) 25°C</th>
<th>Alloy</th>
<th>Magnetic Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gd -&gt; Gd$^{3+} + 3e^-$</td>
<td>-2.40</td>
<td>CoGd</td>
<td>Thermo-magneto-optic (TMO) storage media</td>
</tr>
<tr>
<td>Tb -&gt; Tb$^{3+} + 3e^-$</td>
<td>-2.39</td>
<td>FeTb</td>
<td>TMO storage media</td>
</tr>
<tr>
<td>Standard Electrode Potential (V) 25°C</td>
<td>Alloy</td>
<td>Magnetic Application</td>
<td></td>
</tr>
<tr>
<td>-------------------------------------</td>
<td>----------</td>
<td>----------------------</td>
<td></td>
</tr>
<tr>
<td>Mn → Mn^{2+} + 2e^-</td>
<td>FeMn</td>
<td>recording head</td>
<td></td>
</tr>
<tr>
<td>Zn → Zn^{2+} + 2e^-</td>
<td>CuZn</td>
<td>(Brass*)</td>
<td></td>
</tr>
<tr>
<td>Cr → Cr^{3+} + 3e^-</td>
<td>CoCr</td>
<td>magnetic storage media</td>
<td></td>
</tr>
<tr>
<td>Fe → Fe^{2+} + 2e^-</td>
<td>FeMn</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co → Co^{2+} + 2e^-</td>
<td>CoCr</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni → Ni^{2+} + 2e^-</td>
<td>NiFe</td>
<td>recording head</td>
<td></td>
</tr>
<tr>
<td>1/2 H₂ → H^+ + e^-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu → Cu^{2+} + 2e^-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Au → Au^{+} + e^-</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*standard material for the study of dealloying phenomenon

From the standard electrode potentials it can be observed that the materials considered for magnetic recording are often very reactive. The rare earth metals, gadolinium and terbium are particularly reactive metals and oxidise readily with oxygen or water which may be present in a magnetic recording operating atmosphere. Chromium is known to form a passive protective oxide layer on alloys such as stainless steel but if there is any local attack in the form of pitting or crevice corrosion on the surface such as may occur in a thin film, the resulting corrosion occurs readily.

The other note to make from the standard electrode potentials is that often the metal constituents of the magnetic alloys FeMn, CoCr, FeTb and CoGd have very different standard electrode potentials which indicate very different ion forming tendencies of the constituent metals. This can lead to selective dissolution.
2.2.2. Selective Dissolution

Selective dissolution is the selective removal of one of the components of an alloy. The phenomena was first reported in 1866 and much work has been devoted to it. Dezincification, the selective dissolution of zinc from brass (Pickering 1967, Langenagger 1969, Verink 1972) has received the most attention. Other systems include nickel, aluminium, tin from copper alloys, nickel from alloy steel (Prazak, 1977) and copper from CuAu dental alloys (Hultquist, 1984). Recently Castle and Qiu (1989a, 1989b) looked at the selective dissolution of iron from Fe$_{17}$Cr and Fe$_{15}$Cr$_4$Mo alloy steels to investigate passivation. Most dealloying attacks leave behind a) a noble metal such as gold, copper, silver or b) an inert oxide such as chromium oxide in the case of stainless steel. In this study both iron and manganese are active and this is the case with many of the new alloys developed for the magnetic recording industry.

There are two possible consequences of selective dissolution according to which either constructive dissolution or destructive dissolution results:-

a) a film of the more noble metal forms which gives protection to the alloy against further dissolution or

b) a porous residue is left which offers no protection.

In principle, selective removal of one of the alloying components should always lead to case a). For a porous residue to develop some movement of the more noble metal must occur in order to expose new channels for dissolution. The mechanisms proposed for this transport are outlined in the next section.
2.2.2.1. Mechanisms for Selective Dissolution

Three mechanisms have been proposed in the literature to enable selective dissolution to take its destructive form;

(i) Ionisation-redeposition of the more noble component
(ii) Surface diffusion of the more noble component
(iii) Volume diffusion of the more noble component

The ionisation-redeposition mechanism can be discussed with reference to CuZn alloy (Sugawara et al., 1967). It is based on the theory that the activity of copper in CuZn is greater than the copper activity in pure copper. This can lead to a potential difference on the sample surface between copper rich areas and the bulk CuZn composition areas and thus the copper in the CuZn areas can dissolve and plate onto copper islands. This theory has largely disappeared from the current literature as the noble metal is non-ionisable in the region of selective dissolution which is typically hundreds of mV below the equilibrium potential of the noble metal.

The surface diffusion mechanism, favoured by Forty (1980, 1981), Feller, Swann (1969), Gerischer et al. (1955), assumes that only the less noble metal ionises and enters the solution while the atoms of the more noble metal aggregate by surface diffusion. A protective layer can form by nucleation and growth of the pure more noble metal. Forty (1981) proposed that surface disordering-reordering occurs to accommodate this growth. It has been argued that adatoms of the more noble metal would not accumulate by surface diffusion because of the large overpotential for their dissolution.
In the volume diffusion mechanism, only the less noble metal ionises and enters the solution and atoms of both metals move in the solid phase by volume diffusion. Pickering (19..) used this to explain the solid solution composition of the alloy in the porous residue left after selective dissolution of alloys. He also used it to explain the greater gold buildup in a cold worked sample in AuCu alloys in decreasing copper dissolution. The extra point, line and planar defects would increase effective diffusivity. It was also observed that dealloying occurs faster at slip steps in CuAu alloys. Volume diffusion would be normally considered inoperable on the basis of extrapolation from high temperature diffusivity measurements. Use of such an extrapolation implies that a) equilibrium concentrations of vacancies are established at room temperatures and b) the contribution of diffusion along small-angle grain boundaries and along grain boundaries is negligible at room temperature, but many authors have suggested the effective average diffusion coefficient may be considerably greater than expected from this high temperature data extrapolation. However if the alloy is continuous selective dissolution of the less noble metal requires diffusion through the noble metal enriched layer. This process, even for very thin layers would be slower than surface diffusion. The roughening of the surface which is observed for certain conditions of alloy composition and potential is the main evidence in support of volume diffusion.

2.2.2.2. Predicting Selective Dissolution

There are two approaches in predicting the occurrence of selective dissolution. The first is by Pickering and Wagner (1969) who suggested that conditions for selective dissolution were

\[ E_D - E_a > \frac{kRT}{F} \]  

(2.1)
Where  
\[ E_a = \text{Standard electrode potential of metal a} \]
\[ E_b = \text{Standard electrode potential of metal b in alloy ab} \]
\[ R = \text{Gas constant} \]
\[ T = \text{Temperature in kelvin} \]
\[ F = \text{Faraday Constant} \]

where  
\[ E_a < E_{\text{corr}} < E_b \]

\[ E_{\text{corr}} = \text{Corrosion potential of alloy ab} \]

The greater the difference in standard electrode potential, the greater the tendency for selective dissolution to occur.

Castle (1991) modified this equation to;

\[
E_b - E_a > \frac{s \times 2.3 \times R \times T}{n \times F}
\]

(2.2)

If selectivity \( s > 2 \) then selective dissolution can occur.

Castle (1991) compiled a Table 2.2 of practical values of \( s \) from the literature. There is little evidence in the literature that, for alloys lying above NiCr in the table, that selective dissolution occurs during active corrosion, although Ni enrichment occurs during the active corrosion of stainless steel. Below Ni/Cr selective dissolution does occur. It may be noted
that selective dissolution is composition dependent (Pickering, 1983).

Table 2.2. Practical values of selectivity (Castle 1991).

<table>
<thead>
<tr>
<th>Alloy A/B</th>
<th>Standard Potential (mV)</th>
<th>-Log Concentration of A (s/n_A)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>E_A</td>
<td>E_B</td>
</tr>
<tr>
<td>Mo/Ni</td>
<td>-200</td>
<td>-230</td>
</tr>
<tr>
<td>Ni/Fe</td>
<td>-230</td>
<td>-440</td>
</tr>
<tr>
<td>Fe/Cr</td>
<td>-440</td>
<td>-740</td>
</tr>
<tr>
<td>Co/Cr</td>
<td>-280</td>
<td>-740</td>
</tr>
<tr>
<td>Ni/Cr</td>
<td>-230</td>
<td>-740</td>
</tr>
<tr>
<td>Pd/Cu</td>
<td>623</td>
<td>340</td>
</tr>
<tr>
<td>Au/Ag</td>
<td>1110</td>
<td>799</td>
</tr>
<tr>
<td>Ni/Ti</td>
<td>-230</td>
<td>-860</td>
</tr>
<tr>
<td>Fe/Mn</td>
<td>-440</td>
<td>-1190</td>
</tr>
<tr>
<td>Cu/Ni</td>
<td>340</td>
<td>-230</td>
</tr>
<tr>
<td>Cu/Zn</td>
<td>340</td>
<td>-763</td>
</tr>
<tr>
<td>Au/Cu</td>
<td>1110</td>
<td>340</td>
</tr>
<tr>
<td>Cu/Zr</td>
<td>340</td>
<td>-1430</td>
</tr>
<tr>
<td>Fe/Tb</td>
<td>-440</td>
<td>-2340</td>
</tr>
<tr>
<td>Fe/Gd</td>
<td>-440</td>
<td>-2400</td>
</tr>
<tr>
<td>Co/Gd</td>
<td>-280</td>
<td>-2400</td>
</tr>
<tr>
<td>Au/Zn</td>
<td>1110</td>
<td>-623</td>
</tr>
</tbody>
</table>

The second approach was suggested by Verink and Heidersbach (1972). Their model, applied to dezincification from brass predicted selective dissolution of Zn in the region of overlap of the copper and zinc Pourbaix diagrams shown in Figure 2.3. The selective dissolution of zinc is predicted to occur in the shaded area of the diagram. This has the advantage of predicting the conditions of selective dissolution under conditions of applied
potential and pH. Since the Pourbaix diagrams are theoretically determined and are for equilibrium concentration of a pure metal in its solution of ions, caution should be taken in their interpretation.

Figure 2.3. Verink and Heidersbach model for selective dissolution. Selective dissolution of zinc from brass is predicted in the overlap of the copper and zinc Pourbaix diagrams.

2.2.2.3. Effect of Selective Dissolution on the Polarisation Curve

The shape of the polarisation curve observed when selective dissolution occurs can be represented in the general form as shown in Figure 2.4. (after Pickering, 1983). Examples
of the CuZn (Pickering, 1969) and the CuAu systems (Gerischer, 1955) are presented in Figure 2.5 and 2.6.

Figure 2.4. General shape of the anodic polarisation curve of an alloy showing selective dissolution.
Figure 2.5. Anodic partial currents for zinc and copper for brass.

Figure 2.6. Anodic partial currents for CuAu alloys for gold contents 0-100%.
There is a region of low potential where dissolution of the less noble metal is independent of potential. Above a certain potential, the critical potential $E_c$, the current increases sharply with potential. $E_c$ is a function of alloy composition, increasing with increasing noble metal content. As the $\Delta E$ in equation, the difference in standard electrode potentials vanishes, the polarisation curve takes a form similar to that of the pure metals (curve pure A or pure B in Figure 2.4). This is observed when there is no protection of one of the components by the other to prevent further dissolution.

Region a) in Figure 2.4 is the limiting current region of very low current due solely to the dissolution of the less noble metal A. Dissolution of A is suppressed by a surface layer of the more noble metal B, although it is not clear if this layer is pure B or, B-enriched.

When the layer is protective in this way (constructive dissolution) it can be considered to be similar to the passive region observed in metals and alloys. In this case a layer of B or a B enriched layer takes the place of the reaction product passive layer, for example, gold in AuCu alloys, copper in brass, cadmium in MgCd alloys.

In region b) the dissolution of A increases sharply and surface roughening of a planar surface occurs with pitting and increased porosity.

### 2.2.2.4. Evaluation of Selective Dissolution

A selectivity, or dissolution, coefficient has been used by several authors (Marshakov et al., 1964, Kolotyrkin, 1973) to evaluate the extent of selective dissolution of metals from their alloys. This is done by comparing the concentration of ions in solution with the alloy
composition:-

For example, the dissolution coefficient of A, $Z_A$, from alloy AB is given by:

$$Z_A = \frac{A_{\text{solution}}}{A_{\text{alloy}}} \frac{A_{\text{solution}} + B_{\text{solution}}}{A_{\text{alloy}} + B_{\text{alloy}}}$$

(2.3)

Where

- $A_{\text{solution}}$ = concentration of A ions in solution
- $B_{\text{solution}}$ = concentration of B ions in solution
- $A_{\text{alloy}}$ = amount of A in the alloy
- $B_{\text{alloy}}$ = amount of B in the alloy

If $Z_A > 1.0$ then more A than B is dissolving, and selective dissolution of A is occurring.

If $Z_A < 1.0$ then less A than B is dissolving, and selective dissolution of B is occurring.

and if $Z_A = 1.0$ then equal amounts of A and B are dissolving ie no selective dissolution is occurring.

This approach is very useful for determining selective dissolution of alloys and can be applied to any alloy system, not just simple binary systems as indicated here.

2.2.3. The Importance of Solution Analysis

Solution analysis is important both, in the study both of selective dissolution, and in the
determination of any passivation region. In the former case, regions of constructive dissolution can be revealed by determining partial currents of the alloy constituents. The latter case is examined in Figure 2.7a and b.

Consider the diagram in Figure 2.7a showing a potentiodynamic scan, which measures the total external current flowing i.e. the sum of the anodic and cathodic currents. At the rest potential, the anodic and cathodic currents are equal and the resulting measured external current is zero. From this information alone, it is impossible to determine whether the rest potential, the intersection of the cathodic curve with the anodic curve occurs in the region of transpassivity (intersection 2), or active dissolution (intersection 1), as shown in Figure 2.7b. If the intersection occurs in the transpassive region of the anodic curve, the passive region will not be revealed because of the dominating cathodic current.
Figure 2.7a. A potentiodynamic scan around the rest potential.
2.3. In-situ Oxidation Studies

Solution analysis gives an idea of the corrosion products in solution. To determine the corrosion products on the surface of the sample after exposure, surface analysis can be used. There is, however, an ambiguity which occurs with the possibility of post-solution oxidation, which can occur during the transfer of the sample between the solution and the chamber of the surface analysis instrument. This is particularly a problem with active surfaces, as discussed in a section 4.10 of the thesis. One way of overcoming this ambiguity is to perform the reaction, for example the oxidation, in the analysis chamber, ie perform in-situ oxidation.
Various techniques, including XPS (Fowler 1988, Cohen 1988), AES (Hofmann, 1991) and SIMS (Benninghoven, 1979) have been used to look at the in-situ oxidation of materials in an analysis chamber. The traditional method, involves exposing a material to oxygen for a fixed time, named a Langmuir exposure, within the analysis chamber and then analysing the oxidation products which have formed. Fowler (1988) performed in-situ oxidation on FeMn using XPS and found that manganese oxidised at shorter Langmuir exposure than iron. Cohen (1988) performed a similar study on CoCr and found an interesting series of oxidation stages. Firstly, the chromium oxidised and then the cobalt oxidised, followed by diffusion of cobalt across the chromium rich layer. The resulting layer was then a cobalt rich layer on top of a chromium rich layer.

2.3.1. In-situ SIMS Oxidation Studies

In-situ oxidation studies reported in the literature involve exposing the sample for a fixed exposure time then analysing the resulting products. These techniques allow analysis of the oxide products at an early stage of oxidation. To investigate the oxidation process at an even earlier stage, ie at the very initial stages of oxidation, a novel technique using dynamic SIMS, can be used. Initiated by Gunnar Hultquist at the National University of Singapore, the technique involves simultaneous analysis and controlled formation of oxidation products, rather than just analysis. A sputtered cleaned sample is exposed to various partial pressures of oxygen in the SIMS chamber, and an equilibrium is achieved between the formation and removal of the reaction products under normal dynamic SIMS conditions.

Hultquist (1989a, 1989b, 1990, 1992) used the technique to look at the oxidation of various metals (zinc, copper, chromium, zirconium and iron) with oxygen, water and oxygen and
water systems. Hultquist found that the intensity of the emitted secondary ions for a metal, for example iron, FeX+ and Fe2X+ (X = O, H, OH, H2O), normalised to Fe+, showed a dependence on the oxygen, hydrogen or water pressure during sputtering with argon ions. The normalised yields of (MeO+ + Me2O+)/Me+, for iron, chromium, copper and gold, plotted versus oxygen pressure (Hultquist, 1989a), show a relationship to the reactivity of the metals.

A major emphasis in his work was placed on exploiting the fact that SIMS can detect the hydrogen ion involved in corrosion processes, and that the use of isotopes can help distinguish oxygen in water and molecular oxygen. Using isotopically labelled water, Hultquist (1992) was able to distinguish the source of oxygen in the reaction of iron with oxygen and water. At room temperature a coupled reaction occurs such that 2Fe + H2O + 1/2 O2 -> 2FeOH. At higher temperatures the iron reacts preferentially with water.

This in-situ SIMS technique is explored in this thesis to find out whether it can be used to investigate the oxidation properties of the alloy CoCr and its constituent metals.

2.5. Objectives of This Study

The objective of this study is to understand how to investigate very reactive alloys used in the magnetic recording industry. The techniques used are: a) electrochemistry and b) the in-situ oxidation SIMS. It is important to explore new techniques which can enhance the understanding of the fundamental processes involved in the corrosion of active materials. The electrochemistry study involves the recently developed solution analysis technique of ICP-MS, which allows very low detection limits that have not been possible before. It also
involves a variety of proven techniques such as XPS and SEM, as well as the recently
developed imaging XPS system. The in-situ SIMS study is a very novel way of looking at
the oxidation process and is, as yet, unexplored with this alloy system.
CHAPTER 3
Experimental
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3.1. Electrochemistry

3.1.1. Electrochemical Equipment

3.1.1.1. Electrochemical Cell

The electrochemical cells used are shown in Figure 3.1. Cell (a) consisted of two 15ml pyrex glass chambers connected via a Luggin probe. One chamber held a reference electrode in an aqueous solution of 0.1M sulphuric acid, while in the second, a platinum foil counter electrode (cleaned in aqua regia) was mounted opposite the test piece. This was centrally perforated to allow passage of the Luggin probe which was placed in close proximity (<3x the diameter of the Luggin probe) to the sample surface. The second cell used, (b), was of similar volume to the first, but the pyrex glass chamber holding the sample in solution had
a greater diameter to allow better positioning of the test piece. In this cell the reference electrode was held in a solution of 1.0M aqueous sodium sulphate.

Figure 3.1. Electrochemical cells used in this study.
3.1.1.2. Potentiostat

A Wenking potentiostat, model LT78 was used. The potential to be applied could be preset and monitored throughout the exposure.

The rest potential of the working electrode (ie the sample) with respect to the reference electrode, could be measured by setting the instrument selector switch to 'E'\. The exposure was started by switching to the preset value 'E' within one or two seconds of placing the test piece in the solution. The current flow through the working electrode could be measured by switching 'E' to 'I'.

3.1.1.3. Current Integrator

A long term current integrator, Wenking model EV180, was used in combination with the potentiostat. This instrument consists of a high quality integration capacitor charged by a low leakage operational amplifier. It integrates the input signal up to a precisely set voltage level detected by a discriminator circuit. The integrating capacitor is discharged to zero within a short time and is charged again. The number of discharges is counted by a dual counter, separately for each polarity.

3.1.1.4. Potentiodynamic Princeton Computer Program

For potentiodynamic scans a Princeton electrochemical program was used to step the applied voltage and record the resulting current density. The electrochemical cell was connected to a Princeton potentiostat, model 173 by a model 270 interface. A schematic of the experimental set-up is shown in Figure 3.2. An Apple II computer stepped the voltage over a range of at least +/- 100mV from the rest potential of the system, and displayed the
resulting current density versus potential on the screen.

Figure 3.2. Schematic of experimental set-up for the potentiodynamic investigations.

3.1.1.5. Betacrunch Computer Program for the Calculation of Corrosion Constants

For the Tafel slope to be calculated from a potentiodynamic scan, the gradient of \( \log(\text{current}) \).
density) versus applied potential needs to be constant over a potential range. The region around the rest potential has a rapidly changing current and this makes achieving a constant gradient difficult. The Betacrunch program, modified by Parvizi (1985), uses a method of least squares to fit a theoretical curve, with a constant gradient section, to the set of experimental points. The Tafel constants may then be obtained from the mixed potential region where no Tafel line can be observed.

