Kinetics of O2 Reduction on Oxide-covered Ni-Cr-Mo Alloys

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Graduate Program in Chemistry  
A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy  
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(Thesis format: Integrated-Article)

by

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Graduate Program in Chemistry

A thesis submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
The University of Western Ontario
London, Ontario, Canada

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The thesis by

Xiangrong (Sarah) Zhang

entitled:

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is accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy

Date ___________________________                ________________________________

Chair of the Thesis Examination Board


**Abstract**

Ni-Cr-Mo alloys exhibit exceptional corrosion resistance and are widely used in chemical processing industries. The reliable performance of these alloys under extreme industrial conditions, are generally attributed to the presence of a passive film on the alloy surface. \( \text{O}_2 \) reduction is the most likely cathodic process able to sustain metal oxidation (corrosion) in industrial environments. However, the kinetics of \( \text{O}_2 \) reduction on these oxide-covered alloys has hardly been studied, despite the possibility it may be the rate controlling process for corrosion, especially localized corrosion. The objectives of this research are to characterize the properties of the oxide film on Ni-Cr-Mo alloys, and to investigate whether \( \text{O}_2 \) reduction occurs on oxide-covered surfaces, and, if it does, the conditions under which it occurs and the mechanism of the reaction.

Various surface analytical techniques such as angle-resolved X-ray photoelectron spectroscopy (XPS), synchrotron radiation XPS (SR-XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and SEM are employed to characterize the properties of oxide film on Ni-Cr-Mo alloys as a function of applied potential, temperature and pH. The presence of a layered structure in the passive film (< 5 nm) has been demonstrated on these alloys, with the outermost surface being enriched in Cu (or Cu oxide) and Mo oxide, the intermediate region dominated by Cr/Ni/Cu hydroxides, and the inner region comprising Cr/Ni oxide.

A number of electrochemical techniques are used to measure the reduction of \( \text{O}_2 \) on a series of Ni-Cr-Mo alloys (Alloy C22, C2000, C276, C4 and 625) in 5 mol•dm\(^{-3}\) NaCl solution
over the temperature range of 30-90 °C. Both potentiostatic and cyclic voltammetric (CV) experiments demonstrate that O₂ reduction currents on these alloys are either very small or completely suppressed by the presence of a film grown in the passive region, but revived to different degrees when the film-growth potential was extended into the transpassive region. The impedance properties obtained from EIS measurements show that the polarization resistance reached a maximum in the passive region, and decreased with the increase of film-growth potential in the transpassive region, due to the oxidative injection of cation defects.

**Keywords:** Ni-Cr-Mo alloys, passive film properties, kinetics, O₂ reduction.
Acknowledgements

This thesis would not have been possible without the support of many people. It is my great pleasure to humbly acknowledge all people who have helped and inspired me during my doctoral study.

First and foremost, I offer my sincerest gratitude to my supervisor, Professor David W. Shoesmith, who has supported me throughout my Ph.D study with his patient guidance, encouragement, and knowledge whilst allowing me the room to work in my own way. His perpetual energy and passion for electrochemistry had motivated all his endless stream of ideas and sound advices on my research. Hence, my research life at The University of Western Ontario became smooth and rewarding experience.

I would like to thank Dr. Jamie Noël and Dr. Dmitrij Zagidulin for their assistance in the lab, and invaluable discussion in the meetings, and Dr. Zack Qin for his help in impedance analysis. Special thanks go to Dr. Jigang Zhou at Canadian Light Source, and Mr. Mark Biesinger, Dr. Heng-Yong Nie, Mr. Gary Good, and Mr. Ross Davidson at Surface Science Western, without whose knowledge and assistance this study would not have been successful. Furthermore, I would also like to thank the members in Shoesmith’s and Wren’s groups, both past and present, for the inspiration in research and life, friendship, and fun.

I gratefully acknowledge the U.S. Department of Energy and NSERC of Canada for the funding sources that made my Ph.D work possible.

Finally, my deepest gratitude goes to my parents, my brothers, and especially my husband, for their unflagging love and support throughout my life; this dissertation is simply impossible without them.
This thesis is dedicated to all the people who never stop believing in me …..

my parents

my brothers

my husband, Zhikang

and our son, Steven
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Chapter 1
Introduction

1.1 General

Ni-Cr-Mo alloys are well known high performance Ni-base alloys that exhibit exceptional corrosion resistance under extreme industrial conditions. These alloys are widely used by chemical processing industries, in the areas of energy, health and environmental, oil, gas and pharmaceuticals. For example, a Ni-Cr-Mo alloy, Alloy-22 was chosen as the reference material for construction of the outer barrier of the double-wall waste package by the US Department of Energy for the permanent disposal of nuclear waste in the Yucca Mountain repository in the U.S.A.* [1, 2]. This alloy would provide the primary barrier to the release of radionuclides from the fuel waste form.

The superior corrosion behavior of Ni-Cr-Mo alloys manifests itself in both lower materials loss by general corrosion and in the ability to better withstand localized processes (notably pitting and crevice corrosion), intergranular corrosion and stress corrosion cracking. The reliable performance of these alloys under extreme industrial conditions, is generally attributed to their elemental composition and passive behavior. Ni-Cr-Mo alloys remain passive in most industrial environments due to the formation of a Cr$_2$O$_3$ barrier layer which has an exceptionally low general corrosion rate [3-7]. The combination of high Cr and relatively high Mo contents with the addition of a small amount of W confers on the material excellent corrosion resistance to aggressive conditions.

* The Yucca Mountain project has now been cancelled.
reducing (e.g., sulfuric and hydrochloric acids) and oxidizing (e.g., nitric acid) environments, and a high resistance to localized corrosion processes such as pitting and stress corrosion cracking. In this thesis, a family of five industrially manufactured Ni-Cr-Mo alloys differing in major and minor alloying components were investigated. The major chemical compositions for the Ni-Cr-Mo alloys studied are presented in Table 1.1.

<table>
<thead>
<tr>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Cu</th>
<th>Nb+Ta</th>
</tr>
</thead>
<tbody>
<tr>
<td>C22</td>
<td>56</td>
<td>22</td>
<td>13</td>
<td>3</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>C2000</td>
<td>59</td>
<td>23</td>
<td>16</td>
<td>1.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>625</td>
<td>62</td>
<td>21</td>
<td>9</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C276</td>
<td>57</td>
<td>16</td>
<td>16</td>
<td>4</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>C4</td>
<td>65</td>
<td>16</td>
<td>16</td>
<td></td>
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</tr>
</tbody>
</table>

Even though the Yucca Mountain repository will be located beneath ~300 meters of consolidated tuff rock and ~300 meters above the water table [9], contact of the waste package with groundwater containing dissolved O₂ is possible. Although initially dilute, groundwater containing chloride, nitrate, sulfate, and carbonate anions and sodium, calcium, potassium, and magnesium cations can become concentrated by evaporative contact with the hot waste package surfaces (temperatures up to 160 °C) and solutions with a wide range of pH (from pH ~ 3 to pH > 12) and anion composition could form. Since the service life required in these extreme environments is long, general corrosion and crevice corrosion are considered to be the principle threats to the integrity of the waste packages.
Figure 1.1 illustrates the general mechanism of crevice corrosion on a Ni-Cr-Mo alloy. Crevice corrosion occurs when a metallic surface is in close proximity to another surface. The tight geometry of the crevice results in limited mass transport between the occluded region (inside the crevice) and the bulk solution (outside the crevice). Surface oxidation and dissolution within the crevice consumes the dissolved oxygen in the occluded region and its replenishment is limited by the crevice geometry [10]. The dissolved metal cations hydrolyze to produce acidity within the crevice and chloride ions migrate from the bulk solution into the crevice to maintain electroneutrality. This produces an aggressive acidic saline solution, which rapidly destroys the protective oxide film on the metal surface. As shown in the figure, metal dissolution within the crevice must be supported by the reduction of O$_2$ on the oxide-covered surface outside the crevice. In most corrosion processes, and within the Yucca Mountain repository, the primary oxidant will be dissolved oxygen. This makes the kinetics of O$_2$ reduction on the passive surface very
important in determining passive corrosion rates, susceptibilities to localized corrosion and propagation rates of the crevice corrosion process. With this in mind, the primary goal of this thesis is to investigate the kinetics of O₂ reduction on a series of oxide-covered Ni-Cr-Mo alloys at various temperatures and potentials in a concentrated saline environment, including the candidate material for the high-level nuclear waste disposal package, Alloy-22.

1.2 The Passivity of Ni-Cr-Mo Alloys in Aqueous Solutions

1.2.1 The Thermodynamics of Passivity

Most metals and alloys are covered by a thin protective surface oxide film resulting from reaction with the environment. These protective films are responsible for the phenomenon of passivity. The conditions under which passivation becomes thermodynamically possible can be predicted from a potential (E)-pH diagram, Pourbaix diagram. The condition of equilibrium of a metal with its oxides or hydroxides can be obtained from such diagrams, and indicates the conditions when passivity should be achieved.

Figure 1.2 shows a potential-pH diagram (E-pH diagram) for the nickel-water system [11], the primary metal in Ni-Cr-Mo alloys. The diagram was constructed from the standard potential values and the Nernst equations for possible reactions. For the dissolution of Ni to Ni²⁺

\[
Ni = Ni^{2+} + 2e^- \tag{1.1}
\]
the equilibrium potential (vs. the Standard Hydrogen Electrode (SHE)) is given by the Nernst Equation

$$E = E^o + \frac{RT}{2F} \ln [\text{Ni}^{2+}]$$

(1.2)

where $E^o$ is the standard electrode potential, $R$ is the gas constant, $T$ is the temperature, 2 is the number of electrons involved in the half reaction, $F$ is Faraday’s constant, and is the activity of Ni$^{2+}$ in solution. Since the potential does not depend on pH and only on Ni$^{2+}$ activity, this reaction is represented by horizontal lines (9) in the Pourbaix diagram. The number on the lines represents the log of [Ni$^{2+}$]. However, protons are involved in the reaction of Ni with water to form Ni(OH)$_2$ (reaction 1.3),

![Potential-pH equilibrium diagram for the system Ni-H$_2$O, at 25°C](image)

**Figure 1.2** Potential-pH equilibrium diagram for the system Ni-H$_2$O, at 25°C[11].
\[ \text{Ni} + 2\text{H}_2\text{O} = \text{Ni(OH)}_2 + 2\text{H}^+ + 2\text{e}^- \]  

(1.3)

and the Nernst equation gives a potential that is pH dependent (equation 1.4).

\[ E = E^\circ + \frac{RT}{F} \ln [\text{H}^+] \]  

(1.4)

This reaction is represented by a diagonal line (2) in the right part of the \( E \)-pH diagram. The diagonal lines on the diagram, marked (a) and (b), show the domain for water stability. This is the region of the \( E \)-pH diagram, therefore, that is important in aqueous corrosion.

A Pourbaix diagram can be used to establish the theoretical domains for corrosion, immunity and passivation, as illustrated in Figure 1.3 [11]. The three domains show the

![Figure 1.3](image)

**Figure 1.3** Theoretical domains of corrosion, immunity and passivation of Ni in H\(_2\)O, at 25 °C [11], established with the log of [Ni\(^{2+}\)] = – 6.
potential regions within which the metal will not dissolve (immunity), where a corrosion-product film \( \text{Ni(OH)}_2/\text{Ni}_3\text{O}_4/\text{Ni}_2\text{O}_3/\text{NiO}_2 \) forms and may confer protection against corrosion (passivation), and where dissolved ions are thermodynamically stable (corrosion). Such diagrams can be used to identify when metals are capable of forming passive films, and provide the basis for a preliminary corrosion prediction. The theoretical domains of corrosion, immunity and passivation for the main alloying

**Figure 1.4** Theoretical domains of corrosion, immunity and passivation of Cr (in solutions containing chloride) and Mo, W and Cu (in H\(_2\)O), at 25 °C [11].
elements in the Ni-Cr-Mo alloys studied in this thesis in solutions containing chloride (for Cr) or H₂O (for Mo, W and Cu), are shown in Figure 1.4. Within the region of water stability, Cr, Mo and W never achieve immunity and would dissolve or form surface oxides depending on the pH, whereas Cu is immune to corrosion in water over a wide pH range. Although each metal exhibits very different $E$-pH behaviour, consideration of the diagrams shows that if a Ni-Cr-Mo-W alloy was controlled by the thermodynamic properties of the individual alloying metals, it would be passive over the entire region of water stability, except for extremely alkaline (pH >14) conditions. However, even though it is convenient and instructive to use Pourbaix diagrams to predict the corrosion behaviour of an alloy, the use of individual alloying metal diagrams for understanding alloy behaviour is limited, since corrosion processes are inevitably kinetically driven.

1.2.2 The Kinetics of Passivity

Kinetically, passivity characterizes the condition when a protective film, present on a metal surface, markedly lowers the rate of corrosion, even though active corrosion would be expected from thermodynamic considerations [12]. The nature of passivity is illustrated using an anodic polarization curve, Figure 1.5 [13]. This curve can be divided into a number of regions: Region AB is the metal dissolution or active region, when the current density for metal dissolution increases exponentially with potential; Region B is the active-to-passive transition region, when oxide film formation begins to limit the rate of metal dissolution; and Region C is the passive region when the current is decreased to a lower value. The current maximum is the critical passivating current density ($i_{crit}$), and the potential corresponding to the establishment of full passivity is called the passivation
Figure 1.5  Schematic polarization curve for a passive metal that undergoes active-to-passive and passive-to-transpassive transitions: \((E_{e})_a\) and \((E_{e})_{MO}\) are the equilibrium potentials for the metal dissolution and oxide formation reactions respectively [13].

potential \((E_{pass})\). In the passive region CD/CE, current densities can be as low as \(\text{nA}\cdot\text{cm}^{-2}\) compared to critical passivating current densities which can be as high as tens of \(\text{mA}\cdot\text{cm}^{-2}\). At high potentials in the transpassive (the dashed-dotted line in the potential region D to E) and/or \(\text{O}_2\) evolution region (for potentials greater than point E), cations in the oxide are oxidized to higher, more soluble oxidation states and/or water is oxidized to \(\text{O}_2\). For metals such as iron, nickel, chromium, and nickel-chromium alloys, transpassive dissolution and \(\text{O}_2\) evolution via the oxidation of water often occur together [13]. Transpassive dissolution of Ni-Cr-Mo alloys mainly involves the oxidation of
Cr$_2$O$_3$/Cr(OH)$_3$ to Cr(VI)$_{aq}$ in the form of CrO$_4^{2-}$ [14], and probably NiO/Ni(OH)$_2$ to Ni(III)$_{aq}$ [15-17]. The phase transformations for Mo and W, and the role they play in transpassive behaviour in Ni-Cr-Mo(W) alloys, are still unclear.

Corrosion involves the coupling of the anodic half-reaction for material oxidation to the cathodic half-reaction for the reduction of an oxidant in solution (usually protons or dissolved oxygen). The driving force for corrosion is the difference in equilibrium potentials for the two half-reactions. The schematic in Figure 1.6 [13] illustrates how the current and potentials for each half reaction are related with respect to their equilibrium potentials assuming passivation does not occur. Corrosion occurs when the anodic and cathodic currents are equal in magnitude, but opposite in sign ($i_{corr}$). The potential that results from the coupling of these reactions is the corrosion potential, $E_{corr}$. Therefore,

![Figure 1.6](image-url)  

**Figure 1.6** Current-potential relationships for a metal dissolution process coupled to a reduction half reaction.
even though a material may be capable of exhibiting passivity, its corrosion rate will depend on where the corrosion potential is located in Figure 1.5. Two key conditions are possible: (i) when \((E_{eq})_{M/MO} > E_{corr} > (E_{eq})_a\), the metal will freely corrode since \(E_{corr}\) is in the active region; (ii) when \(E_{corr} > (E_{eq})_{M/MO}\), passivity is possible since the oxide is thermodynamically stable. In the second region, the passive current density will depend on the properties of the oxide such as its chemical stability (i.e., dissolution rate) and its physical properties (i.e., coherence, adherence, porosity).

### 1.2.3 Mechanism of Formation of the Passive Film

Since the properties of passive films determine the overall corrosion behaviour, their nature has been extensively studied and many models have been developed to describe their growth kinetics. The commonly accepted point defect model (PDM) can be used to illustrate the critical features of the current-potential behaviour in the passive region.

The PDM describes passive film processes on the basis of the chemical reactions involved and the physicochemical properties of the metal-film-solution interface [18-20]. The passive film has been found to have a bilayer structure, consisting of an inner barrier layer (bl), whose insulating properties provide the essential corrosion protection, and a hydrous oxide outer layer (ol) that forms from the hydrolysis of cations ejected from the inner layer and confers little extra corrosion protection [21, 22]. In this model, the oxide growth is assumed to occur by the transport of defects through the film. The concept of point defects is adopted from solids in which they directly affect the chemical and electrical properties. This concept has been extended to metal oxides and thin oxide films to explain their chemical and electronic behaviour [23]. The defect species in the oxide
film may be an ion, an interstitial or a vacancy which carries a virtual charge of the opposite sign to the ion that would normally occupy the site. The nature of the defect depends on the metal/alloy and the nature of the growing oxide.