3.1.2. Experimental Procedure

3.1.2.1. Preparation of Sample

1cm² samples with an end tang cut from a rolled sheet of Fe₃₅Mn₄₇ alloy were mounted in bakelite and mechanically polished using a Struers Planopol-2-Pedemax machine to a 1µm finish. Immediately after polishing, the samples were removed from the bakelite and stored over silica gel in a vacuum desiccator. Samples were prepared for electrochemical tests by soldering an electrical contact to the back of the tang. Areas not to be exposed to the solution were coated with lacomit.

3.1.2.2. Potentiodynamic Investigations

Potentiodynamic scans were performed under the control of the Princeton program on samples in the untreated condition and then with various inhibitors. The inhibitors investigated were octadecylamine, triethanolmine, benzatrizole, cyclohexylamine, and 1000, 500, 250 and 100ppm chromate solutions. The resulting current, potential and Tafel constants were determined using the Betacrunch routine.
3.1.2.3. Potentiostatic Investigations

Potentials were selected in the cathodic region where selective dissolution was suspected. A fixed charge transfer (0.05 C/cm²) was passed through the electrode. This was measured using the current integrator. In the case of thin films a fixed time of exposure was used and the charge passed monitored. Most samples were exposed in the cathodic region and hence there was no direct relationship between the cathodic charge passed and the anodic dissolution charge. After each potentiostatic experiment the sample was stored over silica gel in a desiccator and the resulting electrolytic solutions stored in polythene containers before further analysis.

3.2. Solution Analysis

It has already been suggested that the anodic dissolution curve cannot easily be separated from the dominant cathodic curve over much of the potential range. The usual method of using deareated conditions to suppress the cathodic reaction:

\[
O_2 + 2H_2O + 4e^- \rightarrow 4 OH^- \tag{3.1}
\]

cannot be used because the potential range lies in the field for the reaction:

\[
2H^+ + 2e^- \rightarrow H_2 \tag{3.2}
\]

The alternative way in which the anodic current can be determined is by measuring the number of the cations formed, both in solution and in the oxide layer on the surface. For the initial work the mass of oxide was assumed to be negligible and solution analysis used exclusively.
3.2.1. Introduction

Solution analysis techniques used in the literature are wide ranging from the traditional wet chemical analysis to modern high sensitivity, low detection limit techniques now available. Of the modern solution analysis techniques, ICP-MS has great potential for future corrosion studies.

Inductively-coupled plasma source mass spectrometry (ICP-MS) has proved to be an invaluable tool in the field of inorganic analysis. The technique of sampling ions from a plasma and introducing them into a mass spectrometer is little over 17 years old and has reached the stage of commercial practicality with instruments now manufactured by VG Scientific and Sciex. With its low detection limits, high sensitivity, rapid sample throughput and simple data interpretation it is finding a wide range (Jarvis et al., 1990) of applications in the fields of geology (Jarvis, 1988), the petroleum industry, food science, water evaluation (Henshaw, 1989), environmental analysis (Shrammel, 1988), and metallurgy. As the uses of the commercial instrument are expanding, the number of users is increasing and its development is increasing rapidly.

The use of ICP-MS for corrosion studies has only recently been exploited by Castle and Qiu (1989a, 1989b) who used ICP-MS to investigate the passivation of stainless steels. By correlating the results obtained by solution analysis and the surface composition of the corroded samples, a complete analysis of the passivation process could be performed.
3.2.2. Development of ICP-MS

A comprehensive overview of the origins and development of the ICP is dealt with by Gray (1985a), who was involved with the initial development of the technique at the University of Surrey. A brief summary shall be given here.

The technique developed from the well established technique of Inductively Coupled Plasma Source Atomic Emission Spectroscopy (ICP-AES). During the development of the powerful ICP-AES, it became apparent that there could be severe matrix effects which limited the choice of interference free spectral lines for trace elements. In addition the spectra for rare heavy elements were particularly complex and gave relatively poor detection limits.

Atomic mass spectrometry showed the greatest potential for a wide element coverage, element specificity and uniform sensitivity across the Periodic table. The problem with mass spectrometry for inorganic samples was the complex sample preparation required to volatilise and dissociate strongly bound, often refractory materials. Sample throughput was slow and skilled operation and interpretation was required.

To make mass spectrometry viable, a new ion source was required. Ion detection from chemical flames has been investigated, but the gas temperature was too low to ionise most materials (3000K) and the reactive environment was unattractive, so it was suggested that atmospheric plasmas and arcs were used, which could produce a temperature of 5000K. From ICP-AES it was clear that the degree of ionisation was high in the plasma but, for mass spectrometry, the ion extraction from a plasma at atmosphere into a vacuum system of the mass spectrometer was a problem.
After work was carried out on the extraction problem at the Ames Laboratory, Surrey University and Toronto, extraction became possible through a series of different vacuum stages and aperture sizes (Gray et al., 1983). These studies led to the first commercial ICP-MS instruments by 1983. The PlasmaQuad manufactured by VG Isotopes Ltd, UK was based on the development system at Surrey and the Elan by Sciex Inc. based on the work at Toronto.

3.2.3. Instrumentation

A photograph of the VG Isotopes PlasmaQuad ICPMS instrument, used in this study, is given in Figure 3.3. A schematic of the instrument layout is given in Figure 3.4. The sample is introduced through a nebuliser into a high temperature plasma which ionises the sample. The ions produced are then extracted into a quadrupole mass spectrometer.
Figure 3.4. Schematic of ICP-MS instrument layout.
3.2.3.1. Sample Introduction

The most common sample introduction into the plasma is with a pneumatic nebuliser which forms a fine aerosol of droplets of the analyte solution. It is the most convenient of the methods available despite its inefficient consumption of the solution; only 5% of the solution enters the plasma. Any droplets greater than 4μm in diameter are rejected in the spray chamber and drained away. The other techniques used to a lesser extent include electrothermal volatisation (ETV) from a graphite rod or furnace or from a refractory wire or tape. This more complicated method is employed when the level of polyatomic and oxide interferences has to be reduced, for example when the oxide peak from a matrix element coincides with a wanted trace element.

Slurry introduction from a high-solids nebuliser is being used for multielement samples, which are difficult and time consuming to digest but which can be ground to particle sizes of a few microns. Such particles can be transported in the injector gas flow provided they can be nebulised from the initial slurry.

A recent development (Gray, 1985b) to analyse solid samples is laser ablation using a ruby laser to vaporise a solid sample into the injector flow.

3.2.3.2. The ICP Source

A standard argon plasma source of a type originally developed for atomic emission spectrometry, modified to provide a horizontal torch with a plasma tail flame protruding from the side of the shieldbox, is utilised.
The ICP source allows the attainment of sufficiently high temperatures to produce the controlled and uncontaminated environment required for sample conditioning and excitation and rapid and complete introduction of the sample for a sufficient residence time for the processes of desolvation, volatisation, dissociation, excitation and ionisation to occur.

The temperatures obtained in the plasma reach up to 10,000K where the RF energy couples to an outer annulus in the gas stream. From this region the energy is transferred mainly by thermal conduction to the central channel flow of initially cold gas, which is injected at high velocity along the axis of the quartz plasma torch. The plasma produced and its temperature map are given in Figure 3.5a and 3.5b. The cross section of the ICP source is given in Figure 3.6.

Figure 3.5a. Inductively coupled plasma.
Figure 3.5b. Temperature map of plasma.
Figure 3.6. Cross-section of ICP source.

Once the central channel leaves the torch, the temperature begins to drop and when it reaches the extraction aperture, 10mm or 20mm from the coil, the temperature is about 6000K or less.

3.2.3.2. Extraction

The extraction aperture is 0.5 to 0.8mm in diameter in a shallow water cooled cone. Once the gas passes through the aperture into a region at intermediate pressure, it undergoes supersonic expansion. The temperature drops rapidly and the reactions which could change
the composition of the gas are frozen. The gas is then extracted by a sharp skimmer about 10mm behind the aperture to the high vacuum stages, which eventually lead to the quadrupole. The ion lens usually includes a photon stop on the axis to prevent direct photons from the plasma reaching the ion detector and contributing to the background. Ion lenses are used in these second and third stages to focus the ions into the mass analyser, a large quadrupole VG type 12-12s.

3.2.3.3. Detection

The quadrupoles used in ICP-MS systems are of the type developed for organic mass spectrometry consisting of rods of 12-18mm diameter and about 200mm long. The quadrupole mass analyser acts as a filter, along the axis of which, a stable ion path exists for ions of a particular mass to charge ratio. Other ions are deflected away from the axis and lost.

Ions are detected by a channel electron multiplier operated either as a pulse or mean current detector. Single ion monitoring or mass scanning may be employed, synchronised with a digital memory scan for the storage of signal response. A spectrum can be built up in the memory from successive sweeps over the selected mass range. 8 to 10 memory channels are used for each mass peak to give good resolution on the spectrum display. It is faster to accumulate first the incoming signals from the ion detector in the digital memory scan and then transfer all the data at once to computer or hardcopy. The high scan speed of the mass analyser can thus be fully utilised. The number of complete scans is preset to give an integrating time of one minute for most analytical purposes.
It is possible, using computer control, to scan selected peaks only, which greatly reduces the
time spent. The maximum sensitivity can be obtained for a single ion by continually setting
to the required mass, this can produce a sensitivity tenfold improved to a wide mass range.

3.2.4. Operating Conditions
The VG Elemental PlasmaQuad PQ was used to analyse the electrolytic solutions resulting
from the potentiostatic experiments. The aqueous solutions were ideal for ICP-MS analysis,
having no matrix effects. ICP-MS analysis allowed a rapid simultaneous analysis of the iron
and manganese corrosion products with good precision, good sensitivity, easy data
interpretation and excellent detection limits. The detection limits for iron and manganese are
1.62ppb and 0.29ppb respectively and are well below the concentration of the corrosion
products analysed. A standard of 100ppb iron and manganese in distilled and deionised
water was used as a sensitivity standard and run after every third sample to check for drift.
In this case the change was ~3% over three samples which was corrected by linear
correction on subsequent calculations.

A narrow mass range, scanned from 52.94 to 59.94 a.m.u., was utilised to achieve best
sensitivities for iron and manganese. The possible isotopes available with their relative
abundance and main interferences are given in Table 3.1. Manganese is monoisotopic and
suffers no interference. The ICP-MS values obtained for $^{57}\text{Fe}$, which suffers from a small
background interference from $^{40}\text{Ar}^{16}\text{OH}$, are within 3% of the values obtained for $^{56}\text{Fe}$, which
suffered a large background due to $^{40}\text{Ar}^{16}\text{O}$, for the higher concentration solutions. This
indicates that background elimination calculations are effective. $^{56}\text{Fe}$ is preferred because its
high relative abundance (91.7%).
Table 3.1. Isotopes of interest and possible interferences.

<table>
<thead>
<tr>
<th>Isotope</th>
<th>Relative Abundance %</th>
<th>Interference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{54}$Fe</td>
<td>5.84</td>
<td>$^{40}$Ar$^{14}$N</td>
</tr>
<tr>
<td>$^{56}$Fe</td>
<td>91.68</td>
<td>$^{40}$Ar$^{16}$O</td>
</tr>
<tr>
<td>$^{57}$Fe</td>
<td>2.17</td>
<td>$^{40}$Ar$^{16}$O$^+$</td>
</tr>
<tr>
<td>$^{58}$Fe</td>
<td>0.31</td>
<td></td>
</tr>
<tr>
<td>$^{55}$Mn</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

Each sample solution was run three times and the mean determined. To indicate the precision of the runs, two examples are given below for a) a low and b) a high concentration of corrosion products.

Table 3.2. Examples of two ICP-MS experimental runs.

<table>
<thead>
<tr>
<th>$^{55}$Mn (ppb)</th>
<th>Mean Standard Deviation %</th>
<th>$^{56}$Fe (ppb)</th>
<th>Mean Standard Deviation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.8</td>
<td>1.3</td>
<td>7.9</td>
<td>0.5</td>
</tr>
<tr>
<td>342.9</td>
<td>1.3</td>
<td>102.5</td>
<td>4.5</td>
</tr>
</tbody>
</table>
Table 3.3. ICP-MS operating conditions

<table>
<thead>
<tr>
<th>ICP-MS Operating Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Instrument</td>
</tr>
<tr>
<td>Forward Power</td>
</tr>
<tr>
<td>Reflected Power</td>
</tr>
<tr>
<td>Coolant Gas Flow</td>
</tr>
<tr>
<td>Nebuliser Gas Flow</td>
</tr>
<tr>
<td>Auxiliary Gas Flow</td>
</tr>
<tr>
<td>Ion lenses optimised on</td>
</tr>
<tr>
<td>Nebuliser</td>
</tr>
<tr>
<td>Scan Range</td>
</tr>
<tr>
<td>No Channels</td>
</tr>
<tr>
<td>No of Sweeps</td>
</tr>
<tr>
<td>Dwell Time</td>
</tr>
</tbody>
</table>

3.3. Surface analysis

Solution analysis provides information on the corrosion products in the solution. To determine the overall corrosion characterisation, it is important to determine the material deposited on the surface of the corroded sample.

With an active material such as FeMn there exists a possible limitation in using surface analysis which lies in the activity of the surface of the sample after removal from solution. The oxide determined by surface analysis may have resulted either from the dissolution of the alloy in solution or from air oxidation on its consequent removal and storage prior to surface analysis.
3.3.1. Introduction

Surface analysis has been used extensively in a variety of areas to give information on the physical and chemical surface characteristics of materials. The range of techniques available to the analyst is large. The available techniques are summarised in Table 3.4. (Seah et al., 1990). Each of the techniques has advantages and disadvantages; the choice of technique depends on the requirement of properties such as chemical state information, molecular, spatial, depth information in a qualitative or quantitative form. Often several techniques are complementary and can used to give an overall view of the surface characteristics.
<table>
<thead>
<tr>
<th>Technique</th>
<th>Information (E = elemental, C = chemical)</th>
<th>Spatial resolution (best)</th>
<th>Sampling depth monolayers</th>
<th>Sensitivity (order of)</th>
<th>Quantification (√ = easy)</th>
<th>Elements not covered</th>
<th>Specimen preparation (√ = easy)</th>
<th>Ease of use</th>
<th>Extent of support data</th>
<th>Effective take-off year</th>
</tr>
</thead>
<tbody>
<tr>
<td>AES</td>
<td>E*</td>
<td>5 nm</td>
<td>3</td>
<td>0.3%</td>
<td>√</td>
<td>H,He</td>
<td>****</td>
<td>√</td>
<td>****</td>
<td>1968</td>
</tr>
<tr>
<td>Atom probe</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>FIM</td>
<td>E†</td>
<td>1 nm</td>
<td>1</td>
<td>1%</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1968</td>
</tr>
<tr>
<td>HREELS</td>
<td>C</td>
<td>1 mm</td>
<td>1</td>
<td>1%</td>
<td>√</td>
<td>H,He</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>1970</td>
</tr>
<tr>
<td>ISS</td>
<td>E</td>
<td>1 mm</td>
<td>1</td>
<td>1%</td>
<td>√</td>
<td>H,He</td>
<td>*</td>
<td>*</td>
<td>*</td>
<td>1967</td>
</tr>
<tr>
<td>MEIS</td>
<td>E</td>
<td>1 mm</td>
<td>3</td>
<td>1%</td>
<td>√</td>
<td>H,He, Li, Be</td>
<td>*</td>
<td>*</td>
<td>**</td>
<td>1967</td>
</tr>
<tr>
<td>RBS</td>
<td>E</td>
<td>1 mm</td>
<td>100</td>
<td>1%</td>
<td>√</td>
<td>H,He</td>
<td>**</td>
<td>**</td>
<td>***</td>
<td>1967</td>
</tr>
<tr>
<td>SIMS (static)</td>
<td>C</td>
<td>1 μm</td>
<td>2</td>
<td>0.01%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>*</td>
<td>1970</td>
</tr>
<tr>
<td>SIMS (dynamic, imaging)</td>
<td>E</td>
<td>20 nm</td>
<td>10</td>
<td>&lt; 1 p.p.m.</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1968</td>
</tr>
<tr>
<td>SIMS (dynamic, depth prof.)</td>
<td>E</td>
<td>50 μm</td>
<td>10</td>
<td>&lt; 1 p.p.m.</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1975</td>
</tr>
<tr>
<td>SNMS (dynamic, depth prof.)</td>
<td>E</td>
<td>50 μm</td>
<td>10</td>
<td>&lt; 1 p.p.m.</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1970</td>
</tr>
<tr>
<td>UPS</td>
<td>C</td>
<td>5 μm</td>
<td>3</td>
<td>1%</td>
<td>√</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1969</td>
</tr>
<tr>
<td>XPS</td>
<td>[C, E]</td>
<td>5 μm</td>
<td>3</td>
<td>0.3%</td>
<td>√</td>
<td>H,He</td>
<td>****</td>
<td>*</td>
<td>***</td>
<td>1967</td>
</tr>
</tbody>
</table>

1C is available but not with high spatial resolution due to electron stimulated desorption effects.  
2C may generally be deduced.  
3When compared with a close standard.
Since corrosion is concerned with the interaction of a material with its environment, the surface holds important information about the corrosion process. XPS and AES are two of the most widely used surface analysis techniques in corrosion studies.

Castle was one of the first to realise the potential of XPS for determining the initial products of the corrosion reaction, when commercial XPS instruments became available in the early 1970's. Since this time electron spectroscopy has found useful application in a wide range of corrosion research. This is summarised in Table 3.5. (Castle, 1990).
3. Fields of Corrosion Research

Monolayer adsorption

The starting point for both electrochemical and gas phase corrosion of metals, and also of catalysis: it has received much study (see a recent review by Roberts). XPS & UPS have done much to reveal the dissociative nature of adsorption. Segregation to the surface is a related effect influencing corrosion, eg sulphur has been shown to prevent passivation of nickel, see Oudar’s review. SCC is also influenced by segregation to the grain boundary.

Inhibition is a special topic within the general field of adsorption: ES is well suited to the determination of the surface concentration of an inhibitor. Plotting this as a function of the concentration in solution yields the adsorption isotherm which can give information of the nature of adsorption.

1. Very thin films (<3 nm)
Mott and Cabrera[44] showed that the air-formed film on metals and alloys would normally be in this thickness range which is ideal for study by XPS or AES. Measurements have confirmed this together with the prediction that the composition of the film would be close to that of the underlying substrate.

2. The very thin film in aqueous conditions
The composition of the air-formed film is frequently modified by immersing in an aqueous medium, and especially modified by control of the electropotential. In certain cases this will give rise to passivity which is more fully discussed in the text. Passive films are readily studied by XPS since there is little change in their composition when exposed to the vacuum of the spectrometer. The transient films present on the surface during active corrosion are however difficult or impossible to study by the vacuum techniques.

3. The breakdown of passivity
XPS may be useful for the study of surfaces in crevices and hence of crevice corrosion but in general pitting, SCC and crevice corrosion is the province of AES. Specific ions associated with pits may be identified and may even act as sensors of local electropotentials.

4. The thin film (<0.2 μm) - depth analysis
Layers of this thickness, which often protect metals from corrosion in both aqueous and gas phase, are studied by ‘depth profiling’, i.e. using ion beam etching in combination with AES to expose successive layers for analysis. Results may be corroborated by film stripping or in-situ scribing of the surface.

5. Anodic and chemical conversion layers
Anodic films have been studied by depth profiling by numerous authors, usually with a view to establishing the location of additives or the composition of barrier layers.

6. Thick film (>1 μm) - spalling and exfoliation
Films may be examined in cross-section but key interfaces are more usefully examined in plan by XPS[32]. Sulphur segregation is important[45].

7. Selective oxidation and selective dissolution are ideal for study by XPS[24,25].

Table 3.5. Summary of the applications of electron spectroscopy in corrosion research.

To obtain useful information on the corrosion process from surface analysis data it is important to trace back the ‘snapshot’ of the surface state at a given time, which is obtained by XPS and thus reveal its meaning.

This is generally easiest when a passive layer is involved as the surface will remain
unchanged on transfer to the analysis chamber and indeed most of the successful work carried out in surface analysis of corrosion processes involves a passivation state oxide layer. Once one traverses into the immune or active regions, the surface is prone to further oxidation after removal from solution and it is often difficult to distinguish the corrosion products which have formed in solution from those which have resulted from the sample's removal.

3.3.2. X-ray Photoelectron Spectroscopy

XPS analysis uses the principle that X-ray photons incident on an atom cause ejection of electrons from the core levels in the atom (photoemission). The kinetic energy, $E_k$, of the emitted electron is a function of the initial photon energy, $\hbar \nu$ and the binding energy $E_b$ of the core level, which is unique for a particular element.

$$E_b = \hbar \nu - E_k - w$$  \hspace{1cm} (3.3)

$w = \text{spectrometer work function}$

All values on the right hand side of the known or measured. XPS spectra are usually presented as intensity (counts) versus electron binding energy.

Once the photoelectron has been emitted, the ionised atom must relax in some way. This can be achieved by emission of an X-ray photon, known as X-ray fluorescence. The other way is by ejection of an electron, the Auger electron. Auger electron peaks can be seen in the XPS spectrum as broad peaks. Auger Electron Spectroscopy uses this Auger transition but the core hole is usually produced by a finely focused electron beam which can then give good spatial resolution in the sample.
3.3.3. Instrumentation

A photograph of the VG ESCALAB MkII spectrometer used in this study is given in Figure 3.7. A schematic of the instrument is shown in Figure 3.8. The spectrometer basically consists of an X-ray gun to produce X-rays to excite photoelectrons from the surface, an electron analyser to analyse the resulting electrons and, in this case, also an ion gun for Ar ion etching. These are positioned in an analysis chamber under ultra-high vacuum (UHV). Vacuum pressures of the order $10^{-9}$ to $10^{-10}$ mbar are preferred as XPS is a surface sensitive technique and therefore is very sensitive to surface contamination. From gas kinetics, a pressure of $10^{-6}$ mbar can produce a monolayer in 2 seconds; therefore good vacuum conditions are very important to prevent any influence of the gas. The UHV conditions also help increase the number of electrons reaching the analyzer, as collisions are avoided.
Figure 3.7. XPS spectrometer used in this study.
Figure 3.8. Schematic of XPS spectrometer.
3.3.4. Information from an XPS Spectrum

When the specimen is first analysed by XPS, the first step is to take a survey spectrum. A typical survey spectrum for an oxidised FeMn sample is indicated in Figure 3.9. This provides strong photoelectron peaks and their associated Auger peaks resulting from the de-excitation process. The background increases in a step-like manner after each spectral feature. This is a result of the scattering of the characteristic Auger or photoelectrons by the matrix bringing about a loss in kinetic energy. The background can give valuable information on the structure of near surface layers (Castle, 1990). A perfectly clean surface will have a horizontal background or one with a slightly negative slope; if the surface is covered with a thin overlayer, the peaks from the buried phase will have a background with a positive slope, and in the severe case the peak itself will be absent and the only indication will be a change in background slope at the appropriate energy.
3.3.4.1. Chemical State Information

One of the main advantages of XPS as a surface analysis technique is that chemical state information can be obtained from the spectra. Non-equivalent atoms of the same element give rise to core level peaks with measurable different binding energies.

Fine structure in the spectra such as shake-up satellites and multiplet splitting can also aid chemical state determination. Shake up satellites occur when the outgoing photoelectron simultaneously interacts with a valence electron and excites it to a higher energy level. The energy of the core electron is then reduced slightly giving a satellite structure a few eV below the core level kinetic energy. For example, the shakeup satellite on the iron 2p peak
can help distinguish Fe$^{3+}$ and Fe$^{2+}$ in Figure 3.10. (Watts, 1990).

**Figure 3.10.** Shakeup satellites in the iron 2p spectra can help distinguish the Fe$^{3+}$ and Fe$^{2+}$ states of iron.

Multiplet splitting of the photoelectron peak occurs when a compound has unpaired electrons in the valence band and arises from different spin distributions in the electrons of the band
structure. This results in a doublet of the core level peak. For example, NiO, which shows multiplet splitting, can be distinguished from Ni(OH)$_2$, which does not.

### 3.3.4.2. Quantification

Quantification of XPS spectra is usually made using the measured area under the photoelectron peaks following the subtraction of a linear or S-shaped background and sensitivity factors.

The generalised expression for the atomic concentration $C_x$ of a component $x$ in a sample is given by

$$C_x = \frac{I_x/S_x}{\sum I/S}$$

(3.4)

Where $C_x$ = percentage of component $x$ in the sample

$I_x$ = relative peak area of photoelectron from the element

$S_x$ = atomic sensitivity factor

### 3.3.4.3. XPS Depth Profiling

There are two main ways of depth profiling in XPS; destructive and non-destructive.

The latter utilizes the Beer-Lambert equation, which relates the intensity of electrons $I$ from a depth $d$ to $I_o$, the intensity from an infinite clean substrate, the takeoff angle $\theta$ and the inelastic mean free path $\lambda$

$$I = I_o(1 - \exp(-d/\lambda \sin \theta))$$

(3.5)
Therefore

\[ I/I_o = 1 - \exp(-1) \]

if \( d = \lambda \sin \theta \)

Of the electrons that emerge at \( \theta = 90^\circ \) to the sample, 65% will emanate from a depth \( d = \lambda \sin \theta \), 85% from \( d = 2 \lambda \sin \theta \) and 95% from \( 3 \lambda \). By varying the takeoff angle we can obtain information from the top layers using a low value of \( \theta \), for example 15°, or up to \( 3 \lambda \) using \( \theta = 90^\circ \).

Depth information can be obtained by using different X-ray energy. X-rays of different energies can be used to probe the same energy level, yielding photoelectrons of different kinetic energy. In this way, different depths may be analyzed.

eg for Cls Radiation Analysis Depth

- Mg K\( \alpha \) 6nm
- Al K\( \alpha \) 7nm
- Ag K\( \alpha \) 10nm

A similar effect can be obtained by looking at the different core levels using the same X-ray energy. For example Ge3d and Ge2p have different kinetic energies and therefore different \( \lambda \).

Non-destructive depth profiling will only yield information on the outer 5-10nm of a material and is useful on very thin passive films on metals or surface segregation but to get information deeper than this it is necessary to remove material by ion bombardment. Ion
bombardment is carried out in a sequential manner with the ion gun (usually argon ions) switched off while the spectrum is recorded. The resulting data can be presented as elemental intensity versus etch time or depth if the instrument has been calibrated to a known standard such as tantalum oxide.

Because the technique is destructive, it can lead to some sputter induced effects, which may complicate interpretation of the depth profile. A very brief account is given here but there are many references in the literature, for example see Hofmann (1990).

The detrimental effects which may occur during sputter depth profiling can be characterised as follows:

a) Instrumental factors. These include adsorption from the residual gas, impurities in the gas, or non-uniform ion beam intensity. For example small traces of species such as carbon or oxygen from the residual gas in the analysis chamber or from external sources may react with the surface species such as chromium. Even very small amounts of oxygen in the system can make it impossible to obtain metallic chromium by sputtering.

b) Preferential sputtering. Sample characteristics such as surface roughness, alloys or second phases may lead to preferential sputtering. Preferential removal of one compound of the outermost surface of the alloy or oxide due to different sputtering yields. The distortion of the surface composition is usually confined to the outermost layers. The degree of preferential removal of one component should decrease with time since the impoverishment of the preferred component will increase with time. This will eventually lead to a steady state concentration where both components are sputtered at constant rates, which are in the
same ratio as the components in the alloy. This is observed in SIMS analysis.

c) Chemical decomposition. Radiation induced effects such as atomic mixing and decomposition of compounds can be induced by the ion beam though the beam conditions are important. For example some authors have shown that after ion beam bombardment Fe$^{3+}$ in haematite was reduced to Fe$^{2+}$ and further to metallic iron. However, Richardson at Surrey has shown Fe$_2$O$_3$ to be stable which suggests conditions used in this laboratory are less aggressive than those adopted elsewhere.

### 3.3.5. Imaging XPS

In corrosion studies it is often important to investigate what processes occur at local positions on a surface such as pitting, crevice corrosion etc. For this we require analysis with good spatial resolution. Scanning Auger Mapping has been the traditional method of this type of examination but lacks the chemical state information of XPS, in recent years the advent of scatter diagrams has gone some way to obtain some chemical information from Auger analysis. Auger also has problems with charging with insulating oxides which may be present on a corroded surface.

XPS has generally been regarded as an area averaging technique on an area of $\sim 10\text{mm}^2$. If good spatial resolution could be obtained using XPS it would be a major leap forward to understanding the chemical processes involved in local corrosion on surfaces.

People have been striving to attain smaller and smaller areas of analysis for XPS. Many instruments are now equipped with small area XPS facilities, often reaching down to $100\mu\text{m}$
resolution by defining an area on the sample with a transfer lens. A review of routes to small area XPS is given by Drummond et al. (1985). For localised corrosion a resolution of 100μm is more than often insufficient and higher resolution is desirable.

Recent developments have been made which are going some way to achieving better resolution; in particular the commercial instruments the Scienta ESCA 300, the Kratos Analytical PESM and the VG Scientific ESCASCOPE. The Scienta ESCA 300 uses a rotating anode to give high photoelectron yields with a cylindrical hemispherical analyzer (CHA) and a channel plate to produce 2000μm lines with a resolution of 25μm. The Kratos Analytical PESM uses a divergent magnetic field plus an image band pass filter and, though not yet commercially available, may be on its way to producing a resolution of down to 1μm.

The VG Scientific ESCASCOPE has only recently become available, and has been used in this study at the manufacturer’s factory. The resolution achievable is 5μm. The design is similar to the conventional lens plus analyser arrangement of the ESCALAB illustrated in Figure 3.8. but it has the addition of two quasi-Fourier transform lenses (labelled 3 and 5 in Figure 3.11).
Figure 3.11. Schematic of VG Scientific ESCASCOPE. Lenses 3 and 5 are the Fourier transform lenses which retain and invert angular information through the spectrometer analyser.

In the conventional XPS CHA arrangement the energy and spatial information are convoluted in the dispersive plane of the analyser. The ESCASCOPE, however, converts the X-Y
information into angular information $\theta$ at the input of the CHA using a Fourier lens. The angular information is thus retained through the CHA to the exit aperture. A second Fourier lens than inverts the theta information to provide an X-Y image on the image detector. A more detailed description is given by Coxon (1990).

3.4. SIMS 'in-situ' Analysis Technique

Secondary ion mass spectrometry has been widely used in metallurgical (Degreve 1988) and oxidation studies (Benninghoven 1979). Often the technique is used to complement to other surface analysis techniques such as XPS or AES.

The more straightforward applications of SIMS to oxidation studies involve depth profiling through a thick oxide and providing information on oxide layers. In this study a rather more unusual mode, that of in-situ oxidation using dynamic SIMS, is used.

The basis of this technique is to simultaneously oxidise and analyse the material under investigation. In this way the very early stages of the oxidation process can be monitored. The experimental details in this study are given below.

3.4.1. Experimental Procedure

3.4.1.1. Preparation of Samples

The alloy investigated was Co$_{60}$Cr$_{14}$, in the form of a sputter target material. The metals cobalt, chromium, iron and manganese were 99.99% pure, supplied by Goodfellows, Cambridge. 0.5cm$^2$ samples of CoCr, cobalt, chromium, iron and manganese and 1cm$^2$ were polished on 400, 600, 800 and 1200 grit SiC paper: the samples being ultrasonically cleaned.
in water and then in acetone between each grit paper. The polished sample was mounted on the sample stub, and held in position using nickel clips and transferred to the SIMS analysis chamber.

All SIMS experiments were conducted in a VG SIMSLAB instrument. This is shown in Figure 3.12. The ion source was a duoplasmatron using a 79.3%/20.7% Ar/O\(_2\) gas and a quadrupole mass analyzer. Prior to the in-situ exposure, the sample surface oxide, formed during polishing, must be removed. This was achieved by etching the surface using an 79.7% argon/20.3% oxygen mixture feed gas at 9kV, 60nA sample current. A Wien filter was used to remove O\(_2^+\) ions from the beam. This etching was continued for several hours until the SIMS signals reached an equilibrium value, ie the counts for a particular mass remained constant with time. This indicated that an equilibrium had been reached between the formation of new oxide and its removal by ion etching.
Figure 3.12. VG SIMS instrument used in this study.
### 3.4.1.2. SIMS Experiment

A typical mass spectrum of the as-polished sample of Co$_{86}$Cr$_{14}$ is shown in Figure 3.13. In the SIMS experiment, which is central to this study, the masses of interest are selected and the mass analyser used to intergates the counts for a dwell time of 20s on a particular mass peak. This is then repeated for all the masses selected. The SIMS profile of counts for this mass versus etch time is thus produced. The SIMS profile thus produced will change with oxygen pressure and beam current and it is these changes which are monitored.

![Figure 3.13. A typical mass spectrum of an as-polished sample of Co$_{86}$Cr$_{14}$.](image)

### 3.4.1.3. Oxidation of Samples

A diagram of the experimental set-up in the SIMS chamber is shown in Figure 3.14. Oxygen was introduced into the analysis chamber via a leak valve as a 20.3%/79.7% oxygen/argon mixture. The pressure was increased from the base pressure of the chamber, 1x10$^{-9}$mbar,
in increments to $2 \times 10^{-7}$ mbar. After each increment the SIMS profile was allowed to stabilise to an equilibrium value, which was recorded, before the pressure was increased to the next value. This equilibrium is obtained when the rate of formation of the reaction products equals the rate of their removal in the etching process. A schematic of a typical SIMS profile where one mass is monitored with etch time and the oxygen pressure was gradually incremented is illustrated in Figure 3.15.
Figure 3.14. Experimental set-up for the oxidation of samples in the SIMS chamber.
At equilibrium, the rate of formation equals the rate of removal.

$P_1 < P_2 < P_3$

Figure 3.15. A schematic diagram of a typical SIMS profile where the oxygen pressure was gradually incremented.

Under normal circumstances, fractionation patterns are used to determine oxide species on the surface. This, however, requires monitoring quite a few different ions for one oxide state, preferably with negative and positive SIMS mode. Since we are limited to monitoring a maximum of ten masses in one experimental run, it was decided to look at major ions to see if we can obtain information in this way.
CHAPTER 4

Electrochemistry Study on the Corrosion of Fe$_{33}$Mn$_{47}$ Alloy in Aqueous Solution

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4.1. Introduction

From the literature survey in Chapter 2, it is clear that little work has been performed on the alloy FeMn. The alloy has great potential for use in the magnetic recording industry. For successful application in service, it is important that its corrosion properties are determined. FeMn has two reactive components and this is typical of many of the alloys being developed in the magnetic recording industry. FeMn is therefore a representative alloy to investigate.

One important factor in the corrosion of the alloy, which should be investigated, is whether any naturally occurring passive oxide layer could offer protection to the alloy in service. This passivation can be ascertained using electrochemical means by determining the anodic and cathodic reactions of the alloy in aqueous conditions. If the passivation lies below the cathodic line then it is difficult to examine this region by traditional potentiodynamic methods. By using a sensitive solution analysis, such as Inductively Coupled Plasma Source Mass Spectrometry (ICPMS), the corrosion products in solution can be found. Using X-ray Photoelectron Spectroscopy (XPS), the chemical nature of the corrosion products on the surface can be investigated to give an overall idea of the corrosion process.
4.2. Anodic Polarisation Curve of Fe$_{52}$Mn$_{47}$

Potentiostatic experiments were performed on Fe$_{52}$Mn$_{47}$ samples in pure water at nine different potentials ranging from -139mV to -889mV versus SCE using the electrochemical cell b) shown in Figure 3.1. The external current was monitored with time using an ammeter for each sample; the resulting current density plots are given in Figure 4.1. The external current through the cell is the sum of the anodic and cathodic currents; the direction of the net external current is indicated for each sample. The current flowing was integrated over the exposure period to obtain the charge transfer through the electrode. This charge transfer was interrupted at a charge of approximately 0.05C/cm$^2$ and the sample withdrawn from solution. The samples were then stored in a vacuum desiccator for later examination by XPS and SEM. It was observed that the samples tarnished quickly on removal from the solution; this is an important consideration with respect to the surface analysis that followed. The electrolytic solutions were analyzed using ICP-MS.
Figure 4.1. External current density versus time plots for FeMn samples in water held at different potentials.
To calculate the actual anodic current, the corrosion product in solution has to be analyzed. For the calculation of the mean anodic current densities of metal ions dissolving into solution, it was assumed that the dissolution occurred as predicted by the Pourbaix diagrams;

For the dissolution of Fe: \( \text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \)

and for Mn: \( \text{Mn} \rightarrow \text{Mn}^{2+} + 2e^- \)

The mean anodic current densities can be determined from the calculation

\[
    i_z = \frac{X_z \times V \times e \times L \times n}{N_z \times A \times t}
\]

(4.1)

where:
- \( i_z \) = partial current density (A/cm²)
- \( X_z \) = concentration of z in g/ml
- \( V \) = volume of electrolytic cell solution + rinse in ml
- \( e \) = elementary charge in C
- \( L \) = Avogadro’s constant in mol⁻¹
- \( N_z \) = atomic mass of z in gmol⁻¹
- \( A \) = area of sample in cm²
- \( t \) = time in seconds
- \( n \) = number of electrons in reaction = 2

The solution analysis is given in Table 4.1. The partial ion currents have been determined, using equation 1 as a function of electropotential and the sum of these currents is shown in
Figure 4.2. This anodic current has a potential dependence which is characteristic of a material which shows passivation. An active region is observed up to -618 mV SCE, where an active peak is indicated; the current then drops into a passive region, where it has a value typical of passivity (<1 μA/cm²). The passive region is very short and the curve shows transpassive behaviour in which the current increases sharply. The net external current is anodic in the transpassive region, as shown in Figure 4.2.

Table 4.1. ICPMS solution analysis and mean current densities of iron and manganese, calculated from the electrolytic solutions resulting from the electrochemical experiments.
Figure 4.2. Anodic polarisation curve of FeMn in water.

4.3. The Cathodic Curve

The external current in the potentiostatic experiments is the sum of the partial anodic and cathodic currents as follows;

$$ I_{net} = |I_{cathodic}| - |I_{anodic}| $$

(4.2)

The mean anodic current can be obtained by ICP-MS as described above. The mean net
current can be determined by charge transfer, monitored by the charge integrator, and the time of exposure. Hence, the mean cathodic current can be determined using this relationship and the results are given in Table 4.2. The cathodic curve is plotted in Figure 4.3, with the anodic curve obtained by ICP-MS. The cathodic curve increases up to a value of -740 mV SCE, where it reaches a limiting current of 40 μA/cm². The cathodic current obtained in this way represents the mean value over the period of exposure, i.e., it is based on the integral of the curves given in Figure 4.1.

Table 4.2. Mean cathodic current calculated from the ICPMS data and the external current measurement.

<table>
<thead>
<tr>
<th>Potential vs SCE (mV)</th>
<th>Mean Current Density (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Net External</td>
</tr>
<tr>
<td>-139</td>
<td>37.5</td>
</tr>
<tr>
<td>-239</td>
<td>29.4</td>
</tr>
<tr>
<td>-339</td>
<td>10.3</td>
</tr>
<tr>
<td>-439</td>
<td>12.7</td>
</tr>
<tr>
<td>-539</td>
<td>23.5</td>
</tr>
<tr>
<td>-618</td>
<td>62.1</td>
</tr>
<tr>
<td>-789</td>
<td>38.2</td>
</tr>
<tr>
<td>-839</td>
<td>63.7</td>
</tr>
<tr>
<td>-889</td>
<td>46</td>
</tr>
</tbody>
</table>
Figure 4.3. Anodic and cathodic curves for FeMn in pure water.

The point of intersection of the cathodic and anodic curves lies around -300mV SCE. The net external current was anodic at values of potential where the anodic current exceeds the cathodic; it was cathodic when the opposite was true.

Redeposition of material on the surface of the sample presents a potentially serious error in the calculation of anodic and cathodic currents from the solution analysis and measured charge transfer. This is not accounted for in the above account. This problem is dealt with in section 4.5, where it is shown that redeposition modifies the measured current by 20%.
4.4. The Chemical Nature of the Passive Region

The XPS wide scans and narrow Fe2p, Mn2p and O1s scans are shown in Figures 4.4a-d for a sample in the passive region and for the as-polished sample. The manganese enrichment factor and the manganese dissolution coefficient are given in Table 4.3.

Figure 4.4a. XPS wide scans for an FeMn sample in the passive region and for the as-polished sample.
Figure 4.4b. XPS narrow Fe2p scans for an FeMn sample in the passive region and for the as-polished sample.