The essential features of the PDM model are shown schematically in Figure 1.7 [13]. The defect generation and annihilation reactions envisioned to occur at the metal/barrier layer (m/bl) and barrier layer/outer layer (bl/ol) interfaces are depicted in this figure. Reactions (1) and (3) describe the injection of the lattice cation, $M_M^+$, and cation interstitial ($M_j^{x+}$) into the barrier layer, respectively. These species can be transmitted through the barrier layer and ejected into the outer layer or the solution, as described by Reactions (4) and (6). Reaction (2) is the injection of cations into the barrier layer leading to its growth into the bulk of the metal and the generation of oxygen vacancies ($V_{o}^{**}$). These vacancies are transported across the barrier layer and annihilated at the bl/ol interface, Reaction (5). Reaction (7) leads to the destruction of the barrier layer by conversion to the outer layer or dissolution into solution. Figure 1.7 illustrates only the anodic processes occurring during passive corrosion. In the overall corrosion process, Reaction (2) and (3) must be supported by conduction of an electron through the film to reduce an oxidant in the solution.

Briefly, the barrier layer can be viewed as a highly defective semiconductor, in which the defects (cation and anion vacancies and cation interstitials) act as the electronic dopants. Cation vacancies are generated at the oxide/solution interface when a cation is ejected into the outer layer or the solution (Reaction 4), while the annihilation of oxygen vacancies occurs at this same interface when oxygen anions become incorporated into the
Figure 1.7 Schematic description of the point defect model (PDM) for the growth of a passive oxide film [13].
film (Reaction 5). The interfaces at which the vacancies are generated and annihilated are normally separated by no more than a few nanometers. The growth of the oxide film proceeds via a net flow of oxygen vacancies and cation interstitials from the m/bl interface to the bl/ol interface and a net flow of cation vacancies in the reverse direction. Since reactions (2) and (7) result in the generation and breakdown of the barrier layer, respectively, they are lattice-nonconservative, whereas the remaining reactions are lattice conservative. When the rates of these two non-conservative processes are equal, a steady-state will be reached. At steady-state, the film thickness and passive current density become constant; and with increasing potential the film thickens but the passive current density remains constant.

The transport of defects through the film will be controlled by a combination of diffusion due to the presence of a concentration gradient (Fick’s first law) and migration in response to the electric field across the film. The transport of a vacancy involves the interchange of an atom with the vacancy site, such that the transport of a particular lattice atom by a vacancy mechanism is linked to the movement of vacancies. According to this mechanism, the ion is immobile until approached by a vacancy, which allows it to make a single jump in the transport direction. Transport of interstitials occurs through a displacement process, whereby the interstitial ion displaces a normal lattice ion from its site, forcing the normal lattice ion into a new interstitial site. Regardless of the transport mechanism, electrons will be the most mobile species, and their movement will be controlled by the ionic species with the lowest transport coefficient to maintain charge neutrality.
The PDM has been applied to explain and predict the corrosion behaviour of Ni-Cr-Mo alloys, especially Alloy-22, by assuming that, in the passive potential range, the barrier layer is a defective chromic oxide, \( \text{Cr}_{2-x}\text{O}_{3-y} \) [18, 20]. The defect formula indicates that the barrier layer is either cation rich \((x > y)\), due to the predominance of cation interstitials, or oxygen deficient \((y > x)\), due to the predominance of oxygen vacancies. In any event, the barrier layer on Alloy C22 has been shown to be an n-type semiconductor [18]. In this thesis, the PDM is used to explain the properties of the film on Ni-Cr-Mo alloys.

### 1.2.4 Passive Behaviour of Ni-Cr-Mo Alloys in Aqueous Solutions

A wide array of in-situ and ex-situ analytical techniques [3, 5, 19, 24-27] has been employed to assess the passive behaviour and corrosion performance of Ni-Cr-Mo alloys, especially Alloy-22. It is generally accepted that Alloy-22 remains passive in a wide range of environments. The \( E_{\text{corr}} \) in naturally aerated solutions is usually in the range of \(-0.3 \text{ V to } 0.3 \text{ V}\) depending on pH, temperature, anion type and concentration, and immersion time. And the corrosion rate can be < 50 nm/year even in concentrated near neutral brine solutions at 100 °C after more than 100 days immersion [28, 29]. Alloy-22 was observed to have stable passivity in concentrated salt solutions which simulate concentrated ground waters at 80 °C over a wide range of pH values [30]. For mill-annealed Alloy-22, anodic current densities, measured at 95 °C for 48 h, were found to be consistently lower than \(10^{-7} \text{ A}\cdot\text{cm}^{-2}\) and practically independent of chloride concentration (0.028 to 4.0 mol\(\cdot\text{dm}^{-3}\)), pH (0.7 to 8.0), and potential when \(E \leq 400 \text{ mV}_{\text{SCE}}\). Passive corrosion rates < 1µm/year (0.039 µm/year) were estimated from current density
measurements using Faraday’s law. Modeling studies suggest breakdown of passivity leading to enhanced dissolution is unlikely [31].

Recently, a number of studies have been conducted on the passive film properties on Ni-Cr-Mo alloys. Lloyd et al. [3,4,5] determined the film composition and thickness, and the effect of the alloying elements, Cr, Mo and W, on the passivity of a number of Ni-Cr-Mo (W) alloys in acidic solutions. The oxide film was found to be only a few nanometers thick (< 5 nm), and the thickness increased with increasing potential in the passive region. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) showed that the high-Cr alloys were able to build thicker oxides with a layered structure consisting of an inner Cr-Ni oxide layer and an outer Mo/W oxide when anodically oxidized in 1.0 mol\( \cdot \)dm\(^{-3} \) NaCl + 0.1 mol\( \cdot \)dm\(^{-3} \) H\(_2\)SO\(_4\) solution (pH = 1). The presence of Mo and W in the outer regions of the oxide is thought to suppress passive dissolution at high potentials, when Cr (VI) release appears to start. Macdonald et al. [18] found a similar dependence of thickness on potential. The film exhibited n-type semiconducting properties in the passive region \( (E < 0.6V_{\text{SHE}}) \) and p-type semiconductor characteristics in the transpassive region \( (E > 0.6V_{\text{SHE}}) \). Bakare et al. [32] found a similar oxide film composition on Alloy 625, consisting of NiO, Cr\(_2\)O\(_3\), MoO\(_2\), MoO\(_3\), NbO and Nb\(_2\)O\(_5\). In H\(_2\)O\(_2\)-containing supercritical water (SCW) environments, a duplex layer consisting of an outer layer of large-grain oxide and an inner layer of fine-grain oxide was observed on Alloy 625. The duplex-layer structure was identified to be Ni(OH)\(_2\)/NiO/NiCr\(_2\)O\(_4\)/Cr\(_2\)O\(_3\)/alloy matrix from the outer to the inner layer [33].
In conditions where tight crevices exist in hot chloride-containing solutions and at relatively high applied potentials, Ni-Cr-Mo alloys may suffer crevice corrosion. Crevice corrosion of mill-annealed Alloy-22 occurs only at potentials above the repassivation potential at chloride-concentrations > 0.5 mol•dm\(^{-3}\) and temperatures > 80 °C [34, 35]. The repassivation potential for crevice corrosion was measured in a series of electrochemical tests as a function of temperature (80 to 150 °C) at various chloride-concentrations (0.1 mmol•dm\(^{-3}\) to 4 mol•dm\(^{-3}\)) by Cragnolino et al. [31]. The repassivation potential was found to decrease with increasing temperature and chloride concentration. For mill-annealed Alloy-22, the steady-state \(E_{\text{corr}}\) in air-saturated solutions was lower than the crevice corrosion repassivation potential, even in relatively acidic solutions. Therefore, it is anticipated that crevice corrosion is unlikely to occur in the mill-annealed material under naturally corroding conditions. He et al. [36] investigated the crevice corrosion propagation behavior of Alloy-22 in 5 mol•dm\(^{-3}\) NaCl solution at 95 °C by adding CuCl\(_2\) to the solution as an oxidant to raise the corrosion potential, forcing crevice corrosion to initiate. The subsequent active propagation of crevice corrosion resulted in a significant decrease in \(E_{\text{corr}}\). At short times, the crevice corrosion penetration rates were several orders of magnitude greater than the passive corrosion rates. For longer times, the penetration rates decreased significantly as a result of repassivation of crevice corrosion as indicated by the decrease in current density. Based on the time-dependent crevice corrosion penetration rates, the maximum penetration depths over a period of 10,000 years were predicted by extrapolation to be in the range from 1.8 to 5.3 mm, which is ~ 9 to 26% of the available wall thickness for the waste package proposed for the Yucca Mountain repository site.
1.2.5 Factors Affecting the Passive Behaviour of Ni-Cr-Mo Alloys

Corrosion is affected by the properties of both the metal or alloy and the environment. In this section, both the properties of the alloy, such as composition and microstructure which change depending on the fabrication process, and environmental variables are addressed. The most important environmental variables are potential, temperature, pH, and anion type and concentration.

1.2.5.1 Effect of Alloying Elements

Although nickel itself provides corrosion resistance to caustic and mildly reducing environments, the addition of large amounts of Mo and Cr greatly increases the corrosion resistance of the alloy. Other small amounts of alloying elements, such as W, Cu, etc, can impart resistance to corrosion in specific environments, but are primarily added to enhance strength, improve ductility, or to help eliminate the formation of precipitates that are detrimental to the corrosion resistance of the alloy.

Empirically, it has been established that the addition of Cr to Ni alloys greatly improves their resistance to strongly oxidizing acids at elevated temperatures. Electrochemical experiments have shown that Cr additions to Ni result in a narrower active region, a lower passive current density, and a wider passive potential range [37, 38]. This enhanced passivity is generally attributed to a concentration of Cr$^{3+}$ in the inner oxide layer that is higher than the Cr content of the alloy [39, 40]. Comparison of the corrosion behaviour of 6 different Ni-Cr-Mo dental casting alloys in deaerated artificial saliva at pH 5 and 37 °C, showed that the Ni-Cr-Mo alloys with higher Cr (~21%) and Mo (~8%) contents had a
much larger passive range in polarization curves and were immune to pitting corrosion, due to the high Cr (maximum ~ 31-35%) and Mo (maximum ~ 12%) contents of the passive film [41].

Many studies of film composition, based on XPS and Auger electron spectroscopy (AES), indicate that the development of this increased corrosion resistance is primarily due to the growth and defect annealing of a Cr(III) oxide barrier layer at the alloy/oxide interface. XPS and scanning tunneling microscopy (STM) have shown that the passive film on Cr, Fe-Cr, Fe-Cr-Ni and Ni-Cr alloys consists primarily of an inner layer of Cr$_2$O$_3$ and an outer layer of Cr(OH)$_3$ [42-44]. Lloyd et al. [4] studied the passive behavior of 5 Ni-Cr-Mo alloys, C22, C2000, C276, C4 and 625, and found much lower passive dissolution currents, and a much slower attainment of steady-state conditions, on those alloys with > 20% Cr content. The surface analysis by XPS and ToF-SIMS showed that the high-Cr alloys were able to build thicker oxides with a layered structure consisting of an inner Cr-Ni oxide layer and an outer Mo/W oxide. By contrast, such a high-Cr content inner layer and structured elemental distribution were not achieved with alloys having a lower bulk Cr content.

These observations are consistent with the percolation model of passivity described by Newman et al. [45], which states that about 16 at.% Cr is required to yield a finite probability of the existence of an ‘infinite’ cluster of oxidized Cr atoms. This occurs by selective dissolution of the base metal, with Cr atoms remaining in their lattice positions. This leads to the formation of Cr-O-Cr chains, and eventually to a highly connected 3-D lattice that protects the underlying Ni from further dissolution [46]. However, Cr enrichment in the film can also occur by the preferential oxidation of Cr, as suggested by
Marcus [43, 47, 48]. Cr is unique in its ability to preferentially oxidize due to the combination of a low metal-metal bond strength and a high heat of adsorption of oxygen. Thus, the energy released by the adsorption of oxygen is enough to disrupt the Cr-Cr bond (allowing for the formation of Cr-O bonds), but not enough to disrupt other alloying elements that have stronger metal-metal bond strengths, such as Mo or W.

The addition of Mo to Ni-Cr alloys leads to increased resistance to both oxidizing and reducing acids [49]. A study on Alloy-22 and two experimental alloys containing different amounts of Cr and Mo showed that the effect of Mo on the passive corrosion rate was more marked for pH < 3, and that low Mo alloys are more susceptible to localized corrosion and harder to repassivate [7]. The investigation of a series of Ni-Cr-Mo alloys in 1.0 mol•dm\(^{-3}\) NaCl +0.1 mol•dm\(^{-3}\) H\(_2\)SO\(_4\) (pH 1) showed that, in the passive region where Cr dissolution can only occur as Cr(III), additional alloying elements, specifically Mo and W, exerted little influence on passive current densities. However, at higher potentials in the transpassive region at which Cr(VI) release appears to start, the presence of Mo, and especially W, in the outer regions of the oxide suppresses passive dissolution due to the low dissolution rate of the W-containing surface oxide layer [4].

Many studies have attempted to determine the mechanism(s) by which Mo improves the resistance to localized corrosion in chloride-containing solutions. Mo appears to be present in the film as Mo(IV) and Mo(VI) identified as hydrated MoO\(_2\) and MoO\(_4^{2-}\). The MoO\(_4^{2-}\) anions are formed in the solid state along with CrO\(_4^{2-}\), which together are responsible for producing a bipolar film consisting of a cation-selective outer layer containing CrO\(_4^{2-}\) and MoO\(_4^{2-}\) and an intrinsically anion-selective inner layer of Cr(OH)\(_3\). The ion selective properties of this duplex film are considered to be largely responsible
for the development of the barrier layer and the resistance to chloride and OH⁻ ingress. Both of these properties provide greater resistance to breakdown of passivity in chloride media [50].

The role Mo plays in passive corrosion behaviour remains an area of debate. A clear correlation between the Mo content and the passive corrosion rate for Ni-Cr-Mo alloys is not obvious [4, 7]. It has been suggested that Mo(IV) replaces Cr(III) in the passive film and enhances the dissolution rate [50, 51]. But according to Bojinov et al. [52], Mo(IV) increases the overall degree of non-stoichiometry in the film, thereby enhancing the number and generation rate of oxygen vacancies, a process which accelerates the dehydration of the Cr-oxide inner boundary layer and enhances passivity. A more generally acknowledged hypothesis, summarized by Clayton and Olefjord [53], postulates that Mo on the alloy surface preferentially locates at local defects, and slows anodic dissolution because of its higher metal-metal bond strength [47].

Some alloys also contain tungsten (W), added to provide solid solution strengthening. In the segregation behavior within the oxide film, it is claimed that W acts in a similar manner to Mo and is predominantly located in the outer regions of the film [4]. The role W plays in the enhancement of passivity has not yet been studied in detail. However the solubility of W in acidic solutions is 2 to 3 orders of magnitude lower than that for Mo [54] and the dissolution rate of a W-enriched oxide surface would be expected to be lower than one simply enriched in Mo. A suppression of film dissolution rate could lead to a lower current density and a greater steady-state oxide film thickness.
There are also other minor elements in the studied Ni-Cr-Mo alloys that are beneficial to improving alloy hardness, strength, resistance to damage from heat-treating operations, or corrosion resistance in a specific medium. For example, Co can improve the strength of the alloy matrix, which is especially beneficial for high-temperature applications. The addition of Mn helps to reduce the levels of sulfur and carbon impurities by combining with them forming carbides and sulphides. Small amounts of Ti, Cu or Nb can be added to improve age hardening strength such that most types of intermetallic and grain boundary precipitates will not form during manufacture [55]. However, Cu can also be added to improve resistance to reducing acids like sulfuric or hydrofluoric. The deposition of Cu on the surface of 316 sintered stainless steel containing 0.25-5.0% Cu was claimed to improve the corrosion resistance [56]. Seo et al. [57] found that Cu had a detrimental effect on the passivity, although Cu and Mo suppress the anodic dissolution of Fe-26Cr in 1 mol•dm$^{-3}$ H$_2$SO$_4$. The beneficial effect of alloying with Cu was attributed to the stability of deposited Cu on an anodic surface. This may be due to the presence of Cu in solid solution and as Cu-rich phases in the matrix of the alloy, and the formation of a Cu-rich surface layer occurs faster than that of any other alloying elements during active dissolution [58]. The morphology of the deposited Cu was found to vary on the surfaces, but a metallic Cu layer was found by most workers [59].

1.2.5.2 Effect of Microstructure

Materials fabrication processes, such as welding and postweld heat treatments, can induce changes to the microstructure. Such microstructural changes can reduce ductility and impact strength, and promote localized corrosion. It was demonstrated that welding and postweld heat treatments extend the range of susceptibility to localized corrosion of
Alloy-22 to less concentrated chloride solutions, lower temperatures, lower potentials, and higher inhibitor-to-chloride concentration ratios [60]. Mill-annealed Alloy-22 does not appear susceptible to crevice corrosion under natural corrosion conditions. However, for Alloy-22 thermally aged and welded at temperatures at which precipitation of intermetallic Mo-rich phases occurs, the repassivation potential decreases compared to that measured on the mill-annealed alloy. Thermal aging for a short time renders the alloy susceptible to crevice corrosion in the form of severe grain boundary attack even at lower chloride concentrations [31]. Published literature attributes this increased susceptibility to localized corrosion of aged Ni-Cr-Mo-W alloys to the dissolution of the Mo-rich phases and the associated Mo depletion in the alloy [61]. However, a recent study on Alloy-22 shows that Cr-rich precipitates formed, resulting in Cr depletion, during the initial stages of aging. As the aging time was increased, topologically close-packed (TCP) phases, enriched in Mo with possible compositions of Ni$_7$Mo$_6$ or Ni$_3$Mo$_2$, formed, resulting in Mo depletion and corrosive attack [62].