Figure 4.4c. XPS narrow Mn2p scans for an FeMn sample in the passive region and for the as-polished sample.
Figure 4.4d. XPS narrow O1s scans for an FeMn sample in the passive region and for the as-polished sample.

Table 4.3. Manganese enrichment factor and dissolution coefficient for FeMn samples in the passive region and for the as-polished sample.

<table>
<thead>
<tr>
<th></th>
<th>Mn Enrichment</th>
<th>Mn Dissolution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>as-polished</td>
<td>0.87</td>
<td>-</td>
</tr>
<tr>
<td>passivated</td>
<td>0.9</td>
<td>1.12</td>
</tr>
</tbody>
</table>

From Table 4.3 we can see that the surface composition of the passive layer is slightly rich in manganese in both the as-prepared and the passivated surface. The dissolution coefficient for manganese is also greater than unity for this range of potentials, indicating that more manganese than iron is dissolving. Thus iron is concentrating in the sample, either as an enriched metallic phase or as surface material which does not contribute strongly to the XPS signal.
The change in composition of the passive layer with exposure to the solution can be seen in the wide XPS scans in Figure 4.4a. The XPS background slope can give valuable information on the oxide structure, as explained in section 3.3.4. In Figure 4.4a, it can be seen that the background slope in the region of the Fe 2p peak undergoes by far the greatest change after exposure. We observe that the post-peak background of the Fe 2p peak decreases with exposure from steeply upwards post-peak background in the as-polished sample to much less steep background in the water exposed sample. This shows that the iron is buried in the as-polished sample whereas more iron is present on the surface of the exposed sample. In the as-polished sample, the manganese postpeak background is less steep than that of the iron, which suggests that a manganese rich layer lies on top of the iron.

The oxygen 1s peaks in Figure 4.4d. show that the oxide component at 530.3 eV increases relative to the hydroxide peak at 531.5 eV upon exposure, although in both the as-polished and the water-exposed sample the hydroxide peak is dominant. The Fe2p peak (Figure 4.4a) has a metallic component on the as-polished and the water-exposed samples, whereas the Mn 2p peak (Figure 4.4b) only has a metallic component on the as-polished sample. The presence of the metallic components indicate that the passive layer is thin, in the order of <100Å.

In summary, the surface layer of the as-polished sample consists of a thin manganese hydroxide-rich surface on top of an iron/manganese metal layer. There are two possible explanations of the oxide structure after exposure, as shown in Figure 4.5 a) and b).
Figure 4.5. Two possibilities for the structure of the surface layer after exposure.

a) This structure consists of iron rich platelets redeposited from solution on top of a manganese hydroxide rich layer. The fact that iron redeposits on the surface explains the higher net dissolution coefficient of the manganese. Its physical form as platelets means that
the total amount of iron is underestimated in the XPS signal, which is most sensitive to the relative area of the surface phase. The occurrence of iron platelets is in accord with the presence of iron in the surface oxide layer of the passivated structure, in contrast to the buried iron observed in the as-polished sample. The disappearance of the manganese metallic peak suggests that the manganese is preferentially oxidised relative to the iron. The preferential oxidation of manganese may be predicted from thermodynamics, since the heat of formation of manganese oxide is more negative than that of iron oxide. In Cohen's in-situ XPS oxidation study of FeMn (Cohen, 1988) he observed that the manganese component of the alloy oxidised with shorter Langmuir exposures than the iron component.

b) The second possible oxide structure consists of an oxide structure similar to the as-polished sample but a surface roughening between the oxide and the pure alloy has occurred. The manganese has oxidised and the oxide grows into the alloy but the iron remains unreacted. Diffusion of iron into the surface oxide must occur to explain why the spectrum also contains features arising from a surface concentration of iron.

4.5. Redeposition of Material (Estimation of Surface Deposit)

As mentioned in section 4.3., redeposition can cause error in the calculation of anodic and cathodic currents from the solution analysis and measured charge transfer data. This is not accounted for calculation of current densities given in section 4.2. The structure described in a) above, implies that an important contribution to the balance of charge should be ascribed to the surface deposit.

To investigate the contribution of the redeposited material, a sample was exposed at the rest
potential for 20 minutes and transferred within 2 minutes to a scanning electron microscope. This reduced air oxidation which may occur during sample storage. The SEM micrographs of the sample surface are given in Figure 4.6. The structure consists of a layer of crystals over the surface with isolated 'bullseyes' where the centre has small crystals surrounded by a crystal depleted zone and then a matrix of larger crystals. At higher magnification, the hexagonal platelet structure of the crystals can be distinguished. Although this procedure was performed only at the open circuit potential, similar crystal deposits were observed at other potentials, as seen in the SEM micrographs in Figure 4.7.
Figure 4.6. SEM micrographs of the FeMn sample exposed to after at the rest potential and transferred to the SEM within 2 minutes. The structure consists of a layer of crystals over the surface with isolated 'bullseyes' where the centre has small crystals surrounded by a crystal depleted zone and then a matrix of larger crystals.
Figure 4.7a. SEM micrographs of FeMn samples after exposure in water at various potentials.
Figure 4.7b. SEM micrographs of FeMn samples after exposure in water at various potentials.
X-ray analysis of the crystals extracted from the surface on a carbon replica identified an iron rich compound. A Transmission Electron Microscopy (TEM) micrograph and Energy Dispersive X-ray analysis (EDX) of the crystals are given in Figures 4.8 and 4.9. This was in good agreement with microprobe analysis given in Figure 4.10, which also indicated an iron rich compound.

Figure 4.8. TEM micrograph of crystals extracted from the surface of the FeMn exposed for 20 minutes at the rest potential.
Figure 4.9. X-ray analysis of crystals, removed from the surface of the sample in Figure 4.6, on a carbon replica in the TEM.

Figure 4.10. Microprobe analysis of crystals, removed from the sample in Figure 4.6, on carbon coated acetate.
Auger analysis also indicated an iron rich surface (Figure 4.11) in contrast with the manganese rich surface observed with XPS (Figure 4.12). Imaging XPS, obtained by ESCASCOPE, revealed regions of iron rich material at the centre of the 'bullseye' surrounded by a manganese rich ring (Figure 4.13).

Figure 4.11. Auger analysis of matrix material on sample surface after exposure. An iron rich surface is indicated.
Figure 4.12. XPS wide scan analysis of sample surface after exposure. A manganese rich surface is observed by XPS.
In summary, the microanalytical techniques of AES, and TEM-EDX are able to distinguish between a manganese-rich passive layer and the surface-deposit of iron-rich platelets. The area-averaging technique of XPS cannot do this, but the background signature was interpreted to show that there was iron-rich material lying on top of the manganese. ESCASCOPE, with its intermediate range of lateral resolution, shows the platelet deposition to be modified by local electropotentials to give the bullseye rings around pits and inclusions.

**Figure 4.13.** Results from ESCASCOPE imaging XPS of sample surface. There are regions of iron rich material at the centre of the bullseyes structure, surrounded by a manganese rich ring.
From these results, it is clear that there is redeposition of an iron rich material onto the sample surface. This is responsible for an error in the calculation of the anodic and cathodic currents, as this material is not counted in the solution analysis. To obtain the true anodic and cathodic currents, an approximation of the amount of redeposited material should be incorporated into the calculations.

As the SEM micrographs, taken for each sample (Figure 4.7) show, the surface redeposition is not negligible. An allowance can be derived from the images, by estimating the coverage. A schematic of the redeposition is given in Figure 4.14. The deposit appears to be approximately 20% of the available surface at all potentials. The deposit itself, at high magnification, is seen to compose of platelets with a coverage of approximately 50%. ESCA shows the material to be -OOH and to contain Fe(III) and Mn(II) ions. However, the colour changes on exposure to air suggest that, initially, the iron is in the 2+ state. The density of FeOOH is 4.28gcm\(^3\). 50% of the deposit surface is uncovered, 10% of the surface is covered with upright platelets with a thickness of 0.5\(\mu\)m, and 40% of the surface is covered with flat platelets with a thickness of 0.05\(\mu\)m, then the amount of iron can be calculated as follows:
Figure 4.14. A schematic of the redeposition on the surface of the samples.
If $F_{\text{surface}}$ is the mass of iron on the surface then;

$$F_{\text{surface}} = \rho_{\text{FeOOH}} \times V \times C_{\text{surf}} \times \frac{N_{\text{Fe}}}{N_{\text{FeOOH}}}$$

(3)

$$= \rho_{\text{FeOOH}} \times t \times A \times C_{\text{surf}} \times \frac{N_{\text{Fe}}}{N_{\text{FeOOH}}}$$

(4)

Then the number of moles of iron, $M_{\text{Fe}}$, is

$$M_{\text{Fe}} = \rho_{\text{FeOOH}} \times t \times A \times C_{\text{surf}} \times \frac{N_{\text{Fe}}}{N_{\text{FeOOH}}} \times \frac{1}{N_{\text{Fe}}}$$

(5)

Assuming Fe $\rightarrow$ Fe$^{2+}$ + 2e\(^{-}\)

Therefore the charge involved in depositing the material onto the surface

$$= \rho_{\text{FeOOH}} \times t \times A \times C_{\text{surf}} \times \frac{N_{\text{Fe}}}{N_{\text{FeOOH}}} \times \frac{1}{N_{\text{Fe}}} \times 2 \times L \times e$$

(6)

where

$\rho$ = density of FeOOH = 4.28gcm\(^{-3}\)

$t$ = average thickness of the deposit

$= (20\% \text{ at } 0.5\mu m + 80\% \text{ at } 0.05\mu m)$

$= 1.4 \times 10^{-5}$ cm

$A$ = projected unit area = 1cm\(^2\)

$C_{\text{surf}}$ = coverage of deposit = 10%

$N_{\text{Fe}}$ = atomic mass of iron = 56g mol\(^{-1}\)
$N_{\text{FeOOH}} = \text{molar mass of FeOOH} = 89\,\text{g}$

$L = \text{Avogadro's number} = 6.022 \times 10^{23}$

$e = \text{elementary charge} = 1.602 \times 10^{-19} \, \text{Coulombs}$

Substituting these values into the above equation:

The charge involved in the redeposition of material onto the surface:

$$= 4.28 \times 1.4 \times 10^{-5} \times 1 \times 0.1 \times 2 \times 6.022 \times 10^{23} \times 1.602 \times 10^{19} / 89$$

$$= 1.3 \times 10^{-2} \, \text{C/cm}^2$$

From this approximation, it can be seen that the charge involved in the redeposition of the material onto the surface is not negligible, compared to the charge transfer of $0.05 \, \text{C/cm}^2$, and cannot be neglected.

If we assume that the amount of redeposition is approximately equal at all potentials investigated, then the resulting effect on the anodic polarisation and cathodic curve is to raise each of them by the charge $1.3 \times 10^{-2} \, \text{C/cm}^2$. Since the polarisation curve is plotted on a log scale, a factor of 0.2 will, actually, not have such a marked influence on the shape of the curves. Examining the SEM micrographs (Figure 4.7) in the region of passivation, there is less redeposition in this region, if anything. This would imply that the anodic current 'lost' due to redeposition is less than that at other potentials, and this makes the passivation region more pronounced.
4.6. Displacement of the Anodic Polarisation Curve

To investigate the region of passivation further, potentiostatic experiments were repeated at similar potentials on two separate occasions. These sets of experiments shall be referred to as series 2 and 3, and the original set of potentiostatic experiments as series 1. The calculated total anodic currents for series 2 and 3 are compared with those obtained for series 1 in Figure 4.15. It can be observed from Figure 4.15 that each series produced its own anodic polarisation curve, which retained the essential features of the previous one; a steep rise to a peak at potential of -640mV, then a short dip before rising again, less steeply at less negative potentials. However, the anodic polarisation curve for each series is displaced to higher current densities in the order of the series 1, 2 and 3. This breakdown of passivity in the subsequent series 2 and 3 was disappointing and did not have an obvious cause. The SEM micrographs of series 1 did show some pitting on the passivated samples, and this suggested that the alloy was prone to attack. The cause of this attack could be enhanced in the later series. The possible causes of the breakdown of passivity are discussed in the following section.
4.6.1. Factors Influencing the Displacement of the Anodic Polarisation Curve

There are several factors which could influence the displacement of the anodic polarisation curve. These include temperature, pH and specific ions and in this section each of these factors is investigated. Chloride ions are known to enhance corrosion with many alloys. However, the cell was designed with a mercury/mercurous sulphate electrode in neutral sodium sulphate solution to avoid the chloride ions associated with the frequently used
calomel reference electrodes. Therefore, the only active ions which could influence the corrosion of the alloy in the test cell are sodium or sulphate ions arising, possibly, from diffusion through the ceramic frit separating the reference electrode and the test solution.

4.6.1.1. Temperature

All the samples in any one series were run on the same day. The three series were performed at different times over the course of six months as shown in Table 4.4.

Table 4.4. Dates of experimental series 1, 2 and 3.

<table>
<thead>
<tr>
<th>Experimental Series</th>
<th>Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>19/1/89</td>
</tr>
<tr>
<td>2nd</td>
<td>18/5/89</td>
</tr>
<tr>
<td>3rd</td>
<td>22/6/89</td>
</tr>
</tbody>
</table>

It may be argued that the temperature of the laboratory could change with the season. The temperature of the laboratory was recorded on 9/9/88 as 22°C and 13/3/89 as 21°C which suggests that the laboratory temperature probably does not change very much through the year. However, to investigate the influence of temperature on the anodic polarisation curve, potentiostatic experiments were performed at temperatures of 22°C, 32°C and 44°C. All experiments were run within 3 days and covered the active region.

The current densities of iron and manganese, calculated from solution analysis of the resulting electrolytic solutions, are given in Table 4.5. The total current densities (iron + manganese) are plotted as a function of potential in Figure 4.16. There is little difference
between the current densities of the samples run at different temperatures. Therefore, it seems unlikely that a temperature difference of a few degrees, which may result from fluctuations in the laboratory room temperature, should make a tenfold or 100 fold difference, as observed in the current densities of the different series 1, 2 and 3.

Table 4.5. ICPMS data and calculated iron and manganese partial currents for samples exposed at various potentials at temperatures of 22°C, 32°C and 44°C.

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>Potential vs SCE (mV)</th>
<th>ICPMS Data (ppb)</th>
<th>Exposure Time (s)</th>
<th>Current Density (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Mn</td>
<td>Fe</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>-640</td>
<td>335</td>
<td>55</td>
<td>795</td>
</tr>
<tr>
<td>22</td>
<td>-740</td>
<td>402</td>
<td>100</td>
<td>1640</td>
</tr>
<tr>
<td>22</td>
<td>-840</td>
<td>104</td>
<td>13</td>
<td>3125</td>
</tr>
<tr>
<td>22</td>
<td>-940</td>
<td>234</td>
<td>55</td>
<td>2290</td>
</tr>
<tr>
<td>22</td>
<td>-1040</td>
<td>38</td>
<td>13</td>
<td>1965</td>
</tr>
<tr>
<td>32</td>
<td>-740</td>
<td>517</td>
<td>89</td>
<td>2310</td>
</tr>
<tr>
<td>32</td>
<td>-840</td>
<td>57</td>
<td>89</td>
<td>1150</td>
</tr>
<tr>
<td>32</td>
<td>-940</td>
<td>37</td>
<td>3</td>
<td>610</td>
</tr>
<tr>
<td>32</td>
<td>-1040</td>
<td>294</td>
<td>142</td>
<td>700</td>
</tr>
<tr>
<td>44</td>
<td>-640</td>
<td>604</td>
<td>148</td>
<td>1860</td>
</tr>
<tr>
<td>44</td>
<td>-840</td>
<td>158</td>
<td>107</td>
<td>1920</td>
</tr>
<tr>
<td>44</td>
<td>-940</td>
<td>85</td>
<td>37</td>
<td>1015</td>
</tr>
<tr>
<td>44</td>
<td>-1040</td>
<td>116</td>
<td>48</td>
<td>3282</td>
</tr>
</tbody>
</table>
Figure 4.16. The current densities of iron and manganese, for samples held at temperatures 22°C, 32°C and 44°C, calculated from solution analysis of the resulting electrolytic solutions, plotted as a function of potential.

4.6.1.2. PH

The experiments were performed in nominally pure water at neutral pH. Nevertheless, there is a possibility that the pH of the water could change from run to run, owing to small compositional variations between batches, or to contamination of equipment.

The water chosen was deionised and doubled-distilled milli-Q water of very high quality.
The analysis of the water is given in Table 4.6 at three different occasions. It can be seen that the composition is low in dissolved ions and does not vary much between runs.

**Table 4.6.** ICPMS analysis of water used in the electrochemical experiments on three different occasions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Water Analysis (ppb)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>A</td>
</tr>
<tr>
<td>Li</td>
<td>-</td>
</tr>
<tr>
<td>Be</td>
<td>0.21</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
</tr>
<tr>
<td>Na</td>
<td>75.1</td>
</tr>
<tr>
<td>Mg</td>
<td>-</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
</tr>
<tr>
<td>P</td>
<td>-</td>
</tr>
<tr>
<td>Cl</td>
<td>-</td>
</tr>
<tr>
<td>K</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>2.95</td>
</tr>
<tr>
<td>Sc</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>-</td>
</tr>
<tr>
<td>Mn</td>
<td>-</td>
</tr>
<tr>
<td>Fe</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>-</td>
</tr>
<tr>
<td>Ni</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>5.83</td>
</tr>
<tr>
<td>Zn</td>
<td>2.43</td>
</tr>
<tr>
<td>Ga</td>
<td>-</td>
</tr>
<tr>
<td>Ge</td>
<td>-</td>
</tr>
<tr>
<td>As</td>
<td>-</td>
</tr>
<tr>
<td>Se</td>
<td>-</td>
</tr>
<tr>
<td>Br</td>
<td>-</td>
</tr>
<tr>
<td>Rb</td>
<td>0.08</td>
</tr>
<tr>
<td>Sr</td>
<td>0.81</td>
</tr>
</tbody>
</table>
Contamination from the equipment can occur, altering the pH of the sample solution as illustrated by the first electrochemical cell used. This consisted of a mercury/mercurous sulphate electrode in sulphuric acid, connected to the test solution by a ceramic frit, as shown in Figure 3.1. When 0.5M H₂SO₄ was used with reference electrode, the pH of the test solution was 2.5 and with 0.1M H₂SO₄ the pH was 3.

To investigate the influence of pH on the current density, potentiostatic experiments were performed at a constant potential of -938mV SCE on samples in solutions of varying pH from pH1.5 to pH12.8. The sample solutions were prepared by adding 0.1M sodium hydroxide or 0.1M sulphuric acid to 0.1M sodium sulphate solution to adjust the pH to alkaline or acidic.

The resulting current densities, calculated from ICPMS analysis, for samples held in different pH solutions, are given in Table 4.7. The total anodic current densities (iron + manganese) plotted against pH in Figure 4.17. The current density shows a plateau region between pH 3 and 9, and this suggests that small variations from neutral will not greatly affect the current. It is only in the strongly acidic region or strong alkaline region that the pH affects
the current density by an order of magnitude.

**Table 4.7.** ICPMS data and calculated mean current densities for FeMn samples in solutions of various pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>ICPMS Data (Mn, Fe)</th>
<th>Exposure Time (s)</th>
<th>Current Density (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Mn</td>
</tr>
<tr>
<td>1.51</td>
<td>145</td>
<td>516</td>
<td>146</td>
</tr>
<tr>
<td>1.98</td>
<td>150</td>
<td>681</td>
<td>164</td>
</tr>
<tr>
<td>2.53</td>
<td>167</td>
<td>654</td>
<td>196</td>
</tr>
<tr>
<td>3.14</td>
<td>45</td>
<td>&lt; 6</td>
<td>415</td>
</tr>
<tr>
<td>4.15</td>
<td>25</td>
<td>29</td>
<td>1330</td>
</tr>
<tr>
<td>5.65</td>
<td>12</td>
<td>45</td>
<td>1455</td>
</tr>
<tr>
<td>9.45</td>
<td>15</td>
<td>91</td>
<td>795</td>
</tr>
<tr>
<td>9.91</td>
<td>16</td>
<td>&lt; 4</td>
<td>995</td>
</tr>
<tr>
<td>11.1</td>
<td>&lt;0.3</td>
<td>&lt;3</td>
<td>1088</td>
</tr>
<tr>
<td>12.54</td>
<td>0.5</td>
<td>&lt;3</td>
<td>1157</td>
</tr>
<tr>
<td>12.75</td>
<td>&lt;0.2</td>
<td>&lt;3</td>
<td>2234</td>
</tr>
</tbody>
</table>
Figure 4.17. Current density, calculated from ICPMS data, versus pH for FeMn samples held in various pH solutions.