1.2.5.3 Effect of Potential

Providing localized corrosion can not occur, the long-term performance of an alloy in an aggressive environment will be determined by its passive corrosion behaviour and how the rate of this process changes with redox conditions. Accordingly, the redox potential will be an important parameter in determining the long-term degradation of the alloy. Since the surface properties will change depending on the applied potential, practical applications of this technique include increasing passivity by altering the surface oxide or preventing corrosion by supplying electrons to the alloy (cathodic protection).
The variation of the oxide properties on Ni-Cr-Mo alloys with potential has been studied in acidic and neutral NaCl solutions. Lloyd et al. [3] determined the chemical composition and thickness of the oxide films formed on Alloy C22 and C276 after exposure at a sequence of temperatures up to 85 °C at different potentials (200, 500 and 700 mV \( \text{Ag/AgCl} \)) in 1 mol•dm\(^{-3} \) NaCl + 0.1 mol•dm\(^{-3} \) H\(_2\)SO\(_4\) (pH 1) using XPS and ToF-SIMS. As discussed above, the oxide film on both alloys consists of a Mo, Cr, and Ni oxide, with Cr present as Cr\(^{3+}\) and Mo present in several oxidation states. In this potential region, the oxide thickness on Alloy C22 was found to increase with increasing anodic potential, but not for Alloy C276. This absence of film thickening was attributed to the absence of a bilayer structure on Alloy C276.

MacDonald et al. [25] characterized the oxide properties on Alloy-22 by electrochemical impedance spectroscopy (EIS) over the potential range from 0 to 900 mV\( \text{SHE} \). The interfacial impedance (polarization resistance, \( R_p \)) under extreme conditions (e.g., pH = 3, saturated NaCl, 80 °C) was of the order of \( 10^5 \) \( \Omega \)•cm\(^2\), commensurate with a high corrosion resistance. The polarization resistance \( (R_p) \) initially increased with applied potential, within the passive range, due to the establishment of the passive oxide layer. At a sufficiently high potential \( (E > 400 \text{ mV } \text{SHE}) \), which is close to the initiation of the transpassive state, \( R_p \) is observed to decrease with increasing potential, due to thinning of the passive film and the oxidative ejection of Cr(VI) from the barrier layer.

More recently, Jakupi et al. [24] characterized the oxide film properties on Alloy C22 by combining EIS with XPS measurements in near neutral pH, 5 mol•dm\(^{-3} \) NaCl solutions, at 30 °C. A similar variation of film resistance \( (R_{\text{film}}) \) with applied potential was observed. For the range -600 mV \( \leq E \leq -300 \text{ mV (vs. Ag/AgCl in saturated KCl)} \), \( R_{\text{film}} \)}
increased with potential accompanied by an increase in Cr$_2$O$_3$ content. Over the range $300 \text{ mV} \leq E \leq 300 \text{ mV}$, $R_{\text{film}}$ values and the Cr$_2$O$_3$ content of the oxide film achieved their maximum values; and for $E > 300 \text{ mV}$, a decrease in both $R_{\text{film}}$ and Cr$_2$O$_3$ was observed accompanied by a significant increase in the Cr(OH)$_3$ content of the surface. At 30 °C in neutral solutions, $R_{\text{film}}$ on Alloy C22 can reach, or even exceed, $10^6 \, \Omega \cdot \text{cm}^2$.

### 1.2.5.4 Effect of Anions in the Electrolyte

Aggressive halide ions, such as chloride, a common anion in aqueous environments, promote the local breakdown of passive films leading to increased metal/alloy dissolution rates which often result in pitting. Several mechanisms have been proposed to explain the effects of chloride on passive film dissolution, all of which assume that initially chloride is adsorbed on the passive film surface [63]. Following chloride adsorption, three mechanisms are possible: (i) penetration of chloride into the passive film, resulting in the accumulation of chloride at the metal/film interface by the formation of metal chloride; (ii) complexation with the surface cations and thinning of the passive film. A high solubility of the complex would enhance the dissolution and cause thinning of the passive film; (iii) the presence of chloride prevents repassivation of a locally depassivated surface and thus allows pitting.

The Ni-Cr-Mo alloys are much more resistant to acidic chloride solutions than stainless steels. Several recent studies have characterized Alloy-22 corrosion in a wide range of NaCl concentrations [25]. The rate of corrosion of the alloy was found not to depend significantly on chloride concentration ($0.001 < [\text{Cl}^-] < 6.2 \, \text{mol} \cdot \text{dm}^{-3}$). A study of a series of Ni-Cr-Mo alloys in HCl solutions yielded corrosion rates dependent on both acid
concentration and temperature. For example, the temperature limit for the use of Alloy C2000 is \( \sim 60 \, ^\circ\text{C} \) with a concentration maximum of 8 wt.% for a maximum allowable corrosion rate of 0.5 mm/y. A comparison of the corrosion performance of several Ni-Cr-Mo alloys in HCl solutions demonstrated the advantage of using Alloy C2000 at concentrations below 10 wt.%. At higher concentrations (< 20 wt.%), the advantages of Alloy-22 are apparent [64].

Other anions, such as nitrate and sulfate, have been shown to inhibit corrosion. The corrosion of Alloy-22 in chloride-containing environments with pH in the range 5 to -1 was found to be significantly inhibited by the presence of nitrate. When compared to pure chloride solutions, corrosion rates were reduced by three orders of magnitude by the addition of relatively small amounts of nitrate (\( \text{NO}_3^- : \text{Cl} = 0.005 \)) [65]. Also, the addition of nitrate to chloride solutions, even at a low nitrate to chloride molar ratio (~ 0.2), results in a significant increase in the repassivation potential, and inhibition of both the initiation and propagation of crevice corrosion [31]. However, depending on the pH and the nitrate to chloride ratio, the complex interactions of nitrate and chloride can maintain Alloy-22 in either the active, passive, active/passive, or transpassive regions [65]. The presence of sulfate was also found to increase the resistance of Alloy-22 to crevice corrosion at temperatures between 45 and 105 °C [66].

**1.2.5.5 Effect of Temperature and pH**

Temperature can affect corrosion in a number of ways. If the corrosion rate is governed completely by the elementary process of metal oxidation, the corrosion rate should
increase exponentially with an increase in temperature, according to the Arrhenius expression:

\[
r = A \exp \left( \frac{-E}{RT} \right)
\]

where \( r \) is the corrosion rate, \( A \) is a preexponential factor, \( E \) is an activation energy, \( R \) is the gas constant, and \( T \) is the absolute temperature.

The effect of temperature on the passive corrosion behaviour of Ni-Cr-Mo alloys has been studied by a number of researchers. Ashida et al. [67] investigated the effect of temperature on the passive properties of Alloy-22 in simulated ground water solutions (pH 9.8) using a temperature-oscillating heated electrode technique. The \( E_{\text{corr}} \) was found to increase linearly from –293 mV to –256 mV (vs. Ag/AgCl in 3.5 mol•dm\(^{-3}\) KCl) when the temperature decreased from 102 °C to 72 °C, and the passive current density was found to be logarithmically proportional to temperature over the range of 65 to 95 °C. Rebak et al. [68] observed a similar linear relationship between corrosion rate and temperature (30 to 90 °C) on Alloy-22 in both deaerated and aerated simulated acidified water (pH 2.8). Using the Arrhenius expression (1.5), the activation energy for corrosion of Alloy-22 in deaerated and aerated solutions was calculated to be 17 and 23 kJ/mol, respectively. Gray et al. [63] found the corrosion rate to be independent of temperature below 50 °C. Between 50 and 90 °C, however, the corrosion rates in sulfuric and hydrochloric acid increased approximately linearly with temperature. This was ascribed to either an increase in the solubility of Cr species in the passive film, or a possible phase change in the passive layer at 50 °C. In a comparison of Ni-Cr-Mo alloys, Lloyd et al. [3] found the temperature dependence of the passive currents on Alloy C22 was significantly
lower than that for Alloy C276 due to a lower oxide dissolution rate compared to the rate of creation of oxygen vacancies leading to film growth on Alloy C22.

The pH is another important environmental variable which influences the behavior of passive alloy surfaces. The hydrogen ion in solutions interacts with the oxidized surface region of the alloy, especially in the outer-most surface layer generally containing hydroxide-like species in aqueous environments. The properties of such a hydroxide-containing surface, such as thickness and composition, would tend to have a dependence on hydrogen ion concentration, possible through a reaction that can be one step in corrosion:

\[ \text{H}_2\text{O} = \text{OH}^{\text{adsorbed}} + \text{H}^+ + \text{e}^- \]  

(1.6)

Thus, the pH can influence corrosion through this equilibrium reaction. Gray et al. [63] investigated the influence of pH on the corrosion of Alloy-22 in strong acidic conditions (from pH 2 to pH – 1). In hydrochloric and sulfuric acids, the critical pH values for corrosion rates to exceed 100 µm/yr (a convenient metric for passive film breakdown) at 60 °C in 1 mol•dm⁻³ NaCl are near pH ≈ 0.5. At 90 °C, the critical pH values shifted to 0.75 and 0.6 for HCl and H₂SO₄ solutions, respectively. In 4 mol•dm⁻³ NaCl solutions, the critical pH values are approximately 2.5 for both hydrochloric and sulfuric acid solutions. The increase in the corrosion rate in hydrochloric and sulfuric acids with the decrease in pH, was attributed to the increasingly thinner passive film until it eventually reaches zero at pH ≤ 0. It has also been noted that the passive current density on Alloy-22 in pH 9.8 solution at 90 °C was almost the same as at 80 °C in pH 1.5 solution [67]. This implies that a 10 °C increase in temperature has the same influence on passive current as lowering the pH value to 1.5.
These studies show that the influence of alloying elements, microstructure, potential, anion type, temperature and pH on the passive current (or corrosion rate) of Ni-Cr-Mo alloys, especially Alloy-22, is only slight. Figure 1.8 provides a summary of the passive properties and localized corrosion behavior of Ni-Cr-Mo alloys [9].

![Diagram of crevice corrosion and passive dissolution](image)

**Figure 1.8** Summary of the passive properties and localized corrosion behavior of Ni-Cr-Mo alloys [9].

### 1.3 O₂ Reduction Kinetics

If localized corrosion damage is to accumulate in aerated solutions, then metal dissolution inside a creviced area must be supported by the cathodic reduction of O₂ on oxide-covered surfaces outside the crevice. This makes a knowledge of the kinetic parameters for oxygen reduction on Ni-Cr-Mo alloys essential for the development of corrosion models [69]. Despite its importance, the kinetics of this reaction have not been
extensively studied on oxide-covered Ni-Cr-Mo alloys. The influence of passive films on O₂ reduction kinetics is known to be complex [70].

It has been firmly established that in aqueous (neutral and alkaline) solutions, the cathodic reduction of O₂ proceeds along one, or both, of the following two pathways [70]:

(a) direct four-electron transfer process,

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad E_{\text{SHE}}^\circ = 0.401\text{V} \quad (1.7) \]

(b) two consecutive two-electron transfer processes involving the intermediate production of hydrogen peroxide

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \quad E_{\text{SHE}}^\circ = -0.065\text{V} \quad (1.8) \]

followed by

\[ \text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^- \quad (1.9) \]

If both pathways are important, the reaction is described as occurring by a parallel mechanism. Also, under some conditions, the decomposition of H₂O₂ on the electrode surface has been found to be significant,

\[ 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \quad (1.10) \]

The reduction pathway is influenced by many factors. On passive Fe, Ni, and stainless steel, the limiting current for O₂ reduction showed a pH dependence which was attributed to the n-type semiconductive nature of the passive film [71]. The kinetics of O₂ reduction on a graphite electrode modified with adsorbed vitamin B₁₂ also exhibited a pH dependence [72]. In alkaline pH, a Tafel slope of \(-60\text{ mV}\text{•}\text{decade}^{-1}\) was obtained, whereas at pH < 10.9, the Tafel slopes changed to \(-120\text{ mV}\text{•}\text{decade}^{-1}\). The O₂ reduction
reaction on the modified electrode seems to occur via parallel 2-electron and 4-electron pathways, with the 4-electron reduction reaction predominating at more acid pH and at more negative potentials.

The kinetics are also affected by electrode surface treatment [73], O₂ reduction rates on stainless steels increased in the order, chemically treated surface < passivated surface < mechanically polished surface < pre-reduced surface. On pre-reduced and polished surfaces, O₂ reduction was mass transport limited. On passivated surfaces, O₂ reduction currents were lower, due either to a limited access of O₂ to the metal surface or to the modified electronic conductivity of the oxide. Surface chemical treatment with HF/HNO₃ inhibited O₂ reduction. The mechanism of O₂ reduction also changes with surface treatment. On the pre-reduced surface, O₂ was reduced via the four-electron pathway (reaction 1.6). On a polished surface, a parallel mechanism is involved, and about 10% ~ 20% of H₂O₂ was formed. On a passivated surface, the mechanism of O₂ reduction has not been identified. The mechanism of O₂ reduction in neutral solutions was found to vary on bare iron and passive iron [74]. The O₂ reduction on bare iron proceeds through 4-electron pathways with little hydrogen peroxide as an intermediate, and the formation of superoxide radical is the rate-determining step. By contrast, on passive iron, O₂ reduction proceeds through a 2-electron pathway with the formation of H₂O₂ as a reaction product, and the rate-determining step was suggested to be the chemisorption of oxygen. Different from Ni, the rate of O₂ reduction on passive iron is greater than that on bare iron due to a strong catalytic effect of the passive oxide film on iron for the O₂ reduction reaction. For example, at pH = 7, the O₂ reduction current is about 100 times higher than that on bare iron.
On Ni-Cr-Mo alloys, the study of O₂ reduction on Alloy C22 and Alloy C276 showed strong evidence for a predominantly series 2 step, 2-electron O₂ reduction pathway, where kinetic rate constants were estimated at 30 °C in the range of 0.001 to 0.232 cm•s⁻¹ depending on the potential [75]. The kinetics of O₂ reduction have also been explored on bare Alloy-22 over wide ranges of pH and temperature [69]. A diffusion limiting current was found for high cathodic potentials at pH ≥ 4. The limiting current density increased over the temperature range from 20 °C to 70 °C, but decreased with a further temperature increase to 95 °C. This was attributed to competition between an increase in the mass-transfer rate with increasing temperature and a considerable decrease in oxygen solubility in the bulk electrolyte at a temperature of 95 °C. A dual-wave polarization curve indicating two consecutive two-electron transfer processes and the formation of the intermediate, H₂O₂, was observed only at 70 and 95 °C. As expected, the limiting current density also depended linearly on the dissolved O₂ concentration, and was virtually independent of solution pH in the range of 4 ≤ pH ≤ 8. Recently, it was found that increased O₂ concentrations resulted in increased $E_{corr}$ and corrosion rates of Alloy 625 in ammoniacal sulfate solution from 25 to 200 °C [76]. The O₂ reduction current became increasingly diffusion controlled as temperature and oxygen partial pressure were increased, reportedly as the barrier layer thickness and resistance decreased with temperature.

1.4 **Research Scope and Objectives**

Despite these efforts, the influence of the oxide film on Alloy-22, and similar Ni-Cr-Mo alloys, on O₂ reduction is poorly characterized. Since surface analytical methods would
advance our understanding of properties of the oxide film which would determine the kinetics of O₂ reduction and the long-term durability of Ni-Cr-Mo alloys, one goal of this project is to investigate the chemical evolution and electronic properties of the passive film on Ni-Cr-Mo alloys, particularly Alloy-22, as a function of applied potential, temperature, pH, and alloy composition using ToF-SIMS and XPS techniques. A second goal is to study the kinetics of O₂ reduction on Ni-Cr-Mo alloys up to 90 °C in a range of environments similar to those anticipated within Yucca Mountain. A number of electrochemical techniques, including the use of rotating disc electrodes (RDE) and EIS, were employed to measure the influence of environment and alloy substrate composition. The overall goal is to determine kinetic relationships that can be used in models to predict the damage due to crevice corrosion. By analyzing the kinetics behaviour based on surface analytical measurements, we are able to link the corrosion processes to compositional and structural changes that occur within the oxide film. Then it is possible to develop a mechanistic understanding of the mechanism of O₂ reduction on Ni-Cr-Mo alloys.

### 1.5 Reference


Chapter 2
General Experimental

2.1 Introduction

In this chapter, the principles of the electrochemical and surface analytical techniques employed in this project are briefly reviewed. Also the general details of experimental preparation, setup, and procedure are also described. However, the specific details of sample preparation and the values of parameters for specific experiments are given at the beginning of the individual chapters.