The anodic polarisation curve, obtained potentiostatically for samples held at pH3, can be compared to those for Series 1, 2 and 3 in Figure 4.18. The values obtained for the pH3 current densities support the idea that the pH is not the reason for the increase in the current density, since the pH3 values are less than those in series 2 and 3. However, the shape of the pH3 curve does not show the passivation dip in current density observed with the samples run in 'neutral' conditions.
4.6.1.3. Sodium Sulphate Concentration

To investigate the influence of sodium sulphate ions, potentiostatic experiments were performed in solutions of different sodium sulphate concentrations. The ICPMS data and calculated partial current densities for iron and manganese, for samples held in 0.1M and 0.01M sodium sulphate solution, are given in Table 4.8. The total anodic current densities (iron + manganese) for each concentration; 0.1M, 0.01M and 0.00022M, are given as a function of potential in Figure 4.19. The 0.00022M sodium sulphate concentration was
calculated from the measured concentration of sodium in the electrolytic solutions resulting from the potentiostatic experiments from the 1st series. The sodium was assumed to represent the sodium sulphate leaked through the ceramic frit from the reference electrode, since the pure water contained negligible sodium before the potentiostatic experiment.

Table 4.8. Anodic mean current densities for iron and manganese, calculated from ICPMS data, versus potential for 0.1M and 0.01M concentrations of sodium sulphate solutions.

<table>
<thead>
<tr>
<th>Na₂SO₄ (Molar)</th>
<th>V (mV) vs SCE</th>
<th>ICPMS Data (ppb)</th>
<th>Exposure Time (s)</th>
<th>Current Density (µA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>-1038</td>
<td>15 11</td>
<td>1250</td>
<td>1.43 1.02</td>
</tr>
<tr>
<td>0.1</td>
<td>-938</td>
<td>12 45</td>
<td>1455</td>
<td>0.81 2.9</td>
</tr>
<tr>
<td>0.1</td>
<td>-838</td>
<td>243 212</td>
<td>554</td>
<td>42.9 3.61</td>
</tr>
<tr>
<td>0.1</td>
<td>-738</td>
<td>1367 2735</td>
<td>142</td>
<td>926 1822</td>
</tr>
<tr>
<td>0.1</td>
<td>-638</td>
<td>3248 5977</td>
<td>149</td>
<td>2322 4203</td>
</tr>
<tr>
<td>0.1</td>
<td>-538</td>
<td>2422 1659</td>
<td>115</td>
<td>1960 1321</td>
</tr>
<tr>
<td>0.01</td>
<td>-1034</td>
<td>447 132</td>
<td>562</td>
<td>89.9 26.1</td>
</tr>
<tr>
<td>0.01</td>
<td>-934</td>
<td>257 16</td>
<td>1382</td>
<td>21.6 1.33</td>
</tr>
<tr>
<td>0.01</td>
<td>-834</td>
<td>23 3</td>
<td>1205</td>
<td>1.97 0.22</td>
</tr>
<tr>
<td>0.01</td>
<td>-734</td>
<td>340 100</td>
<td>197</td>
<td>197 57</td>
</tr>
<tr>
<td>0.01</td>
<td>-634</td>
<td>764 440</td>
<td>165</td>
<td>541 307</td>
</tr>
<tr>
<td>0.01</td>
<td>-534</td>
<td>773 492</td>
<td>177</td>
<td>532 333</td>
</tr>
</tbody>
</table>

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Figure 4.19. Anodic mean current densities, calculated from ICPMS data, versus potential for different concentrations of sodium sulphate solutions.

From Figure 4.19 it can be seen that, the greater the sodium sulphate concentration, the higher the current density at a given potential.

The anodic polarisation curves for the different sodium sulphate concentrations are compared to the Series 1, 2 and 3 in Figure 4.20. It can be seen that the initial gradient, the Tafel line, calculated to be 50mV/decade, is the same for all curves. The curves are displaced to less negative potentials with increase in sodium sulphate concentration.
Figure 4.20. Anodic polarisation curves for series 1, 2 and 3 compared to the curves for the different concentrations of sodium sulphate solutions.

It seems likely that the increase in the current density is due to a deterioration in the cell frit with time, which allows increasingly more Na$_2$SO$_4$ to diffuse in the test solution.
4.6.1.3.1. Estimation of the Concentration of the Sodium Sulphate for Series 2 and 3

If it is assumed that the displacement of the anodic polarisation curve is due to an increase in sodium sulphate concentration by diffusion across the ceramic frit, then we can estimate the concentration for each series by extrapolation of the current density versus sodium sulphate concentration plot shown in Figure 4.21.

![FeMn in Na2SO4 Solution](image)

**Figure 4.21.** Current density versus sodium sulphate concentration.

The approximate concentration of each series is given in Table 4.9.
Table 4.9. Approximate sodium sulphate concentrations of series 1, 2 and 3 extrapolated from the current density versus sodium sulphate concentration plot in Figure 4.21.

<table>
<thead>
<tr>
<th>Series</th>
<th>Concentration of Na$_2$SO$_4$</th>
<th>Date of Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>0.00022</td>
<td>19/1/89</td>
</tr>
<tr>
<td>2nd</td>
<td>0.0027</td>
<td>18/5/89</td>
</tr>
<tr>
<td>3rd</td>
<td>0.0099</td>
<td>22/6/89</td>
</tr>
</tbody>
</table>

From this we can see that the leakage from the reference electrode increases with time, probably as the ceramic frit deteriorates.

4.6.1.4. IR Drop

Since all the anodic polarisation curves have the same gradient, it is unlikely that the IR drop, between the sample and the reference electrode, had any significant impact, notwithstanding the influence of the leaked salt on the conductivity of the pure water electrolyte.

4.6.2. Concluding Remarks on The Anodic Polarisation Curve of FeMn

The irreproducibility of the anodic curve can be best explained if either Na$^+$ or SO$_4^{2-}$ are specific ions for the corrosion of FeMn. Series 1 shows the best results with the greatest passivation region, and this series will be treated as the reference result for the polarisation curve.

4.7. Breakdown of Passivity

Both the existence of a transpassive region in the anodic polarisation curve and the presence of 'bullseyes' suggest that passivity breaks down rather easily. The breakdown of passivity
can be seen in the displacement of the anodic polarisation curve to higher current densities from the 1st series to series 2 and 3. This has been attributed to an increase in Na\(^+\) and SO\(_4\)^{2-} concentration, the specific ions for the corrosion of FeMn. The passivity, observed in the 1st series, breaks down in the series 2 and 3.

It is interesting to examine this breakdown by comparing the current densities and chemical composition of samples from the series 1, 2 and 3. The current density versus time plots for samples in the region of passivity are given in Figure 4.22. It can be seen that the current density is lowest for the 1st series sample. The net external current density for the 2nd and 3rd series is anodic. It may be noted that the major portion of the anodic polarisation curves, for series 2 and 3, lies above the cathodic curve determined for series 1, and it is at these potentials that the net external current is observed to be anodic.
Figure 4.22. Current density versus time plots for samples in the region of passivity, for samples in series 1, 2 and 3.

There is a change in chemical composition of the surface with the breakdown of passivity. The Fe2p, Mn2p, O1s and the wide scan XPS spectra are given in Figure 4.23a-d for the as-polished and series 1, 2 and 3. The manganese enrichment factors and the manganese dissolution coefficients are given in Table 4.10.
Figure 4.23a. The wide scan XPS spectra for the as-polished and series 1, 2 and 3 for samples in the region of passivity.
Figure 4.23b. The Fe2p narrow scan XPS spectra for the as-polished and series 1, 2 and 3 for samples in the region of passivity.
Figure 4.23c. The Mn2p narrow scan XPS spectra for the as-polished and series 1, 2 and 3 for samples in the region of passivity.
Figure 4.23d. The O1s XPS spectra for the as-polished and series 1, 2 and 3 for samples in the region of passivity.
Table 4.10. The manganese enrichment factors and the manganese dissolution coefficients for series 1, 2 and 3 in the region of passivity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mn Surface Enrichment</th>
<th>Mn Dissolution Coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>as polished</td>
<td>1.14</td>
<td>-</td>
</tr>
<tr>
<td>1st series</td>
<td>1.12</td>
<td>1.12</td>
</tr>
<tr>
<td>2nd series</td>
<td>0.71</td>
<td>1.54</td>
</tr>
<tr>
<td>3rd series</td>
<td>1.06</td>
<td>1.39</td>
</tr>
</tbody>
</table>

Examination of the wide scan spectra in Figure 4.23a reveals that the iron peak becomes dominant with the breakdown of passivity. The post peak background of the Fe2p peak is downward sloping for the 3rd series, in contrast to the horizontal background post peak background in series 1 and 2 and the steeply rising background of the as-polished sample. This shows that the iron is no longer buried at the later stages of the breakdown of passivity.

The metallic component of the Fe 2p peak disappears and the ferric component (Fe³⁺) becomes more prominent relative to the ferrous (Fe²⁺) component with the breakdown of passivity. The disappearance of both the iron and manganese metallic components indicate that a thicker oxide forms with the breakdown in passivity. The O1s spectra shows an increase in the oxide component relative to the hydroxide component for the later series 2 and 3. Series 3 has equal oxide and hydroxide components, which suggests FeOOH may be dominant on the surface.

The manganese dissolution coefficient is higher and a corresponding iron enrichment of the surface occurs as the breakdown increases, as shown in Table 4.8. This indicates that more manganese is dissolving leaving an iron rich surface.

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In summary, the surface composition changes with the breakdown of passivity from a thin (<100Å thick) manganese rich hydroxide layer to a thicker iron rich oxy-hydroxide surface.

4.8. Inhibitor Study

The anodic polarisation curve of FeMn in water shows a shallow region of passivity over a short potential range and a transpassive region. It has been established that a breakdown of the passive layer occurs with sodium sulphate active ions. It is clear that any naturally occurring passivity is very limited, and is relatively unstable since it can be broken down by the presence of low concentrations of active ions. The observation of pits on the passive samples reinforces this viewpoint.

The use of inhibitors in helping to establish the passive layer is well known. It is natural therefore to investigate inhibitors for this alloy.

Several inhibitors, organic and inorganic, known for their protective properties with steel or iron applications, were investigated and are described below.

4.8.1. Organic Inhibitor Study

The organic inhibitors investigated were octadecylamine, triethanolamine, benzatrazole and cyclohexylamine. Potentiodynamic scans on FeMn with each inhibitor were performed and the experimental current density versus potential plots, curve fitted by the program Betacrunch (Parvizi, 1985), are given in Figure 4.24. The corrosion currents and potentials are given in Table 4.11.
Figure 4.24. Potentiodynamic scans on FeMn samples with various organic inhibitors.
Table 4.11. Corrosion currents and corrosion potentials for FeMn samples with various organic inhibitors.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Corrosion Potential vs SCE (mV)</th>
<th>Corrosion Current (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>-861</td>
<td>6.12</td>
</tr>
<tr>
<td>triethanolamine</td>
<td>-797</td>
<td>9.41</td>
</tr>
<tr>
<td>benzatriazole</td>
<td>-637</td>
<td>17.4</td>
</tr>
<tr>
<td>cyclohexylamine</td>
<td>-848</td>
<td>6.64</td>
</tr>
</tbody>
</table>

The organic inhibitors investigated showed little effect on the corrosion currents, and examination of the samples after immersion in aqueous solution showed a tarnished surface for each. The inorganic inhibitor sodium chromate did show a strong influence on the corrosion of the alloy, and this is discussed in the next section.

4.8.2. Inorganic Inhibitor Study

The inorganic inhibitor, sodium chromate, was investigated. The chromate ion is a well known anodic inhibitor and is used in many mixed metal systems. Its influence has been investigated extensively, particularly with the corrosion of iron in aqueous systems.

Potentiodynamic scans were performed on FeMn samples in solutions of sodium chromate at concentrations of 1000, 500, 250 and 100ppm (with respect to the salt). The resulting potentiodynamic scans are given in Figure 4.25. The greatest shift in rest potential occurs with a chromate concentration of 250ppm. The rest potential for the sample treated in 250ppm chromate solution lies at -510mV SCE, which lies in the passive region of the anodic polarisation curve of FeMn in pure water, as determined in Figure 4.2.
Figure 4.25. Potentiodynamic scans on FeMn samples in solutions of sodium chromate at concentrations of 1000, 500, 250 and 100ppm (with respect to the salt).
Table 4.12. Corrosion currents and corrosion potentials for FeMn samples with various concentrations of sodium chromate solutions.

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Corrosion Potential vs SCE (mV)</th>
<th>Corrosion Current (μA/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td>-861</td>
<td>6.12</td>
</tr>
<tr>
<td>1000ppm chromate</td>
<td>-655</td>
<td>0.63</td>
</tr>
<tr>
<td>500ppm chromate</td>
<td>-684</td>
<td>7.36</td>
</tr>
<tr>
<td>250ppm chromate</td>
<td>-538</td>
<td>2.0</td>
</tr>
<tr>
<td>100ppm chromate</td>
<td>-623</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Potentiostatic experiments were performed on FeMn samples in 250ppm concentrations of chromate at potentials of -640, -740, -840, -940 and -1040mV SCE. The samples were removed after a fixed charge was passed, and the samples were stored in a vacuum desiccator for later investigation by SEM and XPS.

The current density versus time plots, for the chromate treated samples are given in Figure 4.26a. The plots all show a similar form: an initial sharp decrease then a decrease at a slower rate. This form is typically expected when some structure forms on the surface. The current densities are slightly lower than the corresponding current densities for the untreated samples. For the chromate treated samples the net external current is always cathodic; this indicates that the anodic curve lies under the cathodic curve. The corresponding current density versus time plots for the untreated samples, given in Figure 4.26b., show a net anodic current at the potentials -640 and -740mV SCE. This is what may be expected as chromate is an anodic inhibitor, i.e., the chromate reduces the rate of the anodic reaction.
Figure 4.26a. The current density versus time plots for FeMn samples in 250ppm chromate solution.
Figure 4.26b. The current density versus time plots for untreated FeMn sample.

4.8.2.1. Surface Examination of the Chromate Treated Samples

The SEM micrographs for the chromate treated and untreated samples are given in Figure 4.27. The chromate treated samples show less redeposition than the corresponding untreated samples.
Figure 4.27a. SEM micrographs for chromate treated and untreated FeMn samples.

(a) untreated sample at -640mV SCE

(b) untreated sample at -640mV SCE

(i) sample in 250ppm chromate solution at -640mV SCE

(ii) sample in 250ppm chromate solution at -640mV SCE
Figure 4.27b. SEM micrographs for chromate treated and untreated FeMn samples.
The chromate treated and untreated samples were examined by XPS. The corresponding XPS spectra are given in Figures 4.28 and 4.29. The quantitative surface analysis results are given in Table 4.13.
Figure 4.28a. XPS wide scan spectra for chromate treated FeMn samples at various potentials.
Figure 4.28b. XPS Mn2p narrow scan spectra for chromate treated FeMn samples at various potentials.
Figure 4.28c. XPS Cr2p narrow scan spectra for chromate treated FeMn samples at various potentials.
Figure 4.28d. XPS O1s narrow scan spectra for chromate treated FeMn samples at various potentials.
Figure 4.29a. XPS wide scan spectra for untreated FeMn samples.
Figure 4.29b. XPS Mn2p narrow scan spectra for untreated FeMn samples.
Figure 4.29c. XPS Fe2p narrow scan spectra for untreated FeMn samples.
Figure 4.29d. XPS O1s narrow scan spectra for untreated FeMn samples.
Table 4.13. Quantitative surface analysis results for chromate treated samples.

<table>
<thead>
<tr>
<th>V (mV) SCE</th>
<th>XPS Analysis (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
</tr>
<tr>
<td>untreated</td>
<td></td>
</tr>
<tr>
<td>-640</td>
<td>5.18</td>
</tr>
<tr>
<td>-740</td>
<td>5.25</td>
</tr>
<tr>
<td>-840</td>
<td>5.27</td>
</tr>
<tr>
<td>-940</td>
<td>4.76</td>
</tr>
<tr>
<td>-1040</td>
<td>4.1</td>
</tr>
<tr>
<td>chromate treated</td>
<td></td>
</tr>
<tr>
<td>-640</td>
<td>0.04</td>
</tr>
<tr>
<td>-740</td>
<td>0.73</td>
</tr>
<tr>
<td>-840</td>
<td>1.17</td>
</tr>
<tr>
<td>-940</td>
<td>0.71</td>
</tr>
<tr>
<td>-1040</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The wide scans show a chromium rich surface for the chromate treated samples at all potentials except at -840mV, where the chromium content is at its lowest value and manganese is dominant. At the other potentials manganese is present to a lesser extent than the chromium, and the iron is only present at very low concentrations (<1.12%). Only at -840mV SCE does the iron concentration approach that of manganese.

The surface composition ratio of chromium to (iron + manganese) for each potential, is given below in Table 4.14. The chromium due to the remaining sodium chromate on the surface has been allowed for in the calculated ratios.
Table 4.14. The surface composition ratio of chromium to (iron + manganese) for each potential.

<table>
<thead>
<tr>
<th>Potential vs SCE (mV)</th>
<th>Cr/(Fe+Mn)</th>
<th>Cr/(Fe+Mn+Cr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-640</td>
<td>0.93</td>
<td>0.48</td>
</tr>
<tr>
<td>-740</td>
<td>0.91</td>
<td>0.48</td>
</tr>
<tr>
<td>-840</td>
<td>0.24</td>
<td>0.19</td>
</tr>
<tr>
<td>-940</td>
<td>0.89</td>
<td>0.47</td>
</tr>
<tr>
<td>-1040</td>
<td>2.03</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Chromium incorporated into the oxide film and accounts for approximately 50% of the metal atoms on the surface, except at -840 mV SCE, where the amount of iron and manganese is greater than the chromium. At this potential there was no sulphur or sodium but twice as much chlorine compared to the other potentials. It may also be noted that this potential showed the most tarnished image of the SEM micrographs though all micrographs, had less corrosion product than the untreated samples.

The wide scans in Figure 4.28a. tend to show manganese and chromium peaks with flat or downward-sloping peaks, except where there is a lot of carbon, causing their slopes increase. The post peak background of the Fe2p peak tends to be much higher, indicating that iron may lie underneath a chromium and manganese rich surface.

The XPS spectra show that chemical states of the elements do not vary much with potential. The chromium 2p peak has a binding energy of 577.3eV, which indicates that it is present in the Cr$^{3+}$ state (Ikemoto, 1976) in the film. The binding energy of the Mn2p peak is 641.6eV which can be assigned to Mn$^{2+}$. The surface contains predominantly hydroxide,
compared to the equal oxide/hydroxide surface of the untreated samples. This hydroxide appears to be associated with the chromium. The sample at -940mV shows almost all hydroxide and has the greatest chromium content (4.77%). It may also be noted that this sample had the lowest current density as a function of time.

4.8.2.1.1. XPS Depth Profile

To achieve more information on the passive layer, it was interesting to depth profile through the untreated and treated samples. A depth profile, for the chromate treated sample held at -640mV SCE was obtained using a VGAG2 ion gun operated at 3kV, 1.5kV focus and $10^6$ Torr Ar gas. This is given in Figure 4.30a. The montages of the XPS spectra are given in Figure 4.30b-e. The corresponding depth profile and montage of the spectra, for the untreated sample are shown in Figure 4.31a-d. From quantification of the etch rate with reference to the tantalum pentoxide standard under similar conditions, using a similar argon ion gun the etch rate was found to be $6Å/min$ (Watts, 1991).
Figure 4.30a. Compositional depth profile for a chromate treated sample.
Figure 4.30b. Montage of XPS wide scan spectra for chromate treated sample. Note the change in background and the emergence of the Fe2p peak with increasing etch time.
Figure 4.30c. Montage of XPS Mn2p narrow scan spectra for chromate treated sample.
Figure 4.30d. Montage of XPS Fe2p narrow scan spectra for chromate treated sample.
Figure 4.30e. Montage of XPS O1s narrow scan spectra for chromate treated sample.
Figure 4.30f. Montage of XPS Cr2p narrow scan spectra for chromate treated sample.
Figure 4.31a. Compositional depth profile for untreated sample.
Figure 4.31b. Montage of XPS wide scan spectra for untreated samples.
Figure 4.31c. Montage of XPS Mn2p narrow scan spectra for untreated samples.
Figure 4.31d. Montage of XPS Fe2p narrow scan spectra for untreated samples.
Figure 4.31e. Montage of XPS O1s narrow scan spectra for untreated samples.
The plot of $\text{Cr}/(\text{Cr}+\text{Mn}+\text{Fe})$ versus etch time is given in Figure 4.32. It can be seen that the chromium is incorporated into the surface layers of the film. The chromium appears, at first inspection, to be associated strongly with the hydroxide, since both the chromium content and the hydroxide component decrease with depth, relative to the oxide component. The iron increases when the chromium decreases. However, caution must be taken in interpretation, since argon bombardment is known to chemically change hydroxide to oxide.