2.2 Electrochemical Experiments

2.2.1 Electrochemical Cell Set-up

A standard three-electrode, glass electrochemical cell was used for all experiments, Figure 2.1. The cell contains a working electrode (WE), a pure platinum (99.95% purity) counter electrode (CE) and an in-house fabricated silver/silver chloride (Ag/AgCl) reference electrode (RE) in saturated KCl solution (199 mV vs. SHE at 25 ºC). The last two electrodes are separated from the main body of the cell by porous frits. A Luggin capillary was employed to minimize the ohmic potential drop due to solution resistance between the reference and working electrodes. The cell has an outer jacket through which silicon oil or deionized water is circulated from a thermostatic bath (Isotemp 3016H, Fisher Scientific) to maintain the temperature of the solution to within ± 1 ºC. The cell
was housed in a grounded Faraday cage to minimize noise from external sources during measurements.

All electrochemical experiments were conducted using a Solartron 1287 potentiostat and a Solartron 1255 frequency response analyzer (FRA) (for EIS experiments), except for the long-term film growth experiments which were performed using a Solartron 1480 MultiStat. Corrware and Zplot software (for EIS) (Scribner Associates) were used to record and analyze the data. Except for the long-term film growth and EIS measurements, experiments were conducted using a rotating disc assembly to eliminate diffusion effects at the electrode surface. An analytical rotator (Pine Instruments) with an ASR speed

![Diagram of the electrochemical cell.](image)

**Figure 2.1** Diagram of the electrochemical cell.
control device was used to control the rotation rate. Generally, a rotation rate of 23.3 Hz was used.

### 2.2.2 Electrolyte (Solution) Preparation

5 mol dm\(^{-3}\) NaCl solutions were used in all experiments to simulate the saline conditions anticipated within the Yucca Mountain waste disposal site. The solutions were prepared from reagent grade NaCl and ultra-pure deionized water (resistivity of 18.2 MΩ cm) obtained from a Milli-Q Academic A-10 system. A fresh solution was used for each experiment. Prior to starting each experiment, the electrolyte solution was purged for at least one hour in either Grade 4.4 oxygen (for all aerated experiments) or UHP argon (Praxair) (for all deaerated experiments); purging was then continued throughout the experiment. The solutions were maintained at pH 7 throughout the experiment by adding 0.1 mol dm\(^{-3}\) HCl and NaOH solutions as required, and monitoring the pH using a pH meter (Orion Model 250A, Thermo Electron Corp.).

### 2.2.3 Electrode (Sample) Preparation

Working electrodes were cylindrical specimens cut from plate materials with a diameter of 1 cm and a height of 0.5-1 cm (alloy compositions are given in Table 1.1). The cylinders were drilled at one end to allow electrical connection to a threaded rod of the same material. Each specimen was encased in a heat-resistant epoxy resin (Dexter Hysol resin EE4183, hardner HD3561) so that only the end surface was exposed to the electrolyte. This yielded the flat disc surface (total surface area of 0.785 cm\(^2\)) required for rotating disc and EIS experiments. Before each experiment, the electrode was
polished sequentially with 180, 240, 320, 600, 800, 1000 and 1200 grade silicon carbide paper, and then ultrasonically cleaned for ten minutes in methanol and finally in deionized water.

2.3 Electrochemical Experimental Methods

2.3.1 Rotating Disk Electrode (RDE)

Electrochemical reactions can only occur at the electrode/solution interface. For reversible reactions, the equilibrium potential is set by the steady-state concentrations of the oxidants and reductants at the interface via the Nernst Equation [1]. Due to the consumption (or production) of electroactive species at the electrode surface, the concentrations of the species in bulk solution and at the interface differ. There are three possible modes of mass transport of electroactive species between the bulk solution and the interface: diffusion, electrical migration and convection. Diffusion is a movement of chemical species down a concentration gradient established by the electrochemical reaction, and the rate of diffusion (the flux) is proportional to the concentration gradient according to Fick’s first laws of diffusion [1]. Migration is the movement of charged species in the electrical field established by the gradient in potential in the solution, and can be eliminated by using a large excess of supporting electrolyte whose ions then carry the charge in the electric field. Contrary to diffusion and migration when transport of the species occurs from one location in solution to another by a molecular mechanism, in the case of convection the movement of whole volume elements of solution takes place. Forced convection is usually applied to enhance the rate of the mass transport process, which can be achieved by stirring the solution with the help of a separate stirrer, or the
electrode itself can rotate (rotating disk electrode, RDE). At the surface of a rotating electrode, a steady-state concentration-distance profile is established and the Nernst diffusion layer approximation can be employed. This diffusion layer treatment assumes a transition point between the bulk of solution where a uniform concentration is maintained by convection, and the diffusion layer within which a concentration gradient exists. In reality, the transition from the convective to diffusive regime is not so sharp as shown in Figure 2.2. However, it is a reasonable approximation to take the distance from the electrode surface to this transition as the diffusion layer thickness ($\delta$), Figure 2.2.

![Diagram](Image)

**Figure 2.2** Diagram of the steady-state concentration gradient established near the electrode/solution interface at a constant electrode rotation rate.

Under forced convection conditions at a RDE a vortex is created, such that the solution continuously flows up towards the surface of the electrode and is pushed out towards the
edges of the electrode and surrounding epoxy. Stable laminar flow is achieved across the electrode surface and turbulence is limited to the edges of the epoxy rather than on the surface of the electrode. Under these conditions a steady-state concentration gradient is established with a thickness ($\delta$) given by

$$\delta = 1.61D^{2/3} \omega^{-1/2} v^{1/6}$$  \hspace{1cm} (2.1)

where $D$ is the diffusion coefficient of reactant species (cm$^2$•s$^{-1}$), $v$ is the viscosity of the solution (cm$^2$•s$^{-1}$), and $\omega$ is the rotation rate of the electrode in radians/s. An increase in $\omega$ reduces $\delta$, and increases the concentration gradient and hence the flux of the reactant to the surface. If the rate of mass-transport is increased to a sufficiently high value by enhanced convection, the surface concentration approaches the bulk concentration, and the current becomes controlled by the interfacial electrochemical kinetics. Under these conditions, the kinetics of the charge transfer reaction can be measured.

The RDE is one of the few electrode systems for which the convective-diffusion equations have been solved for the steady state. Levich analyzed the hydrodynamics at a rotating disk and determined that the mass transfer limited current, achieved at high overpotentials (when $c_s = 0$), $j_L$, is directly proportional to the bulk concentration of the species, $c_b$, and given by the following equation [2],

$$j_L = 0.620 nFAD^{2/3} \omega^{1/2} v^{-1/6} c_b$$  \hspace{1cm} (2.2)

where $n$ is the number of electrons transferred, $F$ is Faraday’s constant, $A$ is the electrode area (cm$^2$), and $c_b$ is the bulk concentration of the reactant (mol•cm$^{-3}$). In this project, a constant rotation rate of 23.3 Hz was used (beyond which the current is independent of the rotation rate) during potentiostatic polarization and cyclic voltammetric experiments.
The Levich equation was then used to calculate the maximum oxygen reduction current assuming mass transport control. These currents were then compared to the measured cathodic currents.

### 2.3.2 Corrosion Potential ($E_{corr}$) Measurements

$E_{corr}$ is the measured potential difference between the working electrode and the reference electrode, when no external potential is applied to the system; i.e., it is the potential under open circuit or natural corrosion conditions. In the absence of an externally applied potential or current, the corrosion reaction is a short-circuited electrochemical reaction with both half reactions occurring on the electrode surface. The electrons generated by the anodic metal oxidation are consumed by the cathodic reduction reaction. Thus, the cathodic reaction provides the driving force for the corrosion process. In this project, the cathodic reactions are oxygen reduction and/or water reduction (proton reduction in acidic solutions). Metal dissolution of alloys containing various alloying elements is complicated since more than one metal cation is produced. On passive alloys, the transferred electrons must pass through the passivating oxide film to the cathodic reactant at the film/solution interface.

As illustrated in Figure 1.6 in Chapter 1, for metal dissolution (oxidation) coupled to one or more cathodic reactions, $E_{corr}$ represents the potential at which the anodic and cathodic currents are equal but opposite in sign and represent the corrosion current ($i_{corr}$). The value of $E_{corr}$ is determined by the type and kinetics of the redox reactions involved, the concentrations of redox species present, and the reactivity of the working electrode surface. Even though a metal/alloy may be capable of exhibiting passivity, the location of
$E_{corr}$ in the polarization curve of the passive metal/alloy, illustrated in Figure 1.5 in Chapter 1, will determine the corrosion rate. For naturally passive metals/alloys, $E_{corr}$ is sufficiently positive to maintain a protective passive oxide on the metal/alloy surface. However, if the solution is insufficiently oxidizing, then $E_{corr}$ may shift to low positive potentials and the corrosion rate increase. If a sufficiently high concentration of a strong oxidant is present, then $E_{corr}$ may increase to a value at which oxidizable elements in the alloy are unstable, and this would be expected to destroy, at least partially, the passive oxide film leading to an increase in corrosion rate.

$E_{corr}$ measurements cannot provide quantitative information about the corrosion rate, only a qualitative comparison of the dependence of the specific material corrosion on experimental perimeters such as the concentrations of oxidant species, temperature and pH. In this thesis, changes in materials and solution temperature in aerated and deaerated solutions cause changes in $E_{corr}$. A decrease in $E_{corr}$, as stated above, indicates that a material is approaching the active state and thereby the corrosion rate would be expected to increase.

### 2.3.3 Potentiostatic Polarization Experiments

Polarization experiments can be performed either potentiostatically or potentiodynamically. In this project, most of the electrochemical data was collected in potentiostatic polarization experiments, in which a constant potential is applied to the working electrode, held for a specific time, and the resulting current recorded as a function of time. Potentials were chosen depending on the purpose of the experiments; for instance, a very low potential (–1 V) was applied to remove any oxide film and clean
the electrode surface. Higher potentials were chosen to grow passive or transpassive films, and to produce the films anticipated under natural corrosion conditions.

During potentiostatic polarization experiments employed in this project, a constant potential was applied for one hour (two hours for Electrochemical Impedance Spectroscopy (EIS) measurements) and the current recorded. Then the potential was increased (or decreased) to the next constant potential, and the current again recorded (illustrated in Figure 2.3). The nearly steady-state currents recorded were then plotted as a function of applied potential in the form of a potentiostatic polarization curve. In this project, potentiostatic polarization experiments were performed on a series of Ni-Cr-Mo alloys over the temperature range of 30-90 °C. During this set of experiments, a rotating disc electrode (RDE) with a constant rotation rate of 23.3 Hz was used to eliminate diffusion effects at the electrode surface.

![Figure 2.3](image-url)  
**Figure 2.3** Potential-time profile for potentiostatic polarization experiments.
Potentiodynamic polarization curves were generated on pure metals (Ni, Cr and Mo) by sweeping the potential from a value below $E_{\text{corr}}$ to another positive value at a scan rate of 0.1667 mV$\cdot$s$^{-1}$, and recording the resulting current point by point as a function of the applied potential. These polarization scans give an overview of the general corrosion properties of different metals and were performed in stagnant solutions, and used to identify the potential regions of reactivity for each metal in this project.

### 2.3.4 Cyclic Voltammetry (CV) Experiments

CV is a commonly employed technique which measures the current response of an electrode to a linearly increasing and decreasing potential [3]. The experiment is usually started at an initial potential at which the electrode process of interest does not occur and the potential scanned at a fixed scan rate to the switching potential and back. When an electrochemically active compound is present in the solution, or the electrode is electrochemically oxidizable, an anodic (positive) current is detected during the anodic scan (from the low initial potential to the high switching potential). When the potential is swept back to the initial potential, a cathodic (negative) current may be observed. Cyclic voltammetry is an excellent technique to survey the reactivity of materials and can provide information on the following: (i) the potential at which oxidation or reduction processes occur, (ii) the oxidation state of the redox species, (iii) the number of electrons involved, (iv) the rate of electron transfer, (v) possible chemical processes associated with the electron transfer, and (vi) adsorption effects [4, 5].

CV experiments were employed in this project to examine the reactivity of the oxide film formed potentiostatically on Ni-Cr-Mo and Ti alloys. The potential profile used in CV
experiments is shown in Figure 2.3. First, air-formed oxides were removed at very negative potential (–1 V) and an oxide film then grown potentiostatically. Starting at the film-growth value, the potential was then swept in the negative direction at a constant scan rate (v_s = 5 mV\textperiodcentered s^{-1}) (forward scan). At a certain potential (the cathodic limit, –1 V), the scan was reversed, and continued in the positive direction until the film-growth potential was again reached (reverse scan). During the forward scan, the reduction of species in the film, dissolved oxygen and/or water take place in different potential regions yielding negative currents, while re-oxidative processes yield positive currents during the reverse scan. As in the potentiostatic polarization experiments, a rotating disc electrode (RDE), rotated at a constant rate of 23.3 Hz, was used to eliminate diffusion effects at the electrode surface.

![Diagram of potential-time profile](image)

**Figure 2.4** The potential-time profile used in experiments involving potentiostatic oxidation followed by cyclic voltammetry.
2.3.5 *Electrochemical Impedance Spectroscopy (EIS)*

EIS is a steady-state technique used to measure the electrical properties of an electrode/electrolyte interface. In an EIS experiment, a sinusoidally fluctuating potential perturbation is applied to an electrochemical system

\[ E(t) = E_0 \sin(2\pi ft) \]  

(2.3)

where \( E(t) \) is the potential at time \( t \), \( E_0 \) the amplitude of the potential signal, and \( f \) the frequency of the sine wave, and the corresponding sinusoidal current response (\( j(t) \)) at the same frequency is measured,

\[ j(t) = j_0 \sin(2\pi ft + \theta) \]  

(2.4)

where \( j_0 \) is the amplitude of the current, \( \theta \) the phase difference between the potential and current signals. If the magnitude of the perturbation is small, then the system steady state is not significantly disturbed by the EIS measurement. The transfer function relating the perturbation and response measured as a function of frequency, is the system impedance represented in a manner similar to Ohm’s law,

\[ Z = \frac{E(t)}{j(t)} = \frac{E_0 \sin(2\pi ft)}{j_0 \sin(2\pi ft + \theta)} \]  

(2.5)

The impedance can also be expressed in terms of real and imaginary components of impedance,

\[ Z = Z' + iZ'' \]  

(2.6)

where \( Z' \) is the real (in-phase) component, \( Z'' \) is the imaginary (out of phase) component and \( i = \sqrt{-1} \). The modulus of the impedance is given by:

\[ |Z| = \sqrt{(Z')^2 + (Z'')^2} \]  

(2.7)
and the phase angle $\theta$ is:

$$\theta = \tan^{-1}\left(\frac{Z''}{Z'}\right) \quad (2.8)$$

An EIS measurement is typically performed over a large range of frequencies covering several decades, from mHz to hundreds of kHz. The measured impedance spectrum can be presented as either Nyquist plots ($-Z''$ vs. $Z'$) or Bode plots ($\log|Z|$ and $\theta$ vs. $\log(f)$). Bode plots have the advantage of showing the full range of frequency information, while Nyquist plots emphasize the low frequency behaviour, which is generally the most important range for corrosion reactions. Both Nyquist and Bode plots will be used in this project.

The interpretation of measured impedance data is carried out either by their comparison to predictions of a theoretical model based on the integration of coupled charge-transport equations, or by fitting to an electrical equivalent circuit, in which the electrical parameters are determined by fitting theoretically calculated impedance plots to the experimentally measured values. The results of this analysis are accepted if the deviation is sufficiently small [3], and the parameter values obtained are meaningful.

In this project, impedance data were obtained immediately after each potential step in a potentiostatic polarization experiment (Figure 2.3). The current response was measured at individual potential input frequencies, using a Solartron 1287 potentiostat coupled to a 1255B Frequency Response Analyzer (FRA) running Zplot software from Scribner Associates. The AC potential stimulus was set at an amplitude of 10 mV and applied sinusoidally over the frequency range 100 kHz to 0.005 Hz. The self-consistency of the
measured spectra is tested with the use of the Kramers–Kronig transformations [6,7] whose violation indicates the studied system is not at steady-state.

The data was interpreted by fitting to an equivalent electrical circuit comprising a number of circuit elements, such as resistors and capacitors. A resistor is independent of frequency and possesses only a real component, so that the current through it is always in phase with the applied potential. Capacitors have only an imaginary component and the current phase shift is $-90^\circ$ with respect to the input potential. A system that has both resistive and capacitative attributes can be described as having a time constant, $\tau$, which is the product of the measured resistance and the capacitance ($\tau = RC$). An example of a simple equivalent circuit that can represent an oxide-covered alloy is shown in Figure 2.5.

![Simple equivalent circuit model representing an oxide-covered alloy.](image)

**Figure 2.5** Simple equivalent circuit model representing an oxide-covered alloy.

This circuit consists of a solution resistance ($R_s$), an oxide film resistance ($R_f$) and an oxide film capacitance ($C_f$). The value of $C_f$ can be used to calculate the film thickness (providing a value of the oxide dielectric constant is available), and $R_f$ is a measure of the passivity of the oxide layer.

The capacitors in interfacial equivalent circuits often do not behave ideally (i.e. the phase shift is not $-90^\circ$). A common reason for this is surface roughness which leads to frequency dispersion. To compensate, constant phase elements (CPE) are commonly used
in place of pure capacitors. The impedance of a CPE is given by:

\[
Z = Z_0 (i2\pi f)^{-n}
\]  

If \( n = 0 \), then the CPE represents a resistor; while if \( n = 1 \), the CPE represents a capacitor. In this project, all capacitors are modeled as CPEs, and hence values of both the CPE and the exponent, \( n \), are reported in fitting results.

A two time-constant circuit, Figure 2.6, may sometimes be required to account for the occurrence of electrochemical reactions at either the alloy/oxide or the oxide/solution interface. In this circuit \( R_1 \) represents the charge transfer resistance of the interface and CPE\(_1\) is the constant phase element used to represent the interfacial capacitance. Several reactions are possible on the oxide-covered alloys used in this project, including oxidation of alloying elements at the alloy/oxide interface, oxidation of cations in the oxide film to soluble higher oxidation states, and reduction of oxygen and/or water at the oxide/solution interface. Overall, analysis of the resulting impedance spectra allows the electrical properties of the oxide film to be determined.

![Figure 2.6](image)

**Figure 2.6**  A two time-constant equivalent circuit representing an oxide-covered alloy.

### 2.4 Surface Analytical Techniques
2.4.1 Scanning Electron Microscopy (SEM) and Energy-dispersive X-ray Spectroscopy (EDX)

SEM is the most widely-used analytical technique to provide high resolution images of surface topography, with excellent depth of field. In SEM, a highly-focused primary beam of electrons, with an energy of 0.5 to 30 kV, is focused on a surface and generates many low energy secondary electrons (< 50 eV), whose intensity is primarily governed by the surface topography of the sample. By measuring the intensity of these secondary electrons as a function of the position of the primary electron beam, an image of the sample surface can be constructed. When combined with an ion beam (usually gallium) milling system utilizing a finely focused ion beam (FIB), an in-situ cross-sectional image of a sample can be obtained. High spatial resolution is possible for SEM when the primary electron beam is focused to a very small spot (< 10 nm), and, when using a primary electron beam with an energy of < 1 kV, a high sensitivity to topographic features on the outermost surface (< 5 nm) can be achieved.

In addition to low energy secondary electrons, backscattered electrons (BSE) and X-rays are also generated by the primary electron bombardment. The intensity of backscattered electrons is correlated to the atomic number of the element in the sample. Hence, some qualitative elemental information can be obtained. More quantitative elemental information can be achieved by Energy-dispersive X-ray spectroscopy (EDX). EDX is an analytical technique used for the elemental analysis or chemical characterization of a sample. The characterization capabilities of EDX are due to the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of
an element's atomic structure to be identified uniquely from one another. By measuring the characteristic X-rays from a specimen in response to irradiation with the incident beam of primary X-rays using an energy-dispersive spectrometer, the elemental composition of a specimen can be determined.

In this project, a Leo 1540 FIB/SEM with CrossBeam (Zeiss) and EDX system (Oxford Instruments) at Western Nanofabrication Facility, and a Hitachi S-4500 field emission SEM equipped with an EDAX™ EDX system at Surface Science Western were used to investigate the surface topography and composition of Ni-Cr-Mo and Ti alloys.

2.4.2 Scanning Electrochemical Microscopy (SECM)

SECM is a surface analytical technique which can determine local chemical information on a microscopic scale. It has been developed for a wide range of applications in the area of chemical activity imaging, due to its ability to probe interfacial electron and ion transfer processes occurring nonuniformly at interfaces [8, 9]. It works by measuring a current on an ultramicroelectrode (UME) immersed in a solution containing an electroactive species (commonly termed a redox mediator) and located in close proximity to a reactive substrate surface. A typical SECM set-up is shown in Figure 2.7 [10]. It uses a piezoelectric based positioner and controller to precisely position the UME (tip) in any of 3 axes at a known scan speed (typically 1 to 20 µm•s⁻¹). A bipotentiostat is employed to simultaneously control the potential of both the tip and the substrate against the reference electrode and to monitor the Faradaic current flow. Hardware on the PC supplies control
signals to the piezo-positioner and collects data from the tip and substrate.

The UME is usually either a conductive disk of noble metal (such as Pt and Au) or a carbon fiber, with a diameter ranging from 2 to 25 µm, set in an insulating sheath of glass. Substrates can be a variety of solid surfaces (such as metals) which perturb the electrochemical response of the tip, and this perturbation provides information about the nature and properties of the substrate and how they vary with position on the substrate surface. In practice, the UME is set at a sufficiently large potential where the tip current is controlled by diffusion of the electroactive species. For a disk-shaped UME, the diffusion-limited current \( j_{T,\infty} \) can be calculated from the relationship [11]:

\[
j_{T,\infty} = 4nFDC_0a
\]  \hspace{1cm} (2.10)

where \( c_0 \) is the concentration of species in the electrolyte, and \( a \) is the tip radius.

**Figure 2.7** Typical SECM set-up.
The most frequent mode of operation of SECM is the feedback mode, where only the tip current is monitored [11]. When the tip approaches closely to a flat substrate, diffusion of the species from the bulk solution to the tip is blocked and the tip current becomes inherently related to the electrochemical activity of the substrate. When the tip is approaching an insulating substrate, the tip current should noticeably decrease (negative feedback) since the concentration of electrochemically active species is limited. However, for a conductive substrate, the tip current should increase due to a regeneration current at the tip (positive feedback). Figure 2.8 illustrates these feedback modes in SECM.

For a substrate with different reactive sites, SECM measurements can be performed by scanning the UME tip laterally across the substrate surface to acquire SECM images. The surface is scanned with the UME tip at an initially fixed separation (i.e., in the constant height mode). However, due to surface topography the tip to substrate separation varies as the scan is performed. Consequently, the tip current contains information on both the surface reactivity and the topography. However, probe approach curves (PACs) can be

![Figure 2.8](image-url)  
**Figure 2.8** Illustration of feedback modes in SECM.
recorded at specific surface sites to separate the influences of topography and localized reactivity. A PAC is produced by recording the normalized current versus normalized distance as the tip approaches a surface site.

In this project, SECM was used in the constant height mode to examine the surface reactivity of a passive Ti alloy. The UME is a 5 µm diameter disk-shaped Pt electrode insulated in a glass sheath with an RG value of 6 (the ratio of the radius of the insulating sheath to the radius of the conductive disk). Ferrocenemethanol (0.9 mmol•dm⁻³) was used as the redox mediator in 0.1 mol•dm⁻³ NaCl solution.

### 2.4.3 X-ray Photoelectron Spectroscopy (XPS)

#### 2.4.3.1 Principles of XPS

XPS, also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a surface sensitive technique that provides the chemical composition (atomic percentage of each component) and the oxidation states elements in material surfaces. It is based on the photoelectric effect, and measures the energies of photoelectrons emitted from atoms when they are irradiated by soft X-ray photons (1 - 2 keV) [12, 13]. When a sample is irradiated with x-rays of known energy, \( hv \), electrons with a binding energy, \( E_b \), are ejected from atoms with a kinetic energy, \( E_{\text{kin}} \) (Figure 2.9) [14]. The relationship between the binding energy and the kinetic energy of the emitted electron (photoelectron) is dictated by the conservation of energy:

\[
E_b = hv - E_{\text{kin}} - W_f
\]

where \( W_f \) is the spectrometer work function.
Figure 2.9  Schematic representation of photoelectron generation in XPS.

XPS has a number of powerful attributes, including a high (and variable) range of sensitivities to structures on the outermost surface (outer few nanometers) of the solid. This surface sensitivity is due to the low inelastic mean-free path (IMFP) of the photoelectrons within the sample, which is between 0.5 and 3.0 nm for most photoelectrons of interest (Figure 2.10) [15, 16]. This makes the technique ideal to study thin films on passive alloys.

A typical XPS spectrum is generated by plotting the measured photoelectron intensity as a function of $E_b$, which corresponds to the characteristics of specific elements in the sample. In addition, the intensity (or area) of the peaks is related to the concentration of that element. Hence, using the peak intensity (or area) and a sensitivity factor for each element, which is an empirically determined factor that sums up all instrumental factors, this technique can provide a relative measure of surface chemical composition. Of particular value is the ability of the technique to measure binding energy variations for an element resulting from different chemical environments and/or oxidation states (chemical
shifts). Distinct chemical states, which are close in energy, can be deconvoluted by obtaining high-resolution spectra and using peak fitting programs to give the percentage of each oxidation state. XPS was used in this project to obtain quantitative analyses of oxide film compositions and the oxidation states of components in the oxide film.

### 2.4.3.2 Angle-resolved XPS (AR-XPS)

Non-destructive XPS profiling techniques are based on either the energy or the emission angle dependence of the mean escape depth (or IMFP) of the emitted electrons. The basis of the angle dependent profiling method is the dependence of escape depth on the angle of the incident beam, Figure 2.11 [17]. It has been shown theoretically by a Monte Carlo simulation [18], and proved experimentally [19], that the intensity of ejected electrons through a medium with no energy loss follows an exponential decay function, i.e.

![Figure 2.10](image)

**Figure 2.10** The inelastic mean free path (escape depth) for various elements as a function of kinetic energy.
\[ I(d) = K \int_{0}^{d} \exp\left(\frac{-x}{\lambda \cos \theta}\right)dx \]  \hspace{1cm} (2.12)

where \( I \) is the electron intensity after traveling a distance \( x \), \( d \) is the depth, \( K \) is a constant related to the instrument, \( \theta \) is the photoemission angle as defined in Figure 2.11, and \( \lambda \) is the photoelectron attenuation length (IMFP). It can be calculated from the integral of this equation that 95% of the information obtained by XPS comes from a depth within three times the IMFP (typically < 5 nm) (assuming \( \theta \) is 0), a distance sometimes referred to as the “sampling depth”. For a given electron energy, at higher photoemission angles, the information is obtained from shallower depths than at lower photoemission angles (as illustrated in Figure 2.12). By varying the photoemission angle, therefore, the effective "sampling depth" can be varied, since the emerging photoelectrons travel through more material at the higher photoemission angles, and only those photoelectrons originating from closer to the surface escape with no energy loss [17]. The most important application of angle resolved XPS (AR-XPS) is in the estimation of the thickness of thin films e.g. contamination, implantation, sputter-altered

![Figure 2.11](image.png)

Figure 2.11  The illustration of photoemission angle (\( \theta \)) in XPS.
Figure 2.12  Schematic representation showing the effect of photoemission angle ($\theta$) on sampling depth in XPS.

and segregation layers [20]. A good reference for the underlying principles and applications of AR-XPS can be found in the book by Briggs and Seah [21].

In this project, two photoelectron take-off angles (measured from the sample surface, 90 – $\theta$), 30º and 90º, were used to analyze the oxide film on Alloy C2000. By comparison of the information obtained at a grazing take-off angle (30º) to that at an angle close to the surface normal (90º), information on the variation of composition with depth can be obtained.

All AR-XPS analyses were carried out with a Kratos Axis Ultra spectrometer using a monochromatic Al Kα source (15 mA, 14 kV). The instrument work function was calibrated to give an Au 4f 7/2 metallic gold binding energy of 83.95 eV. The spectrometer dispersion was adjusted to give a binding energy of 932.63 eV for metallic Cu 2p 3/2. The Kratos charge neutralizer system was used for all the analyses. High-resolution spectra were obtained using a 20 eV pass energy, whereas survey spectra were recorded using a 160 eV pass energy with an analysis area of ~ 300 μm × 700 μm.
2.4.3.3 Synchrotron Radiation XPS (SR-XPS)

Synchrotron radiation is a photon light source generated by high-energy electrons that are centripetally accelerated in the magnetic fields of a storage ring, as shown in Figure 2.13 [22]. This radiation is extremely intense over a broad range of wavelengths extending from the infrared through visible light and ultraviolet into the soft and hard x-rays of the electromagnetic spectrum, which can be used in a wide range of analytical techniques. As an alternative x-ray source, synchrotron radiation has several advantages over conventional sources: (i) the brightness and intensity are very high, many orders of magnitude more than with X-rays produced in conventional X-ray tubes, and, hence the resolution can be very high; (ii) the radiation is highly polarized; and, (iii), most importantly, the photon energy can be changed. The wide tunability in energy allows

![Schematic diagram of the acceleration of electrons in a storage ring and the emission of synchrotron radiation](image)

Figure 2.13 A schematic diagram of the acceleration of electrons in a storage ring and the emission of synchrotron radiation [22].
peaks in an x-ray spectrum to be shifted to exactly the kinetic energy required. In practice, this is often the energy where the mean free path of the electrons is shortest. Hence, by varying the excitation energy at constant photoelectron emission angle, and therefore controlling the kinetic energy, depth profiling is possible.

In this project, SR-XPS was used to investigate the oxide film composition and the variation of this composition with depth of the film on Alloy C22 polarized at 0 V by varying the incident beam energy. The SR-XPS experiments were performed at the spherical grating monochromator (SGM) undulator beamline at the 2.9 GeV third generation Canadian Light Source (CLS). The energy resolution (ΔE/E) of the beamline is 10^{-4} with a flux of > 10^{11} photons/s at the photon energy range of 250-1500 eV. The incident photons were set at 30º to the sample. The resolution of the Scienta 100 electron energy analyser was determined to be 0.1 eV at the pass energy of 100 eV used for this experiment. The incident energies used were 700, 1000, 1200 and 1500 eV, respectively.

2.4.3.4 XPS Data Analyses

All XPS spectra were analyzed using CasaXPS software [23] (version 2.3.16). All spectra were calibrated using the main peak of the C 1s spectrum with a fixed value of 284.8 eV. After calibration, the background from each spectrum was subtracted using a Shirley-type background correction. All survey scans were analyzed to determine the surface composition by using the appropriate sensitivity factors. The high-resolution spectra were fitted using a set of fitting parameters including the full width at half-maximum (FWHM), peak separation, and peak ratios obtained from reference spectra recorded on
reference materials and/or from the literature to obtain the information on oxidation states and the relative compositions for each element.

2.4.4 Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)

2.4.4.1 Principles of ToF-SIMS

ToF-SIMS is a surface analytical technique that uses an ion beam (primary ions) to remove small numbers of atoms and molecules from the outermost layer of a surface and analyzes those that are ionized (secondary ions). A short pulse of primary ions strikes the surface and the secondary ions produced in the sputtering process (illustrated in Figure 2.14) are extracted from the sample surface into a time-of-flight mass spectrometer.

![Figure 2.14 Schematic representation of the SIMS sputtering process.](primary ion beam)

These secondary ions are dispersed in time according to their velocities (which are proportional to their mass/charge ratio (m/z)). Discrete packets of ions of differing mass are detected as a function of time at the detector. In general, the inherent sensitivity of mass spectrometry-based techniques, which is a consequence of the low background that
exists between secondary ions with mass:charge ratios that only differ by a fractional mass unit, gives SIMS a major advantage over other methods of analysis of thin films. ToF-SIMS is capable of detecting ions over a large mass range of 1 to 10,000 atomic mass units at a mass resolution \( \frac{m}{\Delta m} \) of 10,000. The technique is also capable of generating an image of lateral distributions of these secondary ions at spatial resolutions of better than 0.15 microns.

A dual beam mode of operation in ToF-SIMS was used in this project to study the lateral distribution of the thin oxide films on Ni-Cr-Mo and Ti alloys. A very low energy (1 keV) Bi\(^{3+}\) ion beam, with a target current in the range of ~7-8 nA, was employed in the dual beam mode to create a sputter crater, while the analysis of the secondary ions was performed with a higher energy (25 keV), finely focused, monoisotopic \(^{69}\)Ga\(^+\) ion beam. This helps maintain the integrity of the oxide during analysis, allowing for the elucidation of both chemical and structural information. The main advantage of this technique is that a finely focused Ga ion gun achieves a smaller beam allowing for better lateral resolution. In addition, the heavier Bi\(^{3+}\) beam more quickly erodes the surface and enhances the yield of negative secondary ions, which are the ions of interest emitted from an oxide film (e.g., NiO\(^-\)). By using separate beams for erosion and analysis, each beam is specifically suited to its task. This results in high elemental sensitivity and the ability to quickly erode through the surface to obtain the depth profile while maintaining excellent depth resolution, and allows for ultra shallow depth profiling within a passive oxide film to be performed on the nanometer scale [24, 25].

One disadvantage is that the depth scale cannot be quantified due to matrix effects. In a complex structure, such as a Ni-Cr-Mo oxide in which multiple components coexist,
there is a rapid succession of different matrices within a profile. This makes it difficult to accurately determine the depth resolution and depth scale for all components individually, since the sputter rates vary depending on the matrix being analyzed. Also, since standards to match the complex oxide matrix on an industrially made alloy cannot be obtained, the secondary ion intensities cannot be calibrated with any oxide mixtures of known composition. Therefore, the changes of intensity observed as a function of sputtering time in this project should be considered only qualitative.

Another disadvantage of this technique is that, while the low beam current allows for the elucidation of the chemical nature of species in the oxide, more specific characteristics, such as the oxidation state of an ion, cannot be determined. For instance, while a high intensity of \( \text{CrO}_3^- \) clusters detected by the mass spectrometer indicates that Cr was bonded to oxygen in the film, it does not indicate that the oxidation state was +6. Other techniques, such as XPS, are more suited for determining oxidation states of atoms within the oxide film.