**Figure 4.32.** The plot of $\text{Cr}/(\text{Cr}+\text{Mn}+\text{Fe})$ versus etch time for the chromate treated sample.

The oxide is much thinner on the chromate treated samples than on the untreated. After
60mins etch, 38% oxygen remains on the surface of the untreated and only 11% on the chromate treated. The metallic components of both iron and manganese appear after 1min on the treated samples, whereas, the metallic iron peak takes 10 minutes to appear and the manganese between 15 and 60mins. Assuming an etch rate of 6Å/min (Watts, 1991) the thickest oxide would be <106Å on the chromate treated sample.

4.8.2.1.2. Ion Beam Effects

The ambiguity in determining the change in oxide or hydroxide due to ion bombardment has already been mentioned. Further difficulties arise with the reduction of the metal oxides. Fe$^{3+}$, present on the surface of the untreated samples - probably due to air oxidation after removal from the test solution, can be seen to be reduced to Fe$^{2+}$ and eventually to Fe$^{0}$. It is unclear whether the change in the valence state is genuinely associated with the oxide on the surface, or due to the ion beam. Brundle (1977) commented on the reduction of Fe$^{3+}$ to Fe$^{2+}$ after only 1 minute etching. However, other workers (Richardson, 1981, Clayton 1976) this laboratory did not observe reduction of Fe$^{3+}$ under the conditions used in this study.

Manganese is much more stable under the action of the ion beam. The Mn$^{2+}$ is only reduced to Mn$^{0}$ after severe etching (90 minutes) on the untreated samples. It is interesting to note that the chromium in the treated sample is reduced from the Cr$^{3+}$ to Cr$^{0}$ at after a similar etch time to that for the Mn$^{2+}$ to Mn$^{0}$. This may be significant, thermodynamically, to the process.

\[
2\text{Cr} + \text{O}_2 \rightarrow \frac{2}{3} \text{Cr}_2\text{O}_3 \quad \text{-167 kcal/mol}
\]
\[2\text{Mn} + \text{O}_2 \rightarrow 2\text{MnO} \quad -184 \text{ kcal/mol}\]
\[2\text{Fe} + \text{O}_2 \rightarrow 2\text{FeO} \quad -130 \text{ kcal/mol}\]

It is seen that iron has the lowest heat of formation. This means it is more likely to be reduced under the ion beam than the more stable chromium and manganese. This observation about the heats of formation with reference to reduction of various oxides to their respective metals under an ion beam has been discussed by Kim (1974). He suggested that the greater the heat of formation, the less likely the oxide is to be reduced, which is what is observed in this study.

Iron becomes enriched at the surface after extensive etching, and this is probably due the preferential sputtering of manganese.

**4.8.2.2. Discussion on Chromate Formed Films**

Adding chromate reduces the anodic current, as observed in plots of the anodic density against time and the measured net external currents for the potentiostatic experiments. These currents were net cathodic over the potential range -640mV to -1040mV SCE, compared to the untreated samples, which had a net anodic current at -640 and -740mV SCE. A decrease in anodic current is expected for an anodic inhibitor.

A passive film <120Å thick is observed on the chromate treated samples. Chromium is incorporated into the film in this study. This has been observed with chromate treated pure iron (McCafferty, 1988). It is interesting to note that, in this case, the chromium is associated with the manganese, rather than the iron.
The surface produced is hydroxide rich compared to the oxy-hydroxide rich surface of the untreated samples.

An hydroxide rich surface was also associated with the natural passivation of the FeMn samples, as mentioned in the previous section. The as-polished and the 1st series samples, in the passive region of the anodic polarisation curve, both showed hydroxide rich surfaces. Only when the sodium sulphate concentration was increased did the $O^2$ peak increase relative to the $OH^-$. The surface of the chromate treated samples showed manganese on top of iron, and this is what was observed with the natural passive layer of the alloy. When the passive film is most effective there is a manganese rich layer on top of the iron. As passivity breaks down with increase in the active ions $Na^+$ and $SO_4^{2-}$, the iron becomes prominent on the surface.

The anomaly observed at the potential -840mV SCE happened to lie where the anodic polarisation curves all decrease, and this means that the surface would be unstable in this region.

4.8.2.3. Concluding Remarks on Chromate Inhibited Samples

Thin passive oxides can be produced by using a chromate inhibitor. A decrease in the anodic current is observed with the chromate as expected with an anodic inhibitor.

The passive film observed for samples in the passive region of the anodic polarisation curve of FeMn and the passive film formed using chromate inhibitor have some similar characteristics. An effective passive film seems to be associated with a manganese hydroxide
rich layer on top of the iron. In the chromate treated samples, the chromium is incorporated into the passive layer.

The incorporation of chromium into the oxide is in the range of 50% of the metallic components except at -840mV SCE, where manganese dominates. This potential lies in the range where the anodic current decreases rapidly.

4.9. General Discussion

The complete electrochemical (anodic and cathodic) behaviour of the alloy FeMn in water has been determined. This has been successfully achieved using a sensitive solution analysis technique of ICPMS which allows sub-ppb concentrations to be analysed. The anodic polarisation curve shows a short, shallow region of passivation. This region of passivation occurs in a net cathodic region, and would not have been revealed by traditional electrochemical methods. A very sensitive solution analysis technique is required in this study, to allow the relatively low concentrations of corrosion products in solution to be analysed. The amount of dissolution is small compared to many other electrochemical studies as the anodic polarisation of FeMn was determined in water, instead of in a traditional, more aggressive environment with acid or other aggressive ions.

Various factors have been investigated which could influence the corrosion of the alloy in aqueous solution. These factors were temperature, pH and the presence of active ions ie sodium sulphate. Small changes in temperature and pH showed little influence on the corrosion of the alloy. A large influence was, however, observed with the presence of active ions. There is a displacement of the anodic polarisation curve to higher current densities.
with increase in sodium sulphate concentration. The anodic polarisation curve retains the shape of the initial curve and the Tafel gradient is the same for each concentration of sodium sulphate concentration.

It has already been mentioned above, that small changes in pH have little influence on the corrosion of the alloy. The effect of pH was investigated over a wide range from pH 1.5 to pH 12.8, at a constant potential of -940mV SCE, as seen in Figure 4.17. This is in agreement with a similar plot for iron in the literature, Figure 4.33 (Whitman). A plateau region exists over the range of pH values 3 to 9.9. At the higher pH value, the drop in current density could correspond to the formation of insoluble oxides, as reported in the Pourbaix diagrams for iron and manganese in Figures 4.34a and b.

An initial study on the effect of pH on the anodic polarisation curve is shown in Figure 4.17. It can be seen that the polarisation curve produced at pH 3 is similar to that of produced at pH 6. This is in agreement with the current density versus pH plot at constant potential in Figure 4.17. The anodic polarisation curve for the alloy at pH 2.5 shows, however, a large displacement to higher current densities, as observed in Figure 4.35. This could correspond to the large increase observed at pH values > 3 in Figure 4.17. However, the displacement of the anodic polarisation curve must be taken with caution, since the pH results from different concentrations of sulphuric acid in the reference electrodes. The concentrations of sulphuric acid were 1.0M and 0.1M H₂SO₄ for pH 2.5 and pH 3 respectively. Since the polarisation curve at pH 6 was obtained using 1.0M Na₂SO₄ electrolyte in the reference electrode, and because it has already been shown that small changes in sodium sulphate can cause large displacements in the anodic polarisation curve,
the displacement of the anodic polarisation curve, as seen by the pH2.5, may be due entirely, or in part, to an increase in sulphate concentration, and not just, the pH.

Figure 4.33. Current density versus pH for iron (Whitman, 1924).
Figure 4.34a and b. Pourbaix diagrams for iron and manganese. The lines a,b and c represent the range of conditions investigated.
The displacement of the anodic polarisation curve was attributed to an increase in sodium sulphate concentration, which was thought to be probably due to deterioration of the ceramic frit separating the test solution from the reference electrode. By using 'pure' water, the test solution is particularly vulnerable to contamination. It was hoped that by using a neutral sodium sulphate solution reference electrolyte, problems associated with high pH values experienced with sulphuric acid reference electrodes, could be avoided. In addition, using sodium sulphate instead of the commonly used calomel electrode, Cl⁻ ions which are well
known for their aggressive corrosion behaviour, are also avoided.

The anodic polarisation curve was determined in water, so as to be more revelant to the corrosion of the material in its final application. The device would be more likely to be exposed to neutral, atmospherically pure water condensation rather than acidic or highly chlorinated water. In this study, there were problems of contamination from the sodium and sulphate ions leaking across the ceramic frit. There will always be contamination to some extent, particularly as there is a tendency for diffusion from a high concentration to a low concentration solution. One way to overcome this contamination problem from the reference electrode is to use a hydrogen electrode. The stability of such an electrode, for example the Pd/H₂ electrode, is reasonable (see appendix 1). The Pd/H₂ electrode is not as stable as the traditional electrolytic solution electrodes and requires frequent recharging, preferably before each experimental run. The Pd/H₂ electrode should be placed as close to the test specimen as possible, without touching the sample to reduce the IR drop which can occur with low electrolytic concentration solutions. The IR drop is the difference between the nominal applied potential and the actual potential and is directly proportional to the current density and inversely proportional to the specific conductance of the solution. The specific conductance is approximately proportional to the concentration of the electrolyte. Therefore, the lower the concentration, the greater is the effect of IR drop. Dilute electrolytes are more vulnerable to an IR drop effect. However, in this study on the various concentrations of sodium sulphate, the lowest concentration of sodium sulphate showed the lowest current densities effect on the IR drop was minimal. Since all anodic polarisation curves with various sodium sulphate concentrations have the same Tafel gradient, the IR drop influence was negligible.
It is interesting to address the question of selective dissolution. From a theoretical point of view, FeMn should show selective dissolution due to the difference in standard electrode potentials of iron and manganese (-0.44V and -1.18V for iron and manganese, respectively). If the partial current densities of iron and manganese are examined for samples from the anodic polarisation curve in Figure 4.36, some selective dissolution of manganese is observed throughout the range. The selective dissolution is, however, less significant at the more negative potentials. At first glance, this may show the reverse of what Verink and Heidersbach predicted. Based on their model, selective dissolution of manganese should occur in the region of overlap of the iron and manganese Pourbaix Diagrams, as shown in Figure 4.37. This would predict selective dissolution at potentials more negative than -860mV SCE, which in fact, is where (in Figure 4.36.) the manganese and iron concentrations are similar. If another polarisation curve, that for the 3rd series is examined, with 0.01M concentration of sodium sulphate, the opposite effect is observed. This is shown in Figure 4.38. At this concentration of sodium sulphate, the dissolution coefficient of manganese increases with more negative potentials. The apparent discrepancy lies in the fundamental concept of the Pourbaix diagram. The Pourbaix diagram is an equilibrium diagram for pure metal in a solution of its own ions, and does not allow for the presence of active ions such as sodium sulphate. Furthermore, as already shown in section 4.7, redeposition of an iron rich compound occurs. Although this does not have a significant effect on the overall anodic polarisation curve, it could influence the partial iron current more than the manganese partial current. The observed selective dissolution of manganese in Figure 4.36, for FeMn in water, may be misleading, since iron which should be analysed in solution has redeposited. In fact, the regions where the manganese and iron currents are similar show less redeposition than
those at less negative potentials. This suggests that there is no significant selective dissolution of manganese over the range of potentials investigated. To verify or disprove the model of selective dissolution of manganese in the region of overlap of the iron and manganese Pourbaix diagrams based, on the model by Verink and Heidersbach, it is important to accurately calculate the redeposition at each potential, preferably in the absence of active ions.

Figure 4.36. Partial current densities for iron and manganese for the dissolution of FeMn in water.
Figure 4.37. Overlap of the iron and manganese Pourbaix diagrams. The shaded area represents the region where the iron is immune and the manganese is active. This is the region where selective dissolution of the manganese from the alloy FeMn is predicted.
FeMn in Aqueous Solution
Partial Currents for 3rd Series

One significant feature of the anodic polarisation curve for FeMn in water is the large change in current density at a potential of -860 mV SCE. The decrease in current density at this potential may bear some relation to the entrance to the immune region of the iron Pourbaix diagram.

It was initially hoped that, once in the immune region of iron of the Pourbaix diagram, an immune iron rich layer which provide a protective barrier to further dissolution of the alloy.
This, however, was not the case and, if anything, it is a manganese rich layer which is associated with the passive layer. Furthermore, an iron rich layer was observed with the breakdown of passivity.

The natural passivity of the alloy is very vulnerable to corrosion attack, as hinted at by the transpassive region of the anodic polarisation curve and the presence of the 'bullseyes' and by the breakdown of passivity by the active ions, Na\(^+\) and SO\(_4\)\(^{2-}\). This is an important consideration for the practical application of this alloy in service. The material may be exposed to condensate from the environment. If the alloy is used in the thin film form it is even more vulnerable, since once the film is attacked at one point, the whole of the film can be irreparably damaged before a protective passive layer can form. It is imperative that a method be found to produce a durable passive film or another protective layer is imperative. It has already been shown that chromate can form a passive layer on the surface of the alloy. This involves incorporation of chromium into the surface. If incorporation of such an element provides a protective layer, without interfering with the magnetic properties of the device in service, this would be a viable solution.

A variety of techniques have been used to explore the complex nature of the corrosion properties of the alloy. Solution analysis to determine the corrosion products in solution; surface analysis to examine the corroded surface; and external current measurements to monitor the charge transfer with time and determine the cathodic curve. It is apparent that an increasing number of sophisticated instruments are becoming available to the corrosion scientist to unravel corrosion processes. ICP-MS provides the most sensitive detection limits ever available for determination of soluble corrosion products. In addition the ESCASCOPE
is a valuable, recently developed tool which enables the chemical nature of localised corrosion to be investigated as never before possible.

It is important to have new techniques made available and to explore the possibilities and limitations of each. There are ambiguities remaining with the commonly used techniques for corrosion studies. For example, in XPS there are still problems related to analysing an active surface. Once the sample is removed from electrolytic solution, it is no longer at the applied potential, and is therefore subject to a rest potential if residual water exists on the surface, and also to air oxidation, the 'corridor effect'. In this study, the presence of the Fe$^{3+}$ bears witness to air oxidation as it is not predicted to occur under the potentials applied in the test, according to the Pourbaix diagram. It was observed that the samples tarnished quickly after removal from solution.

The problem of post solution oxidation is not as great for the passive films, since the oxide may be sufficient to prevent excessive further corrosion. The chromate treated samples showed little tarnishment after removal from solution.

The other caution is that XPS is an area averaging technique and can lead to ambiguities related to redeposition. XPS was unable to distinguish the local redeposition of iron rich platelets.

There are, however, many advantages of using XPS; it does give an initial idea of what is on the surface including valuable chemical information; it can distinguish hydroxide from oxide and layered structures. This has proved very important in evaluating the passive film,
which is a manganese hydroxide rich surface on top of iron. Further information on the layer structure can be obtained by depth profiling, as illustrated by the studies on the chromate inhibited samples. Depth profiling revealed that the chromium was concentrated in the surface layer, and was associated with the manganese.

The ambiguity of whether oxide products are formed in solution or in air, can be overcome either by having an electrochemical cell attached directly to the spectrometer or by performing a controlled oxidation of the sample in the analysis chamber, and this will be the topic of the next chapter.

4.10. Conclusions

The complete electrochemical behaviour (anodic and cathodic) of FeMn in water has been determined over the potential range -139mV to -889mV SCE. ICPMS has proved to be a valuable tool in this study as it has allowed the determination of the passive region of the anodic polarisation curve which lies below the cathodic curve. Traditional potentiodynamic methods would have been inadequate to achieve this.

The natural passivity is limited to a short potential range and is vulnerable to attack by active ions. The displacement of the anodic polarisation curve to higher current densities was attributed to an increasing concentration of sodium sulphate ions. Small variations in pH and temperature showed little effect on the corrosion characteristics of the alloy.

The passive layer on the FeMn consists of a manganese hydroxide rich surface. A breakdown in passivity was associated with formation of an iron oxy-hydroxide rich layer on the surface.
Redeposition of an iron-rich material occurs on the surface of the alloy. The morphology has the appearance of bullseyes at low magnification. At high magnification this can be seen as loosely packed hexagonal platelets.

Various inhibitors were investigated. The organic inhibitors proved ineffective at improving the corrosion resistance of the alloy. Application of sodium chromate as an inhibitor was found to be effective in reducing the corrosion. Chromate enhanced the passivity of the alloy. The chromium is incorporated into the surface layer.

Using a combination of complementary techniques, such as electrochemical methods and solution analysis with surface analysis, provided essential tools to investigate the overall corrosion of the alloy.
CHAPTER 5
Investigation of the Initial Oxidation of the Alloy Co$_{86}$Cr$_{14}$ and its Constituent Metals with Oxygen using 'In-situ' Dynamic Secondary Ion Mass Spectrometry

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5.1. Introduction

So far, the aqueous corrosion of FeMn, a typical magnetically-active alloy, has been investigated and the complete electrochemical (anodic and cathodic) properties have been determined. Selective dissolution of the alloy occurs over the potential range -139 to -889 mV SCE investigated. It is dependent on sodium sulphate concentration. Surface analysis of the corrosion products formed under these conditions is complicated by the ambiguity that occurs when the sample is removed from the electrolytic solution and air oxidation occurs. The oxide then formed could be the result of the solution, or of subsequent air oxidation. One way of investigating the oxidation of the alloy and determining the oxidation products is to perform the oxidation in an 'in-situ' environment in the analysis chamber with controlled oxidation, and this has been discussed in the literature survey in chapter 2.

Here, the novel technique of dynamic SIMS 'in-situ' analysis, initiated by Gunnar Hultquist at the University of Singapore, is used. Using dynamic SIMS, simultaneous oxidation and analysis is achieved. In this manner, an investigation of the very early stages of the oxidation process is made, i.e. when the oxidation product is of sub-monolayer extent. This investigation is possible because simultaneous analysis and controlled formation of oxidation products, rather than just analysis, are utilised. Gunnar Hultquist used the technique for the study of pure metals with various in-situ environments. Here, the study is extended to give some insight into the interpretation of the SIMS data obtained by this method, and to determine a model for the oxidation of materials. The potential of this novel technique to give information on the selective oxidation of the alloys Fe\textsubscript{33}Mn\textsubscript{47} and Co\textsubscript{86}Cr\textsubscript{14} is examined. The oxidation of the alloys' constituent metals (iron, manganese, cobalt and chromium) is
investigated in order to determine the influence of the individual alloy components on the mechanism of oxide formation.

5.2. SIMS Profiles on the Oxidation of Pure Cobalt and CoCr

Samples of pure cobalt and Co$_{86}$Cr$_{14}$ were sputtered cleaned and exposed to different partial pressures of oxygen the SIMS analysis chamber. For each oxygen pressure, an equilibrium between the formation and removal of the reaction products was attained and this is represented in the SIMS profile, where the counts for a particular mass are constant with time. The resulting SIMS profiles of counts for a particular mass versus time, for the oxidation of pure cobalt and CoCr, are given in Figures 5.1 and 5.2.
Figure 5.1. SIMS profile of the oxidation of pure cobalt.
Figure 5.2. SIMS profile of the oxidation of Co$_{65}$Cr$_{14}$. 

<table>
<thead>
<tr>
<th>Line</th>
<th>Mass</th>
<th>Ion</th>
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<td>1</td>
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<td>Co</td>
</tr>
<tr>
<td>2</td>
<td>52</td>
<td>Cr</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CoO</td>
</tr>
<tr>
<td>4</td>
<td>58</td>
<td>CrO</td>
</tr>
<tr>
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<td>Co$_2$</td>
</tr>
<tr>
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<td>104</td>
<td>Cr$_2$</td>
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<tr>
<td>8</td>
<td>120</td>
<td>Cr$_2$O</td>
</tr>
<tr>
<td>9</td>
<td>60</td>
<td>CoH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>CoCr</td>
</tr>
</tbody>
</table>
5.3. Analysis of SIMS Experiments

As described in Chapter 3, the experiment is concerned with the equilibrium situation of formation of oxide and its removal, when oxygen reacts with a metal surface. There is as yet no physical model to describe this process. The Langmuir model describes the adsorption-desorption equilibrium of gases on metals, but is concerned with the very weak bonds of physisorption. Here, the situation is much more energetic. The surface of the metal is physically bombarded with particles of 9kV energy. This is sufficient to break the stronger chemical bonds of the metal oxide.

A model can, however, be derived, based on the Langmuir model, but allowing for the more energetic nature of ion bombardment and oxide removal. The model of the SIMS 'equilibrium' state is described in the following section.

5.3.1. Description of the SIMS 'Equilibrium' State

The following symbols are used in the description of the sub-monolayer metal oxidation at the surface;

[MeO] = amount of oxidised metal (No. x m\(^2\))

[O] = oxygen available for metal oxidation (No. x m\(^2\))

[Me] = metal available for oxidation; unreacted metal (No. x m\(^2\))

\(j_{\text{beam}}\) = ion beam current density (No. x m\(^2\)s\(^{-1}\))

\(P_{o_2}\) = oxygen pressure (Pa)

At SIMS equilibrium, the rate of change of surface oxide becomes negligible
\[
\frac{d[MeO]}{dt} = \text{zero}
\]

(5.1)

From the law of mass action;

\[
R_{\text{formation}} = k'_{\text{formation}} \times [O] \times [Me]
\]

(5.2)

Where it is assumed that \( k'_{\text{formation}} \) does not depend on the oxide coverage \([MeO]/([MeO]+[Me])\). This is a reasonable assumption for a low coverage for a given metal surface.

From the kinetic theory of gases, at a given temperature;

\[
[O] = \text{const.} \times P_o,
\]

(5.3)

With \( k_{\text{formation}} = k'_{\text{formation}} \times \text{const} \)

\[
R_{\text{formation}} = k_{\text{formation}} \times [Me] \times P_o,
\]

(5.4)

The rate of removal of [MeO] depends on the probability of sputtering by an incident ion;

\[
R_{\text{removal}} = k_{\text{removal}} \times [MeO] \times j_{\text{beam}}
\]

(5.5)

Since at equilibrium;

\[
R_{\text{formation}} = R_{\text{removal}}
\]

(5.6)

180
then;

\[
\frac{[Me] \times P_{O_2}}{[MeO] \times j_{beam}} = \frac{k_{\text{removal}}}{k_{\text{formation}}} = B
\]

Thus;

\[
\frac{[MeO]}{[Me]} = \frac{1}{B \times j_{beam} \times P_{O_2}}
\]

(5.8)

To examine this model it is necessary to identify [Me] and [MeO] with some physical meaning from the data obtained in the SIMS experiment.

The data from the SIMS experiments are obtained in the form of the variation of concentration of a particular ion with oxygen pressure and time. It is essential to understand how the yield of individual ions depends on the surface composition.

5.3.2. Interpretation of the Yields of Me\(^+\) and MeO\(^+\) Detected in the SIMS

The following assumptions are made;

1. The emission of Me\(^+\) originates from both unoxidised, [Me] and oxidised metal, [MeO], but with differing yields.

2. The emission of MeO\(^+\) can only take place from oxidised metal, [MeO], and is therefore a measure of the extent of oxidised metal.
If the above two assumptions are true then plotting Me$^+$ versus MeO$^+$ may give some information on the division of yield distributions from the oxidised and the unoxidised metal. To investigate this possibility, the emissions of the ions involved in the oxidation of the pure cobalt were examined.

The emissions of Co$^+$ versus CoO$^+$ from a cobalt surface oxidised at different oxygen pressures, for a beam current of 20nA, are shown in Figure 5.3a. It may be noted that the emission of Co$^+$ increases with CoO$^+$ which suggests that assumption 1, that Co$^+$ originates from both unoxidised and oxidised metal, is well founded, since if Co$^+$ came from just the unoxidised metal, then Co$^+$ emissions would decrease with oxide coverage, ie with oxygen pressure and CoO$^+$. Moreover, the slope increases and becomes linear at high oxygen pressures, showing that the efficiency of production of Co$^+$ from Co$_{oxid}$ is much greater than that of Co$^+$ from Co$_{unoxid}$. 
Figure 5.3a. Emissions of Co\(^+\) and CoO\(^+\) from a cobalt surface oxidised at different oxygen pressures, for a beam current of 20nA.

The plots for the different beam currents show a similar trend. Moreover, when the points derived from all beam currents are plotted on a single graph, it is seen that the curves have a common locus, whose tangent, if extrapolated to lower values of Co\(^+\), as shown in Figure 5.3b, is seen to pass through the origin. This tangent, therefore, represents the part of the Co\(^+\) signal which is originating from the oxidised metal. However, the actual data deviates from this line, at low oxygen pressures and CoO\(^+\) values, giving a family of curves whose intercepts on the Co\(^+\) axis depend on beam current. These data deviate because of the influence of the Co\(^+\) derived from Co, which has its greatest exposure at low oxygen pressures.
Figure 5.3b. Emissions of Co\(^+\) and CoO\(^+\) from a cobalt surface for beam currents of 5, 20 and 60nA. The common locus of the curves has a tangent, which if extrapolated to lower values of Co\(^+\), passes through the origin.

Assuming that the experimental Co\(^+\) data comprises the sum of components from the oxidised and unoxidised states, it follows that the contribution from the unoxidised metal will the oxidised contribution subtracted from the experimental data. The calculated curve for the Me\(^+\) from the unoxidised metal, for a beam current of 20nA, is given in Figure 5.3c.
Figure 5.3c. Illustration of the relationship between the unoxidised component, \( \text{Co}_{\text{unoxid}}^+ \), oxidised component, \( \text{Co}_{\text{oxid}}^+ \), and the experimental data, \( \text{Co}_{\text{expt}}^+ \). The unoxidised component curve is determined by subtracting the oxidised component curve from the experimental data curve.

The calculated curves for the unoxidised metal for all three currents investigated (5, 20 and 60nA), are given in Figure 5.3d.
Figure 5.3d. Calculated curves for the unoxidised metal for all three curves.

The experimental line has initially a strong contribution from the unoxidised metal at low values of CoO⁺, but as pressure is increased and CoO⁺ is increased; this diminishes and the Co⁺ arises almost entirely from the oxidised metal.
The gradient of the oxidised metal line, \( \frac{d\text{Co}^+}{d\text{CoO}^+} \), is approximately 100. This can be interpreted as representing the fractionation of the CoO\(^+\) to Co\(^+\). It shows the probability of the CoO\(^+\) remaining as such is 1/100. It also shows that this is independent of the beam currents investigated.

### 5.3.2.1. Interpretation of the Co\(^+\) Component from the Unoxidised Surface

It has already been shown that the Co\(^+\) from the metal decreases with increase in CoO\(^+\). This is what might be expected, since the amount of unoxidised metal will decrease with increase in oxygen pressure and oxide coverage. It would be useful to determine what factors influence its decrease, since these variations should reveal the equilibrium oxide coverage at the different oxygen pressures.

At CoO\(^+\) = 0 the contribution of Co\(_{\text{unoxid}}^+\) is at its maximum and corresponds the emission of Co\(^+\) from completely unoxidised metal. This intercept, Co\(_o\), is dependent on beam current. When the values of Co\(_o\) are plotted versus beam current, in Figure 5.4, it can be seen that there is a linear relation between Co\(_o\) and beam current passing through the origin, as would be expected. This is taken as confirmation that Co\(_{\text{unoxid}}^+\) is correctly identified as the component derived from the exposed metal.
5.3.3. Summary of the Interpretation of Co\(^+\) and CoO\(^+\)

In the previous two sections, an interpretation on the emitted ions Co\(^+\) and CoO\(^+\) has been determined. Co\(^+\) comprises two components: a) from the oxidised material and b) from the unoxidised metal. The contribution from the oxidised metal increases from the origin such that Co\(^+\)/CoO\(^+\) is a constant. The ratio Co\(^+\)/CoO\(^+\) represents the fractionation of CoO\(^+\) to Co\(^+\). The probability of CoO remaining as such is 1/100.

The Co\(^+\) from the unoxidised metal decreases from a maximum at CoO\(^+\)=0 at P\(_{O2}\)=0. The actual value of Co\(^+\) at CoO=0 is in direct proportion to the beam current.
5.4. Results on Pure Cobalt

From the previous section expressions for the unoxidised and oxidised metal components have been derived. This enables us to examine the model derived in equation (5.8). In Figure 5.5, MeO/Me is plotted versus $P_{O_2}/j_{\text{beam}}$. It can be seen that the values obtained for the different beam currents lie on the same curve. The initial section of the curve shows linearity, indicating that the oxidation of cobalt obeys the model described in equation (8) up to a value of $P_{O_2}/j_{\text{beam}} = 6 \times 10^{-11}$. The gradient of the linear section, which represents $1/B$, is found to have a value of $7 \times 10^9$. 
Figure 5.5. MeO/Me plotted versus $P_{O_2}/j_{beam}$ for pure cobalt.

After the initial linear section, the curve appears to show an increasing rise with $P_{O_2}/j_{beam}$ increasing to an infinite value of MeO/Me. This can be expected on examination of equation (5.8). As the oxygen pressure is increased, the amount of unreacted surface will decrease while the amount of oxidised surface will continue to increase. The function MeO/Me will then tend to infinity.
5.5. Empirical Model of the Oxidation of Cobalt

So far, a means of interpreting the SIMS data to extract values that represent the oxidised and unoxidised metal has been established. The model in equation (8) works for low oxygen pressures but not higher values. It is possible to extend this to all the values of oxygen pressures investigated. This is done by introducing an empirical model for the oxidation.

The variation of the unoxidised metal with oxygen pressure is first examined. The function that best describes the dependence of Co_{unoxid}^+ on P_{O2} is exponential, as seen in Figure 5.6a, where \( \log_e(C_{o_{unoxid}}^+) \) is plotted versus oxygen pressure, for the different beam currents. The gradients of the graphs of the different beam currents are in the ratio 1:4.3:14 which is in approximately the inverse ratio to the beam currents 5:20:60. This suggests there is some further beam current dependence. If \( \log_e(C_{o_{unoxid}}^+) \) is plotted versus \( P_{O2}/j_{beam} \), as in Figure 5.7., curves are obtained which are parallel to each other.
Figure 5.6a. \( \log_{10}(C_{\text{unoxid}}^+) \) plotted versus \( P_{O_2} \).
Figure 5.7. Log$_e$ $C_{o_{unox}}$ plotted versus $P_{O_2}$.

\[ \log_e C_{o_{unox}} = \frac{-\lambda \times P_{O_2}}{j_{beam}} + \log_e k \]  

(5.9)

where

- $\lambda$ is the common gradient = $6 \times 10^9$.
- $K$ = the intercept with the y-axis which is current dependent when $P_{O_2} = 0$;

\[ \log_e C_{o_{unox}} = \log_e k \]  

(5.10)

therefore;
\[ C_{o_{\text{unoxid}}} = k \] (5.11)

Also \( C_{o_{\text{unoxid}}} = C_o \) at \( P_{O_2} = 0 \)

so,

\[ C_o = k \] (5.12)

From Figure 5.4, where \( C_o \) is plotted versus \( j_{\text{beam}} \), it can be seen that \( C_o \) is directly proportional to \( j_{\text{beam}} \), with a gradient \( N_{Co} = 1086 \). \( N_{Co} \) can be seen to represent the ionisation fraction of Co in the ion beam in the absence of oxygen.

it follows that;

\[ k = C_o = N_{Co} \times j_{\text{beam}} = 1086 \times j_{\text{beam}} \] (5.13)

substituting into equation 5.10;

\[ \log_e C_{o_{\text{unoxid}}} = \frac{-\lambda \times P_{O_2}}{j_{\text{beam}}} + \log_e [N_{Co} \times j_{\text{beam}}] \] (5.14)

An equation for the relationship between the \( C_{o_{\text{unoxid}}}^+ \) and the beam current and oxygen pressure can now be written as follows:-

(5.15)
\[ C_{\text{unoxid}} = j_{\text{beam}} \times N_{\text{Co}} \times e^{-\frac{\lambda \times P}{j_{\text{beam}}}} \]

where

\[ \lambda = 6 \times 10^4 \text{ nA/mbar} \]

\[ N_{\text{Co}} = 1086 \text{ nA}^{-1} \]

To test this equation we plot the value of \( C_{\text{unoxid}} \) calculated from \((\text{Co}^+_{\text{exp}} - 100\text{CoO}^+)\) versus \(j_{\text{beam}} N_{\text{Co}} e^{-\lambda P/j_{\text{beam}}}\). This is given in Figure 5.8. The data points for the different beam currents are indicated. As shown in Figure 5.8 there is very good correlation for the 5 and 20nA beam currents and reasonable agreement for the 60nA current.
Figure 5.8. $C_{\text{mol,oxid}}$ calculated from $(Co_{\text{exp}}^{+} - 100CoO^+)$ plotted versus $j_{\text{beam}} N_{C_0} e^{(\gamma p)}$.

5.6. Comparison of the Empirical Model with the Theoretical Model

Two models have been determined. MODEL I, a theoretical model based on the Langmuir model, describes the oxidation of cobalt such that:

$$\frac{[MeO]}{[Me]} = \frac{1}{B \times j_{\text{beam}} x P_{O_2}}$$

MODEL I
MODEL II, is an empirical model, which describes the decrease of unreacted metal with oxygen pressure such that:

\[ C_{o_{\text{unoxid}}} = j_{\text{beam}} \times N_{Co} \times e^{\frac{\lambda \times P}{j_{\text{beam}}}} \]

MODEL II

It would be very interesting to compare the two models. It has already been observed that the linear section of the plot of MeO/Me against P_{O2}/j for the theoretical model has a gradient of 1/B which is equal to 7x10^9. This gradient is similar to the value of \( \lambda \) in the empirical model. This linear section of the theoretical model corresponds to the sub-monolayer coverage where the Langmuir type model works. At P_{O2}/j_{beam} equal to 6x10^{-11}, the model is no longer applicable as a thicker oxide is forming. Model II applies to all pressures investigated. It may be noted that at the higher pressures, the determination of the unreacted metal from the experimental data may include large errors due the subtraction of two large numbers.

Model I can be rewritten in terms of \( \theta \), the fractional coverage of the surface of oxide thus;

\[ \frac{\theta}{1-\theta} = \frac{P_{O2}}{B \times j_{\text{beam}}} \]

(5.16)

for small values of \( \theta \), i.e. at low oxygen pressures;
\[
\frac{\theta}{1-\theta} = \theta
\]  
(5.17)

hence;

\[
\theta = \frac{P_{O_2}}{B \times j_{beam}}
\]  
(5.18)

The function \(e^{x}y\) can be expanded as a series expansion.

For model II let

\[
y = \frac{\lambda \times P_{O_2}}{j_{beam}}
\]  
(5.19)

The expansion for \(e^y\) is;

\[
e^{-y} = 1 - y + \frac{y^2}{2!} - \frac{y^3}{3!} \ldots
\]  
(5.20)

For small values of \(P_{O_2}\) and hence \(y\);

\[
e^{-y} = 1 - y
\]  
(5.21)

hence;

\[
e^{-\frac{\lambda \times P_{O_2}}{j_{beam}}} = 1 - \frac{\lambda \times P_{O_2}}{j_{beam}}
\]  
(5.22)

Therefore, an approximate value for \(C_{O_2\text{fuel}}\) at low values of \(P_{O_2}\) can be determined such
that;

\[ C_{o,\text{unox}} = N \times j_{\text{beam}} \times \left(1 - \frac{\lambda \times P_{o_2}}{j_{\text{beam}}}\right) \]

(5.23)

now;

\[ N \times j_{\text{beam}} = C_{o_0} \]

(5.24)

substituting and rearranging the equation gives

\[ 1 - C_{o,\text{unox}} \frac{\lambda \times P_{o_2}}{C_{o_0} j_{\text{beam}}} \]

(5.25)

If \( \theta \) = the fractional coverage of oxide then

\[ \frac{C_{o,\text{unox}}}{C_{o_0}} = 1 - \theta \]

(5.26)

Hence

\[ 1 - (1 - \theta) = \frac{\lambda \times P_{o_2}}{j_{\text{beam}}} \]

(5.27)

Therefore

\[ \theta = \frac{\lambda \times P_{o_2}}{j_{\text{beam}}} \]

(5.28)
It can be seen from equations 18 and 28 that the two models are indistinguishable at low pressure of oxygen and that $1/B$ is equivalent to $\lambda$ under these conditions. There is also agreement between the experimentally derived values $\lambda$, using model II in Figure 5.7, and the initial gradient $1/B$ using model I, in Figure 5.5.

5.7. The Oxidation of Other Metals and Alloys

5.7.1. Oxidation of Pure Chromium, Iron and Manganese: Results and Discussion

In order to make use of the SIMS data in determining the selective oxidation of the alloys, it is necessary that an interpretation for the other metals ions is determined. The interpretation for cobalt worked very well and an expression was obtained for amount of unreacted metal with oxygen pressure.

In Figure 5.9a-c, the corresponding plots of $\text{Me}^{+}$ versus $\text{MeO}^{+}$ for pure chromium, iron and manganese are given. It can be seen that the plots are very different in shape to the cobalt data. This makes a similar deconvolution of $\text{Me}^{+}_{\text{ox}}$ and $\text{Me}^{+}_{\text{met}}$, as applied to the cobalt data, impossible. Possible reasons for the different behaviour are discussed in section 5.8.
Figure 5.9a. Emissions of Cr$^+$ versus CrO$^+$ for pure chromium.

Figure 5.9b. Emissions of Fe$^+$ versus FeO$^+$ for pure iron.
Examining the data from the alloy Co$_{98}$Cr$_{14}$ and plotting Me$^+$ versus MeO$^+$ for the constituent metals, as shown in Figure 5.10, it is observed that the cobalt and chromium show a similar behaviour to that of their respective pure metals (Figure 5.3 and 5.9). The gradient of the tangent to the curves is equal to 77. This is very similar to the value of 100 obtained for the ratio of CoO$^+$/Co$^+$ in a separate experiment, in which a thick oxide was formed on the alloy, as reported in Appendix 1.
Figure 5.10a. Emissions of Co⁺ versus CoO⁺ for the constituent metal, cobalt, in Co₈₀Cr₁₄.
Figure 5.10a. Emissions of Me$^+$ versus MeO$^+$ for the constituent metal, chromium, in Co$_{86}$Cr$_{14}$.

Applying a similar deconvolution to the cobalt in the alloy, it follows that the cobalt in the alloy has two components which contribute to the Me$^+$ signal. The relationship for the unreacted cobalt in this case is:

\[
C_{O_{\text{unoxid}}} = j_{\text{beam}} \times N_{\text{Co}} \times e^{-\frac{\lambda \times p_{\text{O}_2}}{j_{\text{beam}}}}
\]

(5.29)

where;

\( \lambda = 5 \times 10^9 \text{nA/mbar} \)
When tested for verification in Figure 5.11, there is very good agreement with the data in which $j_{\text{beam}} = 20 \text{nA}$, and reasonable agreement for the 5 and 60nA data.

Figure 5.11. Verification of the model for the oxidation of CoCr with oxygen.

5.8. Discussion

An important interpretation of the SIMS data has been achieved. The oxidised and
unoxidised components of Co$^+$ in the SIMS data has been interpreted with reference to oxidation of cobalt. This has allowed the oxidation of cobalt to be modelled empirically, using this in-situ SIMS experiment over the range of pressures investigated. The model is in the form;

$$C_{\text{oxid}} = j_{\text{beam}} \times N_{\text{Co}} \times \frac{1}{j_{\text{beam}}}$$

A theoretical model has also been developed, which is based on the Langmuir model of adsorption. At low pressures of oxygen, the two models are indistinguishable. At the higher oxygen pressures $P_{\text{O}_2}/j > 6 \times 10^{-11} \text{ mbar/nA}$, the theoretical model breaks down. It is predicted, that at this value, the coverage exceeds one monolayer, and this is thought to be the reason for the model's breakdown.