Dynamic SIMS is another mode of operation. Operated in dynamic mode, the sputtering phenomenon is the same as for static SIMS (ToF-SIMS). However, the primary beam is high enough in energy (\( \sim 1 \mu A \cdot \text{cm}^{-2} \)) to result in a drastic change of the chemical composition and structure of the surface. This technique is inherently “destructive” due to the collisional interaction of the primary ions with the sample, although the extent of the surface damage can be controlled by an appropriate optimization of the parameters of the primary ion source. The dynamic SIMS (D-SIMS) mode is characterized by the use of high density, DC primary ion beam currents providing typical sputter rates in the range \( 0.5-5 \text{ nm/s}^{-1} \). Under such conditions most chemical bonds are broken and only atoms or
polyatomic fragments are ejected from the sample surface as neutrals or ions. This restricts D-SIMS applications to elemental and isotopic depth profiling or mapping. The detection range of this technique extends from matrix element levels down to trace element levels in the ppb range. It was only used in this project to map the locations of deuterium and iron in a corroded Ti-2 surface.

2.4.4.2 SIMS Experimental Details

An ION-ToF time-of-flight secondary ion mass spectrometer (ToF-SIMS IV) was used to obtain the ToF-SIMS spectra. A 1 keV Bi\(^{3+}\) ion beam was used to sputter an area of 200 \(\times\) 200 \(\mu\text{m}^2\) on the specimen and negative secondary ions were collected from a 100 \(\times\) 100 \(\mu\text{m}^2\) area within the sputter crater using a 25 keV monoisotopic \(^{69}\text{Ga}\)\(^+\) primary ion beam. A smaller analysis area was used within the sputter crater dimensions to avoid edge effects. Each ToF-SIMS mass spectrum was calibrated using the exact mass values of at least 3 known species in the spectrum collected during profiling.

A Cameca IMS-3f SIMS instruments equipped with Cs\(^+\) and O\(^+\) ion sources was used to obtain the dynamic-SIMS image on corroded Ti-2 surface.

2.5 References


4. F. Marken, A. Neudeck, and A.M. Bond, *Cyclic voltammetry*. In: Scholz F (ed)


Chapter 3
Characterization of Film Properties on Ni-Cr-Mo Alloys

3.1 **Introduction**

The primary goal of the studies described in this chapter is to investigate the composition and structure of anodically-grown oxide films on Ni-Cr-Mo (W) alloys as a function of applied potential, temperature and pH. Anodic oxide films were grown on 2 Ni-Cr-Mo (W) alloys, Alloy C22 and Alloy C2000, at various potentials, temperatures and pH values and analyzed using AR-XPS, SR-XPS and ToF-SIMS.

3.2 **Experimental Details**

All experiments were performed on materials supplied by Haynes International, Kokomo, Indiana. The alloy compositions are shown in Table 1.1, Chapter 1. Prior to measurements, the surface of each specimen was wet-polished with a series of SiC papers up to 1200 grit, and then polished successively with 5.0, 0.3, and 0.05 μm alumina powder suspensions. Specimens were then swabbed with cotton under running water to reduce the chances of staining, and finally rinsed with large amounts of deionized water. Specimens were immersed first in acetone and then in ultra-pure deionized water and ultrasonicated for 10 minutes to remove any attached polishing residue, rinsed again with large amounts of ultra-pure deionized water, and immediately placed in the electrochemical cell.
A constant potential was applied to the electrode, immersed in a stirred deaerated solution of 5 mol•dm$^{-3}$ NaCl, for 44 hours to grow a passive oxide film. All potentials were measured against a saturated Ag/AgCl reference electrode. The potentials investigated were 0 V for C22 and –0.4, 0, and 0.6 V for C2000 to represent near-passive, passive and transpassive regions, respectively [1]. Experiments were performed at either room temperature (22 °C), 50 °C or 90 °C. The pH of the solution was adjusted to 7, 4 or 1 with 0.1 mol•dm$^{-3}$ HCl and 0.1 mol•dm$^{-3}$ NaOH.

After film-growth, the specimen was immediately removed from the cell, rinsed and ultrasonicated for 2 minutes in ultra-pure deionized water (at the same temperature as the solution in the cell) to remove any electrolyte left on the specimen surface. The specimen surface was then dried in a stream of argon gas, placed in a small tin box and stored in a desiccator. Subsequently, the specimen was analyzed using SEM (FIB/SEM) imaging, XPS and ToF-SIMS.

### 3.3 Results

#### 3.3.1 SEM (FIB/SEM) and ToF-SIMS Imaging

Figure 3.1 shows SEM micrographs of the surface of Alloy C2000 after polarization at 0 V. The micrograph in Figure 3.1a shows the presence of a uniform film on the surface, except for a few dark spots which maybe either polishing residue or dried electrolyte. The alloy microstructure is almost visible suggesting the presence of a very thin film. Figure 3.1b shows a cross section of the specimen surface. Only an extremely thin line can be observed between the deposit on the surface and the base alloy, indicating that the film is
Figure 3.1  SEM micrographs of the surface of Alloy C2000 after polarization at 0 V
(25 ºC, pH 7) for 44 hours: (a) top-view; (b) cross-sectional view.

Figure 3.2  SEM micrograph of the surface of Alloy C2000 after polarization at 0.6 V
(25 ºC, pH 7) for 44 hours.
too thin to be resolved by this technique. However, the thickness of the passive film on Ni-Cr-Mo (W) alloys has been determined to be a few nanometers (generally less than 5 nm) [2].

Figure 3.2 shows a SEM micrograph of the surface of Alloy C2000 after polarization at 0.6 V for 44 hours. The surface is not uniformly covered by the light grey film observed at 0 V. Some areas are covered by a dark grey product, suggesting the film grown has undergone transpassive dissolution at this potential. However, the compositional differences between the light and dark grey areas could not be resolved by EDX analysis due to the thinness of the film.

These surfaces were also examined by ToF-SIMS. The ToF-SIMS images (top view) of the surfaces of Alloy C2000 after polarization at 0 V and 0.6 V are shown in Figure 3.3, in which the lighter areas indicate a higher content for the species indicated. It can be seen that, for the film grown at 0 V, the various species in the film are uniformly distributed on the surface, but this is not the case for the film grown at 0.6 V. The images for chromium hydroxide related species show some lighter spots than the surrounding areas, the size of the spots matching the size of the dark grey areas in the SEM image (Figure 3.2) for this sample. This indicates the enrichment of chromium hydroxide in the dark grey areas in the SEM image. The images also show an enrichment in MoO₃⁻, compared to MoO₂⁻, and, although less obvious, Ni and Cu hydroxides at the expense of the corresponding oxides.
**Figure 3.3** ToF-SIMS images (top view, 100 µm×100 µm) of the surface of Alloy C2000 after polarization at (a) 0 V (25 °C, pH 7); (b) 0.6 V (25 °C, pH 7).

### 3.3.2 SR-XPS Analyses on Alloy C 22 after Polarization at 0 V

#### 3.3.2.1 Survey Spectrum

Due to the dependence of the IMFP on the excitation energy of the x-ray beam, depth profiling can be achieved with SR-XPS by varying the excitation energy. Figure 3.4 shows the survey spectra recorded at various excitation energies on Alloy C22 after polarization at 0 V. Clear changes in the survey spectra were observed at the different
Figure 3.4  Survey spectra recorded on Alloy C22 after polarization at 0 V (22 °C, pH 7, 44 hours) at various excitation energies (1000, 1200, 1500 eV).

Figure 3.5  Surface composition determined from the survey spectra (Figure 3.4) recorded on Alloy C22 after polarization at 0 V (22 °C, pH 7, 44 hours) at various excitation energies (1000, 1200, 1500 eV).
excitation energies, suggesting a variation of film composition with depth in the film. The XPS survey spectra detected peaks for Ni 2p, Cr 2p, Mo 3d, O 1s and C 1s, but the C 1s peak was not included in the spectral quantification. The surface compositions, determined from these spectra, are shown in Figure 3.5. The decrease in the content of oxygen indicates an increase in probe depth with increasing beam excitation energy. In addition, the elemental compositions vary with excitation energy. The content of Mo is at a maximum at an excitation energy of 1000 eV, indicating enrichment of Mo in the outer region of the film. The Cr content achieves a maximum at an excitation energy of 1200 eV, indicating an enrichment of Cr in the inner regions of the oxide: this is most likely close to, or at, the oxide/alloy interface, since the analysis at an excitation energy of 1500 eV penetrates into the substrate alloy (as indicated by the Ni high-resolution spectrum, Figure 3.6). Similarly, the increase in Ni content with increasing energy indicates the depletion of Ni in the outer region and enrichment in the inner region of the film. The extremely high content of Ni at an excitation energy of 1500 eV confirms that the analysis reached the substrate alloy at this high excitation energy. The observed segregation of alloying elements in the oxide film is in agreement with the results of Lloyd et al. in acidic solutions [3].

3.3.2.2 High-resolution Spectra

Figure 3.6 shows the high-resolution XPS spectra of Ni 2p recorded on Alloy C22 after polarization at 0 V at various excitation energies (1000, 1200, 1500 eV). The scans show the multiplet splitting of the Ni 2p 3/2 and Ni 2p 1/2 peaks, but only the Ni 2p 3/2 region was analyzed in detail. The high-resolution spectra were deconvoluted after a Shirley background correction, indicating the presence of metallic Ni and Ni $^{2+}$ compounds. The
Figure 3.6  High-resolution Ni 2p XPS spectra recorded on Alloy C22 after polarization at 0 V (22 °C, pH 7, 44 hours) at various excitation energies (1000, 1200, 1500 eV).

Figure 3.7  A fitted high-resolution Ni 2p spectrum recorded on Alloy C22 after polarization at 0 V (22 °C, pH 7, 44 hours).
spectra can be fitted using the parameters for NiO and Ni(OH)$_2$ determined by Biesinger [4]. An example of the fitted spectra is shown in Figure 3.7, and Figure 3.8 shows the results as a function of excitation energy. The metallic Ni content increases with excitation energy, as the depth probed reached the alloy substrate at high excitation energies. Also, with an increase in excitation energy, the amount of Ni(OH)$_2$ decreases, suggesting it is enriched in the outer region of the film relative to NiO.

![Figure 3.8](image)

**Figure 3.8** Relative compositions of Ni species in an Alloy C22 surface after polarization at 0 V (22 °C, pH 7, 44 hours) as a function of excitation energy.

A similar analysis of Cr 2p high-resolution XPS spectra at various excitation energies is shown in Figure 3.9. Both of the multiplet splitting peaks of Cr 2p are shown, but only the Cr 2p 3/2 region was fitted with the fixed parameter values for Cr metal, Cr$_2$O$_3$ and Cr(OH)$_3$ determined by Biesinger [4]. The fitted spectra show that the amount of
Figure 3.9  (a) High-resolution Cr 2p XPS spectra recorded on Alloy C22 after polarization at 0 V (22 °C, pH 7, 44 hours) at various excitation energies (1000, 1200, 1500 eV); (b) Example of a fitted spectrum; (c) Relative percentages of the Cr species in the alloy surface as a function of beam excitation energy.

Cr(OH)$_3$ decreases and that of Cr$_2$O$_3$ increases with increasing excitation energy, indicating Cr(OH)$_3$ is enriched in the outer region of the film and Cr$_2$O$_3$ in the inner region, as observed for Ni (OH)$_2$ and NiO.

3.3.3 Angle-resolved XPS Results for Alloy C 2000

3.3.3.1 The Influence of Potential

Alloy C2000 specimens were polarized at – 0.4 V, 0 V and 0.6 V, respectively, and then
analyzed by XPS at take-off angles of 30º and 90º. This allowed us to determine the influence of applied potential on the film properties such as composition, the oxidation states of alloying elements, and the variation of film composition with depth. Three potentials are chosen to cover the ranges from incomplete passivation to transpassivity [1]. The survey spectra for these specimens for both angles are shown in Figure 3.10. The survey spectra detected Ni 2p, Cr 2p, Mo 3d, C 1s, O 1s and a barely visible small peak for Cu 2p. Generally, similar spectra are obtained at – 0.4 V and at 0 V at both take-off angles, while the spectra obtained at 0.6 V are significantly different.

The surface compositions determined from the survey spectra are shown in Figure 3.11. The oxygen content of the surface is higher at an angle of 30º than at 90º, as expected since the depth probed at 90º penetrates into the base alloy. Also the oxygen content increases with an increase in applied potential indicating an increase in film thickness at 0.6 V. The cation composition of the oxide film, corrected for contributions from the metallic substrate which are determined from high-resolution spectra, is determined by excluding the oxygen contribution in the spectral quantification, Figure 3.12. The film was found to be composed of ~ 40 - 70% Cr, 20 - 45% Ni, 10 - 20% Mo and a small amount of Cu. Comparison to the nominal composition of Alloy C2000 (Table 1.1 in Chapter 1), shows a clear enrichment of Cr and a depletion of Ni in the film, especially for the film grown at a potential of 0.6 V.

Comparison of the atomic contents measured at take-off angles of 30º and 90º, shows that the amount of Cu and Mo is higher at an angle of 30º than at 90º for all three potentials, suggesting their enrichment in the outer region of the film. Similarly, Cr and Ni are found to be enriched in the inner region. The variation of Cr and Ni at the two take-off angles
Figure 3.10  The survey spectra recorded on Alloy C2000 after polarization at –0.4 V, 0 V and 0.6 V (22 °C, pH 7, 44 hours) at take-off angles of (a) 30º and (b) 90º.
Figure 3.11  Surface composition determined from the survey spectra (Figure 3.10) recorded on Alloy C2000 after polarization at –0.4 V, 0 V and 0.6 V (22 °C, pH 7, 44 hours) at take-off angles of 30° and 90°.

Figure 3.12  Film cation compositions determined from the survey spectra (Figure 3.10) recorded on Alloy C2000 after polarization at –0.4 V, 0 V and 0.6 V (22 °C, pH 7, 44 hours) at take-off angles of 30° and 90°, corrected for contributions from the metallic substrate.
changes when the film was grown at 0.6 V. The amount of Cr is much lower and that of Ni slightly higher at 30º than at 90º. This is consistent with the transpassive oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution into the solution. At this potential the destruction of passivity allows the transport of Ni through the film and its dissolution at the oxide/solution interface. This Cr/Mo segregation in the film is consistent with the SR-XPS results on Alloy C22, and with the results of Lloyd et al. on Ni-Cr-Mo alloys in acidic sulphate solution [3].

High-resolution scans of Ni 2p, Cr 2p, Mo 3d, Cu 2p, O 1s and C1s were carried out for all three potentials. An example of the O 1s spectrum is shown in Figure 3.13, and can be fitted with three component peaks. The peak at 529-530 eV, comprising approximately

![Graph showing O 1s spectrum](image_url)

**Figure 3.13**  High-resolution O 1s spectrum recorded on Alloy C2000 after polarization at 0 V (22 ºC, pH 7, 44 hours) at a take-off angle of 90º.
20% of the total O 1s spectral area, can be attributed to $O^{2-}$ in the oxide. The major peak at 531-532 eV, comprising 70-80% of the total O 1s spectral area, can be attributed to hydroxide species or defective sites within the oxide, and the small peak at ~ 533 eV may be due to adsorbed water or, possibly, adsorbed $O_2$ [5]. The relative amounts of $O^{2-}$ and $OH^-$ obtained by fitting the O1s spectra at the three potentials are shown in Figure 3.14. Large amounts of hydroxide are found in the film at all three potentials, but especially at 0.6 V. In addition, higher hydroxide and lower oxide contents were observed at 30º than at 90º, indicating hydroxides are located in the outer, and oxides in the inner, regions of the film.

![Figure 3.14](image)

**Figure 3.14** Relative percentage of oxide and hydroxide species in the Alloy C2000 surface after polarization at – 0.4 V, 0 V and 0.6 V (22 ºC, pH 7, 44 hours) at take-off angles of 30º and 90º.

The Ni 2p spectra were deconvoluted into contributions from metallic Ni, NiO and
Ni(OH)$_2$ using the parameter values published by Biesinger et al. [4-5]. The relative percentages (Figure 3.15) show that similar amounts of metallic Ni were detected after polarization at – 0.4 V and 0 V at both angles, suggesting similar film thicknesses at these potentials, consistent with the results from the survey spectra. As expected, the content of metallic Ni detected at 30º is smaller than at 90º. No metallic Ni was detected at both take-off angles at 0.6 V, indicating the presence of a much thicker film after polarization at this potential. Comparison of the relative amounts of Ni(OH)$_2$ and NiO measured at 30º and 90º shows that the amount of Ni(OH)$_2$ is much higher and that of NiO much lower at 30º than at 90º, indicating enrichment of Ni(OH)$_2$ in the outer region of the film relative to NiO, consistent with the analyses of the O 1s spectra.

Figure 3.15  Relative percentages of Ni species in the Alloy C2000 surface polarized at – 0.4 V, 0 V and 0.6 V (22 ºC, pH 7, 44 hours) at take-off angles of 30º and 90º.
The Cr 2p spectra were fitted using the same parameter sets for Cr metal, Cr$_2$O$_3$ and Cr(OH)$_3$ as used for the SR-XPS spectra [4, 6], and the relative percentages obtained are shown in Figure 3.16. It was found that the amount of metallic Cr decreases with the increase in film-growth potential from −0.4 V to 0.6 V, indicating an increase in film thickness, in agreement with the Ni 2p results. Comparison of the relative percentages of Cr(OH)$_3$ and Cr$_2$O$_3$ measured at 30° and 90°, shows that the amount of Cr(OH)$_3$ is much higher and that of Cr$_2$O$_3$ much lower at 30° compared to 90°, indicating an enrichment of Cr(OH)$_3$ in the outer region of the film relative to Cr$_2$O$_3$, consistent with the results for Ni(OH)$_2$ and NiO, and also with the results obtained for Alloy C22 obtained by SR-XPS.

![Figure 3.16](image-url)

**Figure 3.16** Relative percentages of Cr species in the Alloy C2000 surface polarized at −0.4 V, 0 V and 0.6 V (22 °C, pH 7, 44 hours) at take-off angles of 30° and 90°.

The Mo 3d high-resolution scans were fitted with spin-orbit pair intervals set at 3.13 eV
and the parameters determined by McIntyre et al. [7]. Mo was found to be present in the film in a range of oxidation states (IV, V, and VI). Figure 3.17 (a) shows an example of a fitted Mo 3d spectrum, and the relative percentages of Mo species in the film, obtained from such a fit, is shown in Figure 3.17 (b). The percentage of metallic Mo is found to decrease with increasing film-growth potential, consistent with the presence of a thicker film at higher potentials. Comparison of the relative percentages of Mo species measured at 30° and 90° shows that the amount of Mo(VI) is much higher at 30° than at 90°, indicating an enrichment of high oxidation states of Mo in the outer region of the film. At 0.6 V the percentage of Mo(VI) increases markedly. Also, the percentage of Mo(V) measured at 90° is significantly larger than that at 30° at 0.6 V. In fact, at 30° the percentage of Mo(V) decreases with increasing potential whereas at 90° it increases. These results indicate a conversion of lower Mo oxidation states in the inner regions of the film at 0 V to higher oxidation states in the outer regions of the film at 0.6 V.

A typical Cu 2p 3/2 high-resolution XPS spectrum is shown in Figure 3.18. A single peak with a binding energy ranging between 931.8 eV and 932.9 eV was obtained on all specimens. This is close to the BE value for Cu metal and cuprous oxide, which are within 0.1eV of each other and can not be distinguished by XPS [8]. The well known shake-up satellite peak (5 - 10 eV higher on the BE scale than the principal Cu 2p 3/2 line), indicative of the presence of the expected [8] Cu(II) species [9-10], was not observed. The absence of Cu(II) species in the film may be due to the decomposition of Cu(OH)₂ to Cu(I) under X-ray exposure in the spectrometer [8].
Figure 3.17  High-resolution XPS spectra of Mo 3d recorded on Alloy C2000 after polarization at – 0.4 V, 0 V and 0.6 V (22 ºC, pH 7, 44 hours) at take-off angles of 30º and 90º: (a) a fitted spectrum; (b) Relative percentages of Mo species in the alloy surface.
Figure 3.18  High-resolution XPS spectrum of Cu 2p recorded on Alloy C2000 after polarization at 0 V (22 ºC, pH 7, 44 hours) at a take-off angle of 90º.

3.3.3.2 The Influence of Temperature

To study the influence of temperature on the film properties, Alloy C2000 specimens were polarized at 0 V at room temperature (22 ºC), 50 ºC and 90 ºC, and then analyzed by XPS at take-off angles of 30º and 90º. A potential of 0 V is chosen since the passive film is expected to be fully developed at this value [1]. The survey spectra recorded are shown in Figure 3.19, and surface compositions obtained from these spectra and the cation content of the film (corrected for contributions from the metallic substrate which is determined from high-resolution spectra) are shown in Figure 3.20. These analyses show that the oxygen content of the surface greatly increases at both angles with increasing film-growth temperature, indicating an increase in film thickness with temperature. The
Figure 3.19  Survey spectra recorded on Alloy C2000 after polarization at 0 V (pH 7, 44 hours) at various temperatures (a) at the take-off angle of 30º; and (b) a comparison between two take-off angles at 90ºC.
Figure 3.20  (a) Surface composition of Alloy C2000 determined from the survey spectra (Figure 3.19) measured at take-off angles of 30º and 90º after polarization at 0 V (pH 7, 44 hours) at various temperatures; (b) Film cation compositions corrected for contributions from the metallic components determined from high-resolution spectra.
cation composition of the film (Figure 3.20 (b)) shows a clear variation of film composition with temperature. The Ni content in the film increases, whereas the Cr and Mo contents decrease with temperature. The lower Cr and Mo contents may be attributed to their higher solubility at higher temperatures.

Compared to the nominal composition of Alloy C2000 (Table 1.1 in Chapter 1), Cu is significantly enriched in the outer regions of the film, especially at intermediate temperatures. This may be due to the higher dissolution rate of Mo oxide from the outer regions of the film at intermediate and high temperatures which slightly changes the layer structure of the film. This can be observed from the film cation compositions between the two take-off angles. At 90 °C, Cr and Cu, but not Mo, are strongly enriched in the outer regions of the film, and Ni is still enriched in the inner region of the film. Meanwhile, the film growth process is enhanced by the high temperature, maybe in both the inner and outer regions, even though the dissolution rate of the outer regions of the film is higher. The enhanced film-growth process leads to a thicker film at higher temperatures indicated by the increased oxygen contents with increasing temperature, Figure 3.20 (a).

High-resolution XPS spectra for O1s, Ni 2p, Cr 2p and Mo 3d were obtained at take-off angles of 30° and 90°, and the surface compositions determined are shown in Figure 3.21. The results for oxygen consistently show larger amounts of hydroxides in the outer regions of the film, and smaller amounts of oxide in the inner regions. The data obtained at the take-off angle of 30° shows the hydroxide content in the film increases with temperature, indicating the growth of a thicker hydroxide outer layer at high temperatures; whereas, at the take-off angle of 90°, the content of oxide significantly increases for the
Figure 3.21  Surface compositions (from high-resolution XPS spectra) of Alloy C2000 after polarization at 0 V (pH 7, 44 hours) at various temperatures measured at take-off angles of 30° and 90° (a) O 1s  (b) Ni 2p  (c) Cr 2p and (d) Mo 3d .
film grown at 90°C, indicating a thicker oxide inner layer at this temperature.

The results for Ni, Cr and Mo (from high-resolution spectra) show that the relative amounts of metallic states for all elements decrease with the increase in temperature, indicating an increase in film thickness, and consistent with the increasing oxygen content with temperature obtained from the survey spectra. The comparison of the relative composition for Ni and Cr for the two take-off angles shows a higher percent of hydroxides were detected at the smaller take-off angle (30°), demonstrating that the hydroxides of Ni and Cr are enriched in the outer region of the film, and the oxides in the inner region, in agreement with O 1s spectra. With increasing temperature, the Ni(OH)$_2$ content increases and the Cr(OH)$_3$ content decreases, suggesting a higher dissolution rate for Cr(OH)$_3$ at high temperatures, whereas the contents of both NiO and Cr$_2$O$_3$ increase in the inner region indicating a thicker inner layer at high temperatures. The results for Mo show that the higher oxidation states (Mo(VI) and Mo(V)) are enriched in the outer surface at low or mild temperatures, but at 90°C, the percentage of Mo(VI) decreases and is no longer enriched in the outer region, By contrast, the contents of Mo(V) and Mo(IV) increase significantly and are enriched in the outer region, suggesting a higher dissolution rate for Mo(VI) at high temperatures [11].

3.3.3.3 The Influence of pH

To study the influence of pH on the film properties, three Alloy C2000 specimens were polarized at 0 V for 44 hours at pH 1, pH 4 and pH 7, respectively, at room temperature (22 °C), and then analyzed by XPS at take-off angles of 30° and 90°. The survey spectra measured at a take-off angle of 30°, are shown in Figure 3.22. The spectra vary only
marginally. The surface compositions (Figure 3.23) determined from the survey spectra show that the oxygen content increases with an increase in pH, indicating an increase in film thickness with pH. Figure 3.23 (b) shows the variations in cation composition of the films, corrected for contributions from the metallic substrate determined from high-resolution spectra. With a decrease in pH, the relative amounts of Mo and Cr in the film are greatly enhanced, while the Ni content decreases, especially in the inner region, as indicated by the considerably larger pH-dependence observed at 90º compared to 30º. The relatively high Mo and Cr and low Ni contents in the surface at low pH can be attributed to the much higher dissolution rate of Ni species in acidic solutions [12]. Loss of Ni is the primary anodic dissolution process. Its loss leads to, or is accompanied by, an

![Figure 3.22](image)

**Figure 3.22** Survey spectra recorded on Alloy C2000 after polarization at 0 V (44 hours) at various pH values at room temperature (22 ºC) measured at a take-off angle of 30º.
Figure 3.23  (a) Surface composition of Alloy C2000 determined from survey spectra (Figure 3.22) measured at take-off angles of 30° and 90° after polarization at 0 V (22 °C, 44 hours) ; (b) Film cation compositions, corrected for contributions from the metallic components, determined from high-resolution spectra.
increased relative Cr content in the inner layer; i.e. the anodic release of Ni from the inner layer increases with decreasing pH.

The relative compositions obtained by fitting high-resolution XPS spectra for O 1s, Ni 2p, Cr 2p and Mo 3d measured at take-off angles of 30° and 90°, are shown in Figure 3.24. The results for O 1s show that large amounts of hydroxide are present in the outer region of the film, and small amounts of oxide in the inner region, consistent with previous observations (above). The hydroxide content decreases and the oxide content generally increases as pH decreases. The results for Ni and Cr show that the percentages of metallic states decrease with an increase in pH, indicating that the film thickness increases with pH. Comparison of the results for Ni and Cr at the two take-off angles shows a higher percentage of hydroxides are detected at 30° compared to 90°, consistent with the enrichment of hydroxides of Ni and Cr in the outer region of the film. Also, the percentages of hydroxides of Cr and Ni greatly decrease with decreasing pH, indicating a higher dissolution rate of hydroxides in acidic solutions leading to a thinner hydroxide outer layer. The results for Mo show that the higher oxidation states of Mo (Mo(VI) and Mo(V)) are enriched in the outer region of the film. In acidic solution (pH 1), the relative percentage of Mo(VI) decreases while the Mo(V) and Mo(IV) contents slightly increase, suggesting dissolution of Mo(VI) from the outer region of the film in acidic solutions even though the total relative amounts of Mo increases.
Figure 3.24 Surface compositions (from high-resolution XPS spectra) recorded on Alloy C2000 after polarization at 0 V (22 °C, 44 hours) measured at take-off angles of 30° and 90° (a) O 1s  (b) Ni 2p  (c) Cr 2p  and (d) Mo 3d .
3.3.4 ToF-SIMS Analyses on Alloy C 2000

3.3.4.1 The Influence of Potential

ToF-SIMS depth profiles were recorded for all Alloy C2000 specimens. Figure 3.25 shows the profiles for the negative ions detected after polarization at – 0.4, 0 and 0.6 V, respectively, for 44 hours in neutral solutions at room temperature (22 ºC), and Figure 3.26 shows the cross-sectional images for the ions reconstructed from the sputtering profiles. Since the sputtering rate is unknown, conversion of sputtering times can not be used to calculate film thickness. However, according to Lloyd et al. [3], the passive film thickness on this alloy in acidic solutions (pH 1) is about 2 ~ 3 nm. As stated in Chapter 2, the negative ions detected do not necessarily represent the species which exist in the oxide, i.e., the oxidation state of an ion can not be determined. The sputtering profiles
Figure 3.25  ToF - SIMS profiles recorded on Alloy C2000 after polarization at (a) – 0.4 V, (b) 0 V and (c) 0.6 V (22 °C, pH 7, 44 hours). The vertical dashed line represents the peak location of Cr(OH)$_3^-$.
Figure 3.26 ToF - SIMS cross-sectional images for Alloy C2000 reconstructed from sputtering profiles after polarization at (a) – 0.4 V, (b) 0 V and (c) 0.6 V (22 ºC, pH 7, 44 hours).
show that each species exhibits a maximum in intensity at a specific time, indicating its location within the film. From the variation in these times, a layered structure of the film can be inferred. Based on peak locations, Cu and Mo oxides segregate to the outer surface of the film, hydroxides of Cr, Ni and Cu are located at intermediate depths, and the inner film region is enriched in Cr and Ni oxides. This layered structure is consistent with the XPS results and can be observed in the cross-sectional ToF-SIMS images shown in Figure 3.26, where the lighter color indicates the location of each species in the film. The much longer sputtering time required at 0.6 V, suggests the film thickness greatly increases at such positive potentials.

While quantification of species can not be achieved by this technique, the relative concentrations of various species can be determined if it is assumed that the various oxide components have identical sputtering efficiencies. Figure 3.27 shows the Cr\(_2\)O\(_3\)/MoO\(_3\)\(^-\) (solid line) and Cr\(_2\)O\(_3\)/CuO\(^-\) (dotted line) ratios from the sputtering profiles. The increasing Cr\(_2\)O\(_3\)/MoO\(_3\)\(^-\) and Cr\(_2\)O\(_3\)/CuO\(^-\) ratios obtained from the outer to the inner regions of the film indicates the tendency for the alloy to form a Cr rich inner oxide layer. The shorter sputtering time required to reach a peak in the Cr\(_2\)O\(_3\)/CuO\(^-\) ratio, compared to that for Cr\(_2\)O\(_3\)/MoO\(_3\)\(^-\), indicates a more emphatic surface segregation of Cu than of Mo, i.e., Cu is segregated to the surface of the film, as shown in Figure 3.26. This is consistent with the XPS results.

The Mo results are consistent with published literature, which claims Mo is segregated to the outer regions of the film as a high-valency cation [13]. The larger Cr\(_2\)O\(_3\)/MoO\(_3\)\(^-\) and Cr\(_2\)O\(_3\)/CuO\(^-\) ratios obtained on the specimen polarized at 0 V compared to that at −0.4 V, show there is an increase in Cr\(_2\)O\(_3\) content of the inner regions of the film with potential.
The lower \( \text{Cr}_2\text{O}_3^-/\text{MoO}_3^- \) ratio obtained after polarization at 0.6 V clearly shows the loss of \( \text{Cr}_2\text{O}_3 \) from the film as \( \text{CrO}_4^{2-} \) [14], and the absence of peaks in the \( \text{Cr}_2\text{O}_3^-/\text{MoO}_3^- \) and \( \text{Cr}_2\text{O}_3^-/\text{CuO}^- \) ratios at 0.6 V indicates the destruction of the Cr rich inner layer, leading to a highly defective film [15].

**Figure 3.27** \( \text{Cr}_2\text{O}_3^-/\text{MoO}_3^- \) (solid line) and \( \text{Cr}_2\text{O}_3^-/\text{CuO}^- \) (dotted line) intensity ratios from ToF-SIMS sputtering profiles recorded on Alloy C 2000 after polarization at – 0.4 V (black), 0 V (red) and 0.6 V (blue) (22 °C, pH 7, 44 hours). The vertical dashed and solid lines represent the locations of the peak \( \text{Cr}_2\text{O}_3^-/\text{CuO}^- \) and \( \text{Cr}_2\text{O}_3^-/\text{MoO}_3^- \) ratios, respectively.

### 3.3.4.2 The Influence of Temperature

Figure 3.28 shows the ToF-SIMS sputtering profiles obtained after polarization at 0 V at
Figure 3.28  ToF - SIMS sputtering profiles recorded on Alloy C2000 after polarization at 0 V (pH 7, 44 hours) at (a) 50 °C and (b) 90 °C. The vertical dashed line represents the peak location of Cr(OH)$_3$.$^-$.
Figure 3.29 ToF-SIMS cross-sectional images, reconstructed from sputtering profiles, for Alloy C2000 after polarization at 0 V (pH 7, 44 hours) at (a) 50 ºC and (b) 90 ºC.

50 ºC and 90 ºC, respectively, and Figure 3.29 shows the cross-sectional images reconstructed from these profiles. The profiles and cross-sectional images at 50 ºC are similar to those obtained at this potential at room temperature (22 ºC), but this is not the case at 90 ºC. For example, Mo oxide is no longer enriched at the outer surface of the film due to a higher dissolution rate at high temperatures, consistent with XPS results.
Also, longer sputtering times are required to define the profiles, especially at 90 °C. The significant difference in scale (sputtering time) of the profiles observed as the temperature increases, indicates the film thickness significantly increases, in good agreement with XPS results. The variations in the $\text{Cr}_2\text{O}_3^-$/MoO$_3^-$ and $\text{Cr}_2\text{O}_3^-$/CuO$^-$ ratios with temperature are shown in Figure 3.30. The increasing $\text{Cr}_2\text{O}_3^-$/MoO$_3^-$ and $\text{Cr}_2\text{O}_3^-$/CuO$^-$ ratios from the outer to the inner regions of the film at low and intermediate temperatures, indicate the tendency for the alloy to form a Cr rich inner oxide layer at these temperatures. The lower values of the ratios observed at 50 °C compared to room

![Figure 3.30](image)

**Figure 3.30** $\text{Cr}_2\text{O}_3^-$/MoO$_3^-$ (solid line) and $\text{Cr}_2\text{O}_3^-$/CuO$^-$ (dotted line) intensity ratios determined from ToF-SIMS sputtering profiles recorded on Alloy C 2000 after polarization at 0 V (pH 7, 44 hours) at 22 °C (black), 50 °C (red) and 90 °C (blue). The vertical dashed and solid lines represent the peak location of $\text{Cr}_2\text{O}_3^-$/CuO$^-$ and $\text{Cr}_2\text{O}_3^-$/MoO$_3^-$ ratios at 22 °C, respectively.
temperature (22 °C) suggest a relative loss of Cr$_2$O$_3$ from the film at higher temperatures. Also the increased sputtering time required to reach the peaks at 50 °C indicates a thicker outer layer of the film in which Cu and Mo oxides are enriched. The significant decrease in the value of the ratios and the disappearance of the peak in the ratios at 90 °C, indicate a significant loss of Cr$_2$O$_3$ from the film relative to Mo and Cu oxide, consistent with XPS results.