The objective of the initial study was to investigate whether this technique could be used to look at the selective oxidation of the alloys Co$_{86}$Cr$_{14}$ and FeMn. This has been partly successful: the oxidation of cobalt in the pure metal and the cobalt in the alloy Co$_{86}$Cr$_{14}$ has been characterised. It can be seen that the behaviour of cobalt in the alloy Co$_{86}$Cr$_{14}$ is similar to that of the pure cobalt metal, suggesting no influence of the alloy component chromium on the oxidation.

The objective as a whole is only partly fulfilled, as values of the unoxidised components of the other metals chromium, iron and manganese, were unobtainable from the SIMS data. This limits the application of this technique, at present, until an interpretation of the data for these metals is found.
The difference in behaviour between the cobalt and the other metals; iron, manganese and chromium is not clear at the moment, but it may lie in the different reactivities of the metals with oxygen. The corresponding Gibbs Free energies are given below:

\[
\begin{align*}
4/3 \text{Cr} + \text{O}_2 &\rightarrow 2/3 \text{Cr}_2\text{O}_3 & -167 \text{kcal/mol} \\
4/3\text{Mn} + \text{O}_2 &\rightarrow 2/3\text{Mn}_2\text{O}_3 & -152 \text{kcal/mol} \\
3/2\text{Fe} + \text{O}_2 &\rightarrow 1/2\text{Fe}_3\text{O}_4 & -133 \text{kcal/mol} \\
2\text{Co} + \text{O}_2 &\rightarrow 2\text{CoO} & -102 \text{kcal/mol}
\end{align*}
\]

Cobalt is the least reactive metal. This suggests that the initial decrease of unreacted metal, which is observed for the cobalt, can not be easily distinguished for the more reactive metals, since the reaction takes place rapidly at low oxygen pressures. Indeed, for the most reactive metal, chromium, the amount of unoxidised metal may be minimal. This makes the deconvolution of the SIMS data, into oxidised and unoxidised components not possible. A similar treatment of the oxidation for the metals iron, manganese and chromium cannot, therefore, be achieved in the same manner.

If a model for each of the pure metals could be determined, as has been achieved for the cobalt system, it would lead to a greater understanding of the oxidation process at very low oxide coverages. It can be seen how the amount of unreacted cobalt varies with oxygen pressure. If this were extended to alloy systems, the occurrence of selective oxidation could be determined by looking at the remaining unreacted material at a particular oxygen pressure.

The shape of the Me versus MeO curves can yield information on the oxide growth
mechanism. It could provide valuable information on more complex systems, such as alloys. In the CoCr alloy investigated here, the Me vs MeO curve for the constituent metals in the alloy resembled that of the pure metals. This implies that the cobalt and chromium oxidise independently at these low oxygen pressures.

The gradient, which decreases with increasing MeO in the case of the chromium, iron and manganese, may represent a change in the oxide stoichiometry or oxide structure. For example chromium, which is known to form a network structure, may initially form a 2D structure across the surface and then, once this is complete, a 3D structure is built up. This may explain why the gradient Cr/CrO is initially high, implying that the fractionation of CrO to Cr is relatively easy. Once the 3D structure has formed, the chromium oxide is more closely bound and the fractionation is much more difficult; hence the gradient is less steep. In the case of cobalt, which could form more of an island type growth, the strength of the Co-O bond is constant throughout the oxygen pressures investigated. At the moment interpretation of the MeO/Me ratio is speculative and requires much further study.

5.9. Conclusions

The oxidised metal and unoxidised metal components have been successfully deconvoluted for cobalt. The oxidation of cobalt has been modelled over the oxygen pressure range investigated. There is agreement between the theoretical and empirical models determined at low oxygen pressures.

The cobalt component in the alloy Co88Cr14 behaves in a similar way to that of the pure
metal, which suggests that the cobalt oxidises independently from the chromium in the alloy.

The objective to use 'in-situ' SIMS to investigate the selective oxidation of metals and alloys has been partly successful, since although the cobalt oxidation has been modelled, it has not been possible to deconvolute the oxidised and unoxidised components of the metals iron, manganese and chromium. The reason for the difference in behaviour lies in the different reactivities of the metals. Cobalt is the least reactive, which allows the deconvolution of Co$^+$ into Co$^+_{\text{unoxi}}$ and Co$^+_{\text{oxid}}$ to be achieved, using data obtained at low oxygen pressures.
CHAPTER 6

General Discussion

In the previous two chapters, the oxidation of the two magnetically-active alloys has been examined using two very different analysis techniques. Both the ICPMS technique and the novel application of SIMS have only recently been developed. It is interesting to note that such studies would previously have been impossible.

It is useful to compare these apparently very different techniques. The main points of comparison are summarised in Table 6.1.

Table 6.1. A comparison of the electrochemical study and the 'in-situ' SIMS study.

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<td><strong>Other Techniques</strong></td>
<td>XPS</td>
<td></td>
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<td></td>
<td>- Used to examine surface after exposure.</td>
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<td></td>
<td>- Gives chemical state and surface layer structure information.</td>
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<td>- Still ambiguity of post solution oxidation.</td>
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<td>If thicker oxides are examined than could relate MeO/Me ratio or fractionation pattern to chemical state information from XPS which can apply to thin oxide layers studied</td>
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<tr>
<td>SEM</td>
<td>Examine localised corrosion and redeposition</td>
<td></td>
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<tr>
<td>AES</td>
<td>High lateral resolution with local elemental information</td>
<td></td>
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<tr>
<td>ESCASCOPE</td>
<td>Chemical state mapping of localised corrosion</td>
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<tr>
<td>TEM</td>
<td>Analysis of corrosion product on surface</td>
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The most striking feature of both the electrochemical study and the SIMS study is that they are both concerned with the conditions where the reaction is very slow. This means at low
oxygen pressures, for the SIMS study, or, in the case of the electrochemical study, where the potential is in the cathodic region. The amount of reaction can be carefully controlled. The controlling factors in the electrochemical study are the electropotential, the exposure time and the solution conditions such as the presence of active ions, pH and temperature. In the SIMS study the amount of reaction is determined by the oxygen pressure.

To study such slow reactions, as are being considered here, ie submonolayer oxide coverage for the SIMS experiment, and corrosion current densities down to $< 1 \mu A/cm^2$ for the electrochemistry experiment, it is necessary to have sensitive analysis techniques.

In electrochemistry a very sensitive solution analysis technique is required to detect the corrosion products in solution. This is achieved using Inductively Coupled Plasma Source Mass Spectrometry (ICPMS) which can detect sub-ppb level concentrations. In the SIMS study we use a unique application of simultaneous oxidation and removal to achieve a very low oxide coverage and use SIMS to detect the oxide species with high sensitivity.

The measurement of the corrosion products, resulting in both cases from the fragmentation of the surface, is concerned with the detection of ions. These are ions formed from the dissolution of the alloy in solution or emitted from the oxide surface into vacuum. The SIMS study measures the oxidation products immediately allowing simultaneous oxidation and removal and immediate detection of the corrosion products within the same instrument. For the electrochemical study the corrosion products are stored after each experiment, for solution analysis remote from the source of production.
In both the ICPMS and the SIMS analyses, as the names imply, the resulting data are in the form of mass spectra. In ICPMS, the data represent the total amount of ions in a given sample solution after a fixed external charge has been passed through the cell. For the SIMS a SIMS profile which monitors specific masses with time. An equilibrium is reached at a certain oxygen pressure where the rate of oxide formation equals the rate of its removal is obtained. The SIMS profile is then constant with time. This equilibrium value is the value of interest. In SIMS changes can be monitored in real time. In the electrochemical study only a qualitative idea can be achieved as to the processes occurring in the solution by monitoring the external current with time. The added complication, which is particularly acute in the interpretation of the data around the rest potential, is that the external current is the sum of the anodic and cathodic reactions. The currents can be inseparable until the value for the mean anodic current is determined, by, for example an external source such as solution analysis.

The values obtained by the analysis techniques are used in either the mean current density calculations, dissolution coefficients or in SIMS for the oxide coverage.

Interpretation of the data produced can create ambiguities for both studies. In SIMS, there is still ambiguity in the determination of the oxidised and unoxidised species, particularly for the more reactive metals. In the electrochemical study, there is a problem when redeposition of material onto the surface of the sample occurs and this material is not detected by ICPMS.

Models are used to describe the corrosion or oxidation properties of the materials with each technique. In the electrochemical study the model is in the form of an anodic polarisation
This anodic polarisation curve is specific for the solution investigated; ie it is dependent on the active ions present, the temperature and the pH. It gives an indication of the extent of corrosion at any given electropotential and reveals regions of different electrochemical behaviour, such as passivity, transpassivity and active regions. From the SIMS study it was possible to derive an expression for the oxide coverage with oxygen pressure.

Since the study concerns metals of different reactivities, ie very different standard electrode potentials, and differing heats of formation of oxides, different oxide formation behaviour or dissolution rates are likely.

Selective oxidation in the electrochemistry study is determined by the amount of each material in solution and can be modelled by obtaining partial currents for the different alloy components. There is ambiguity in the electrochemistry study due to the preferential redeposition of one metal rich phase with respect to the other. Is the apparent selective dissolution actually only due to the redeposition of the other? In the SIMS study, selective oxidation would be shown by the differing oxide coverages of different metals at a given oxygen pressure. At the moment, it is only possible to monitor the less reactive metals, such as cobalt. The cobalt in the alloy did behave in a similar way to that of the pure metal, which suggests that the alloy components oxidise independently at such low oxide coverages.

For the more reactive metals the oxidised and unoxidised components are indistinguishable. Another model has to be developed in order to interpret their data to be able to determine if any selective oxidation is occurring.
To determine the complete electrochemical properties of FeMn in water, it is necessary to employ complementary techniques to the solution analysis study. As already mentioned, some information can be obtained from monitoring the external current. This also enables the mean cathodic curve to be determined. In this study, XPS has been widely used to monitor the corrosion products remaining on the surface, and to give an idea of the oxide chemistry and layer structure. For example, the chemical nature and layer structure of the passive layer on an FeMn sample was determined. The local corrosion and redeposition can be examined by SEM. The specific subject of the redeposited crystals was examined by Auger, ESCASCOPE and TEM-EDX. Each has its own advantages and limitations. It sometimes requires a variety of techniques to give an overall idea of the corrosion process.

With 'in-situ' SIMS, the additional techniques which can be used are limited, particularly as the oxide coverage is so low and the oxidation is performed in-situ. Either other analysis techniques have to be attached to the instrument or the oxide has to be formed at a later stage of development. For example, a thicker oxide could be formed outside the instrument and then analysed by both SIMS and XPS. By comparing either the MeO/Me ratio or the SIMS fractionation pattern to the XPS chemical state information, a correlation between the SIMS data and the XPS data could be found which could aid in the determination of the specific oxide formed.

To determine selective oxidation for thicker layers, and obtain chemical state information, 'in-situ' XPS could be used. This technique uses simultaneous formation and removal of oxide products. The preliminary results on stainless steel look promising (Appendix 3).
In summary, the techniques used to look at the corrosion of the magnetically active alloys have revealed new tools to examine the oxidation process. An electrochemical study involving ICPMS to look at small concentrations of corrosion products, coupled with surface analysis and external current measurements, can give a very good idea about the corrosion properties of the alloy in question. The SIMS study is involved with the oxide growth in the very initial stages and has proven to be a very sensitive technique for this application.

So far, the experimental methods have been examined. The thesis is a study of possible techniques to investigate the corrosion properties of magnetically active alloys. Are FeMn and Co₈₆Cr₁₄ reasonable examples of materials to be examined? They are both magnetically active; FeMn antiferromagnetic and Co₈₆Cr₁₄ ferromagnetic. They consist of metals with very different reactivities which leads to the possibility of selective dissolution or oxidation.

For the SIMS study, since most of the materials were very reactive it lead to difficulties in interpretation of the oxidised and unoxidised species. It was initially hoped that water exposures should be applied to FeMn in a similar way as in the in-situ oxygen experiments. However, this proved very difficult since the isotopes of iron lie at masses 54, 56, 57 and 58 and monoisotopic manganese lies at mass 55. Once the H⁺ ion was introduced the interpretation of the corrosion products became very complicated. The mass separation with cobalt and chromium is greater so any SIMS work is easier with Co₈₆Cr₁₄. Cobalt is less reactive than iron, manganese or chromium: this made the interpretation of the unoxidised and oxidised components and eventual modelling of the oxidation process possible. In the electrochemical study, FeMn, which would have shown up selective dissolution in the region overlap of the Pourbaix diagrams showed little sign of this, suggesting that immune iron can not protect the alloy. Due to the active nature of the FeMn, air oxidation did create post
solution ambiguities in the consequent XPS analysis. However, many of the 'new' alloys being developed in the magnetic recording industry are reactive metals so FeMn was a representative material to investigate.
CHAPTER 7

Conclusions
The objective of this study was to understand how to investigate the very reactive alloys used in the magnetic recording industry. This has been done using two very different approaches in the investigation the oxidation of two magnetically active alloys, FeMn and CoCr. One approach is an electrochemistry study, which involves a combination of solution analysis and surface analysis techniques. The other investigates the very early oxidation process using an in-situ SIMS technique.

The first approach is a more traditional technique and yields information on the corrosion properties of the alloy of interest, in this case the FeMn, in a relatively straightforward manner. The results obtained can be interpreted and the combined solution and surface analysis give a clear idea of the corrosion processes occurring in solution. The advantage of using a sensitive solution analysis technique, as opposed to traditional potentiodynamic scans, is that features of the anodic polarisation curve which lie beneath the cathodic curve, can be revealed. This was particularly important in this study as the region of passivity would never have been determined by potentiodynamic scans alone. The only ambiguity in the study lies in the post solution oxidation of the sample on removal from solution. This is not a problem if a passive layer is formed, as is the case when chromate is used as an inhibitor. The breakdown of passivity, which occurs with increase in sodium sulphate concentration, can be monitored both as an increase in corrosion current density and by the resulting chemical changes observed in the XPS data. Other influences on the corrosion of the alloy, such as temperature, pH and presence of inhibitors, can be similarly investigated.
This combined electrochemical and surface analysis technique can be recommended for the
determination of the corrosion properties of other magnetically-active alloys.

The SIMS study proved to be less straightforward, particularly with the interpretation of the
basic SIMS data. This is, maybe, not so surprising as SIMS, as a technique, is very much
less well understood than the established techniques of AES and XPS. The study nonetheless
drew out some very interesting aspects of the oxidation of cobalt, which have never before
been available at such an early stage of a metal’s oxidation. Further progress has to be
made into the SIMS data interpretation before the potential of this technique will be fully
realised.

The general conclusions on each study are given below;

The complete electrochemical behaviour (anodic and cathodic) of FeMn in water has been
determined over the potential range -139mV to -889mV SCE. ICPMS has proved to be a
valuable tool in this study as it has allowed the determination of the passive region of the
anodic polarisation curve which lies below the cathodic curve. Traditional potentiodynamic
methods would have been inadequate to achieve this.

The natural passivity is limited to a short potential range and is vulnerable to attack by active
ions. The displacement of the anodic polarisation curve to higher current densities was
attributed to an increasing concentration of sodium sulphate ions. Small variations in pH and
temperature showed little effect on the corrosion characteristics of the alloy.
The passive layer on the FeMn consists of a manganese hydroxide rich surface. A breakdown in passivity was associated with formation of an iron oxy-hydroxide rich layer on the surface.

Redeposition of an iron-rich material occurs on the surface of the alloy. The morphology has the appearance of bullseyes at low magnification. At high magnification this can be seen as loosely packed hexagonal platelets.

Application of sodium chromate as an inhibitor was found to be effective in reducing the corrosion. Chromate enhanced the passivity of the alloy. The chromium is incorporated into the surface layer.

The application of in-situ SIMS to the oxidation of CoCr and pure metals cobalt, iron, manganese and chromium has been explored. The unoxidised and oxidised components have been successfully deconvoluted for cobalt. A model for the oxidation of cobalt has been determined. The cobalt component in the alloy Co$_{88}$Cr$_{14}$ behaves in a similar model to that of the pure metal, which suggests that the cobalt oxidises independently from the chromium in the alloy.
CHAPTER 8

Suggestions for Future Work

This thesis is an essential starting study for future work into determining the oxidation properties of magnetic alloys.

There is much further work required in the interpretation of SIMS data, which is still in its infancy, compared to the well established techniques of XPS and AES.

It would be useful to develop a model to distinguish the oxidised and unoxidised components for the more reactive metals. From this point the model for the oxidation of these metals could then be determined.

What does the MeO/Me ratio actually mean? Would it be possible to relate it to the stoichiometry of the oxide. Maybe this would be possible if SIMS and XPS were performed on thick oxides and the MeO/Me ratio related to a specific oxide compound?

The model for the oxidation of metals could be extended to water studies and a similar model produced for the oxidation of metals with water. This may also give information which is important to the electrochemistry study as it involves the H\(^+\) ion.

As far as the electrochemistry study is concerned it is important to determine the effect of post solution oxidation, ie the corridor effect. By attaching the cell in an enclosed chamber with an inert atmosphere, directly to the preparation chamber it would avoid the ambiguity
of air oxidation after removal from solution. An alternative method would be to use oxygen 18 labelled water and do a SIMS analysis to determine the origin of the oxygen.

The natural passivity of FeMn is very limited. Ways in which this passivity could be extended should be further explored. Chromate did show enhanced passivity in this study. Studies should be performed in which the chromium is incorporated into the alloy, either by alloying, or by use of inhibitors. If alloying is used, the effect of chromium incorporation should be investigated for its influence on the magnetic properties, as well as the corrosion properties of the alloy. Active ions were found to have a great effect on the corrosion of the alloy. To avoid contamination of active ions from the diffusion of ions across the ceramic frit, a Pd/H₂ reference electrode may be the answer.

The studies performed on the bulk samples should be extended to the thin film form. Eventually field trials on the actual device in service should be performed.

The combined electrochemistry study using solution and surface analysis is a powerful combination for looking at the overall corrosion of materials. This could be extended to other alloy systems of interest to the magnetic recording industry.
9. References


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Appendix 1

A Pd/H₂ electrode was produced by charging a piece of palladium in dilute sulphuric acid for 5 minutes using a 1.5V battery. The stability of a Pd/H₂ electrode was monitored with time, as shown in Figure A1.1. Reasonable stability was achieved. If a Pd/H₂ electrode were used, instead of a traditional calomel or sodium sulphate electrode, the presence of active ions, such as sulphate or chloride ions, could be minimised.

Figure A1.1. Potential of Pd/H₂ electrode versus time.
Appendix 2

A Co<sub>80</sub>Cr<sub>14</sub> sample was oxidised in air at 200°C for 18 hours. The resulting oxide was analysed using SIMS with a 5kV and 20nA beam current. The resulting depth profile is given in Figure A2.1. The ratio of CoX⁺/Co⁺ with etch time is shown in Figure A2.2. The ratio for Co⁺/CoO⁺ is approximately 100 for the surface layers is the oxide layer. This value is similar to the Co⁺/CoO⁺ ratio obtained for the very thin oxide obtained in the in-situ oxidation study on Co<sub>80</sub>Cr<sub>14</sub>, in Chapter 5.

Figure A2.1. SIMS etch profile of oxidised Co<sub>80</sub>Cr<sub>14</sub>.
Figure A2.2. CoX⁺/Co⁺ ratios plotted versus etch time.
Appendix 3

A study was made by the author and Cecile Laurent, a French student on secondment to the Surface Laboratory at the University of Surrey on the feasibility of using a dynamic 'in-situ' XPS oxidation of materials. The technique evolved from the in-situ SIMS study. In this case there is an equilibrium reached between the formation and removal of products, and the oxidation products are analysed using XPS. This has an advantage over SIMS, as chemical state information can be directly obtained. The initial study on the oxidation of stainless steel looked quite promising. The chromium enrichment in stainless steel increases linearly with increase in oxygen pressure over the pressure range 0.5 to 1.5 \times 10^8 \text{ mbar}. There appears to be a saturation point, with a chromium enrichment factor of approximately two, at pressures \( > 2 \times 10^8 \text{ mbar}. \)
Figure A3.1. Chromium enrichment factor versus oxygen pressure.