3.3.4.3 The Influence of pH

Figure 3.31 shows the ToF-SIMS sputtering profiles obtained after polarization at 0 V in pH 4 and pH 1 solutions (at room temperature) for 44 hours, respectively, and Figure 3.32 shows the ToF-SIMS cross-sectional images reconstructed from the sputtering profiles. Compared to the profiles and images obtained in neutral solution (Figure 3.25 (b)), there is only a marginal difference in the profiles for these pH values, except for the peak locations, shorter times being required to define the profiles, especially at pH 1. The differences in scale (sputtering time) of the profiles and the narrower regions in the images (Figure 3.32) occupied by the species in the surface as pH decreases, indicate the film thickness decreases with decreasing pH, in good agreement with XPS results. However, the layered structure of the film remained similar in the thinner film grown in acidic solutions. The variations in Cr$_2$O$_3^-$/MoO$_3^-$ and Cr$_2$O$_3^-$/CuO$^-$ ratios in the film with pH are shown in Figure 3.33. The increasing Cr$_2$O$_3^-$/MoO$_3^-$ and Cr$_2$O$_3^-$/CuO$^-$ ratios from the outer to the inner region of the film, indicating the tendency for the alloy to form a Cr rich inner oxide layer, were observed at all three pH values. The decrease in the value of the ratios and the sputtering time of the peaks as pH decreases, indicate a relative loss of Cr$_2$O$_3$ from the film and a thinner outer layer in which Cu and Mo oxide are enriched in
acidic solution.

**Figure 3.31** ToF - SIMS sputtering profiles recorded on Alloy C2000 after polarization at 0 V (22 °C, 44 hours) at (a) pH 4 and (b) pH 1. The vertical dashed line represents the peak location of Cr(OH)₃.
Figure 3.32  ToF - SIMS cross-sectional images, reconstructed from sputtering profiles, for Alloy C2000 after polarization at 0 V (22 °C, 44 hours) at (a) pH 4 and (b) pH 1.
Figure 3.33  Cr$_2$O$_3^-$/MoO$_3^-$ (solid line) and Cr$_2$O$_3^-$/CuO$^-$ (dotted line) intensity ratios from ToF-SIMS sputtering profiles recorded on Alloy C 2000 after polarization at 0 V (22 ºC, 44 hours) at pH 7 (black), pH 4 (red) and pH 1 (blue). The vertical dashed and solid lines represent the peak locations of the Cr$_2$O$_3^-$/CuO$^-$ and Cr$_2$O$_3^-$/MoO$_3^-\$ ratios at pH 7, respectively.

### 3.4 Discussion

The properties of passive and transpassive oxide films on Alloy C22 and Alloy C2000 have been studied as a function of potential, temperature and pH. The potentials studied were – 0.4 V, 0 V, and 0.6 V, to represent the near passive, fully passive, and transpassive regions, respectively, on these alloys. In the passive film (0 V), in which the influence of Cr is expected to dominate since Cr(III) should be stable at this potential, the presence of a layered structure has been demonstrated. All the surface analyses show consistently
high levels of hydroxides in the outer layer compared to oxides in the inner layer, and Cu (or Cu oxide) and Mo oxide are enriched in the outermost surface. This confirms that the enrichment of Cr (and Ni) oxides at the alloy/oxide interface, is the critical feature in achieving passivity, while, Mo (and Cu) oxides segregate to the oxide/solution interface. The observed Cr/Mo segregation process in the film, which yields a bipolar film structure, is consistent with observations made on Mo-containing stainless steels [16] and the results of Lloyd et al. on Ni-Cr-Mo alloys in acidic sulphate solution [3]. It has been claimed that the Mo(VI) in the outer layers of the oxide is stabilized as MoO$_4^{2-}$ by the high electric field, leading to the deprotonation of OH$^-$ within the film, and that this supplies O$_2^-$ to enhance the formation of a protective Cr$_2$O$_3$ inner layer [17]. However, according to the results of Lloyd et al [2], such a Cr/Mo segregation process in the film is only observable on high-Cr alloys such as Alloy C22 and C2000.

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The segregation of alloying elements in passive films is a well known phenomenon, and can be attributed to either preferential oxidation of one alloying element in the alloy or preferential dissolution of other elements from the film, or both [18]. The accumulation of a Cu layer on the surface of Ni-Cr-Mo alloys has not been observed previously. The deposition of Cu on the surface of 316 sintered stainless steel containing 0.25-5.0% Cu was claimed to improve the corrosion resistance [19]. Seo et al. [20] found that Cu had a detrimental effect on the passivity, although Cu and Mo suppress the anodic dissolution of Fe-26Cr in 1M H$_2$SO$_4$. The beneficial effect of alloying with Cu was attributed to the stability of deposited Cu on an anodically oxidized surface. It was proposed that this may be due to the presence of Cu in solid solution and Cu-rich phases in the matrix of the alloy, and the rapid formation of a Cu-rich surface layer during active dissolution [21].
The morphology of the deposited Cu was found to vary on the surfaces of ferritic and austenitic steel [22], but a metallic Cu layer was found by most workers [23]. The oxidation state of the Cu layer, shown here to be deposited on the surface of Alloy C2000, is hard to determine by XPS and ToF-SIMS techniques, due to the possibility of the reduction of Cu(II) species to Cu(I) under X-ray exposure [8]. Also the closeness of the BE for Cu metal and cuprous oxide, makes their separation in XPS spectra impossible. The CuO found in the top surface of Alloy C2000 from ToF-SIMS sputtering profiles and images may be due to the ion interactions in the sputtering/analysis chamber in the instrument, and is not necessarily representative of the oxide composition.

The mechanism of passive film growth and break-down on Ni-Cr-Mo(W) alloys can be explained by the point defect model (PDM), which postulates that the oxide is composed of a bilayer, or duplex structure, as demonstrated in this study [24]. The bilayer consists of an inner, defective chromic oxide with cation interstitials being the principal defect (primary passive film or barrier layer) formed directly from the alloy, and an outer precipitated hydrous oxide layer formed by hydrolysis of cations ejected from the inner layer. The expression for the steady-state thickness of the barrier layer ($L_{ss}$), derived in this model, is given by [25],

$$
L_{ss} = \frac{1}{\varepsilon} \left[ 1 - \alpha - \frac{\alpha d}{\varepsilon} \left( \frac{\Gamma}{x - 1} \right) \right] + \frac{1}{\varepsilon} \left( \frac{2.303 n}{\alpha, x} - \beta \left( \frac{\alpha d}{\varepsilon} \left( \frac{\Gamma}{x - 1} \right) + 1 \right) \right) \rho H + \frac{1}{\alpha, \kappa K} \ln \left( \frac{k_p}{k_v} \right)
$$

(3.1)

where $\alpha$ is the polarizability of the barrier layer/outer layer interface; $\varepsilon$ is the electric field strength in the oxide film; $\beta$ is the dependence of the potential drop at the bl/ol interface.
on pH, $\alpha$, and $\alpha_d$ are the transfer coefficients for the generation of oxygen vacancies ($V_0^{\ast\ast}$) and the oxide dissolution reaction, respectively; $x$ and $\Gamma$ are the oxidation states of Cr in the barrier layer (assumed to be 3) and in solution (3 or 6), respectively; $k_1^o$, and $k_7^o$ are the standard rate constants for the generation of oxygen vacancies and oxide dissolution, respectively; and $\gamma = F / RT$.

In the passive region where no change in oxidation state occurs upon ejection of a cation from the barrier layer ($\Gamma = x$), the thickness of the passive film (barrier layer) will vary linearly with the applied potential ($V$), temperature and pH, in agreement with our experimental observations. In the transpassive range, the oxidative ejection of Cr(VI) species from the barrier layer, leading to the generation of an excess of cation vacancies ($\Gamma > x$), will cause a decrease in barrier layer thickness with increasing potential. This is consistent with our results showing the barrier layer is destroyed at very positive potentials.

The AR-XPS and ToF-SIMS analyses show that the film thickness increases with increasing potential, and the relative Cr content of the film increases while that of Ni decreases. The observation of an increasing film thickness with increasing potential is consistent with the results of Lloyd et al. [2] and MacDonald et al. [26]. The observed variations in cation composition of the film with potential indicates Ni is more readily dissolved than Cr as the potential increases, which is also in agreement with the results of Lloyd et al. [2]. Compared to near passive (~0.4 V) and transpassive (0.6 V) films, the passive film (0 V) was found to have the greatest oxide content relative to hydroxide, i.e., the thickest inner oxide layer relative to outer layer. Also the passive film shows the
highest Cr$_2$O$_3$ content in the inner regions of the film. These observations indicate an improved passivity in the passive region as indicated by the impedance results presented in later chapters (Chapter 4 and 6) and those published previously [1, 26].

The composition and structure of the passive film change considerably when the film-growth potential is extended into the transpassive region (0.6 V). A much thicker but non-uniformly distributed film was observed. The transpassive oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution, leads to the destruction of the Cr$_2$O$_3$ enriched inner layer, as indicated by the extremely low relative oxide to hydroxide content in the AR-XPS results, and the loss of a peak in the Cr$_2$O$_3$$^-$/MoO$_3$$^-$ intensity ratio obtained from ToF-SIMS sputtering profiles. The oxidative dissolution of Cr(III) leads to the introduction of a large number of cation vacancies in the film and a decrease in polarization resistance [1, 26]. This destruction of passivity allows the transport of Ni through the film and its dissolution at the oxide/solution interface. Also, the percentage of Mo(VI) increases markedly, indicating a conversion of lower Mo oxidation states in the inner regions of the passive film to higher oxidation states in the outer regions.

Once the Cr stability within the film becomes threatened at higher potentials, then the influence of Mo and, maybe W, in resisting corrosion appears to increase. Characterization of the influence of W is difficult, since the XPS analyses exhibit only a marginal W peak in the spectra. However, it has been claimed that W behaves identically to Mo and is predominantly located in the outer regions of the film, suggesting a common role for both elements [3].
As the temperature increases, film growth is enhanced and the film thickness increases markedly for both the outer hydroxide and inner oxide layers, as indicated by the increasing hydroxide content in the outer region and oxide content in the inner region with increasing temperature. In addition the Ni content of the film increases significantly, whereas the Cr and Mo contents decrease with increasing temperature. Cu becomes enriched in the outer regions of the film, especially at intermediate temperatures. This variation of film composition with temperature may be due to the higher dissolution rate of Cr and Mo in the outer region of the film at higher temperatures. At intermediate temperature (50 ºC), the Cr₂O₃ content in the inner layer decreases, as indicated by the decreases in Cr₂O₃/MoO₃⁻ and Cr₂O₃/CuO⁻ intensity ratios. At 90 ºC the disappearance of the peak and the low values of the ratios, indicate a significant loss of Cr₂O₃ from the inner layer. This loss of Cr₂O₃ in the inner layer, and Cr/Mo segregation in the film as temperature increases, is consistent with XPS results, and results in the decrease in the polarization resistance described in Chapter 4 and increase in corrosion rate observed by others [27]. In addition, the observed temperature threshold for crevice corrosion on Alloy C22 (60 ºC in 1 mol•dm⁻³ NaCl) [28] may be attributed to the significant loss in Cr₂O₃ in the inner layer at temperatures above 50 ºC.

Both XPS and ToF-SIMS analyses demonstrate a decrease in film thickness as the pH decreases from pH 7 to pH 1, especially in that of the outer region of the film, as indicated by the decreasing Ni and Cr hydroxides and Mo(VI) contents with decreasing pH. With a decrease in pH, the relative amounts of Mo and Cr in the film are greatly enhanced, while the Ni content decreases. This can be attributed to a much higher dissolution rate of Ni in acidic solutions [12]. ToF-SIMS profiles show the presence of a
Cr$_2$O$_3$ rich inner layer and Cr/Mo segregation remained in acidic solutions, but the slight decrease in the Cr$_2$O$_3$$^-$/MoO$_3$$^-$ and Cr$_2$O$_3$$^-$/CuO$^-$ intensity ratios as pH decreases, indicate a relative loss of Cr$_2$O$_3$ from the film in acidic solution. One would expect a complete loss of Cr$_2$O$_3$ from the film would result in a breakdown in passivity, and Gray et al. [27] observed an extremely high corrosion rate (10$^4$ µm/year) on Alloy-22 at pH -0.5 HCl or H$_2$SO$_4$ solutions and the disappearance of passive film when pH < 0 in these solutions.

### 3.5 Summary and Conclusions

The passive and transpassive properties of oxide films on Alloy C22 and C2000 at various potentials, temperatures and pH values were investigated by surface-sensitive techniques such as SR-XPS, AR-XPS and ToF-SIMS and SEM. The presence of a layered structure in the passive film has been demonstrated on these alloys, with the outermost surface being enriched in Cu (or Cu oxide) and Mo oxide, the intermediate region dominated by Cr/Ni/Cu hydroxides, and the inner region comprising Cr/Ni oxide.

As potential increases from – 0.4 to 0.6 V, the film thickness increases, and the relative Cr content of the film increases while that of Ni decreases. The passive film (0 V) has a relatively thicker inner oxide layer and higher Cr$_2$O$_3$ content in the inner layer, compared to the near-passive film (– 0.4 V). When the film-growth potential is extended into the transpassive region (0.6 V), the composition and structure of the film change considerably. The transpassive oxidation of Cr(III) to Cr(VI) in the barrier layer of the film and its subsequent dissolution leads to the loss of the Cr$_2$O$_3$-rich inner layer and the destruction of passivity.

As temperature increases, the film-growth process is enhanced and the thicknesses of
both the outer hydroxide layer and inner oxide layer increase. Also, the Ni content of the film significantly increases, whereas the Cr and Mo contents decrease with increasing temperature. Cu is significantly enriched in the outer regions of the film, especially at intermediate temperatures. An increasing loss of Cr$_2$O$_3$ in the inner layer was observed as the temperature increases, which becomes very significant at 90 °C, and the observed loss of Cr/Mo segregation in the film may eventually lead to passivity breakdown.

Both XPS and ToF-SIMS analyses have demonstrated a decrease in film thickness as pH decreases from 7 to 1, especially in the outer region of the film. With a decrease in pH, the relative amounts of Mo and Cr in the film are greatly enhanced, while the Ni content decreases. ToF-SIMS profiles show the presence of a Cr$_2$O$_3$-rich inner layer and that Cr/Mo segregation remained significant in acidic solutions. However, a relative loss in Cr$_2$O$_3$ from the film was observed as pH decreases. A complete loss in Cr$_2$O$_3$ from film leading to a breakdown in passivity in extremely strong acidic solutions would be expected.

### 3.6 Reference

5. M. C. Biesinger, B. P. Payne, L. W. M. Lau, A. Gerson and R. S. C. Smart, 

6. M. C. Biesinger, C. Brown, J. R. Mycroft, R. D. Davidson and N. S. McIntyre, 


15. M. Bojinov, G. Fabricius, T. Laitinen, K. Makela, T. Saario and G. Sundholm, 


Chapter 4

The Kinetics of O₂ Reduction on Oxide-covered Alloy C22

4.1 Introduction

This chapter describes the application of various electrochemical techniques to the investigation of the kinetics of O₂ reduction on the oxide-covered Ni-Cr-Mo (W) alloy, Alloy C22, at temperatures up to 90 °C in a concentrated saline environment. $E_{corr}$ was measured in both O₂-saturated (aerated) and Ar-saturated (deaerated) 5 mol•dm⁻³ NaCl solutions at 70 °C to simulate natural corrosion environments. Potentiostatic polarizations followed by EIS measurements were performed over different potential ranges, including both the passive and transpassive regions, at various temperatures from 30 °C to 90 °C. Cyclic voltammetric experiments were conducted on surfaces pre-oxidized at different potentials (-0.6 V to 0.6 V vs. Ag/AgCl) at 70 °C to examine how the film-growth potential influenced the O₂ reduction kinetics and surface reactivity (redox transformations).

4.2 Experimental Details

Freshly-prepared 5 mol•dm⁻³ NaCl solutions were used in all experiments. Prior to starting each experiment, the electrolyte solution was purged for at least one hour in either O₂ or Ar, and purging continued throughout the experiment. The solutions were maintained at pH 7 by adding 0.1 mol•dm⁻³ HCl and NaOH solutions as necessary.
Each specimen (working electrode) was encased in a heat resistant epoxy resin with an exposed total surface area of 0.785 cm². Before each experiment, the working electrode (WE) was polished sequentially using 180, 240, 320, 600, 800, 1000 and 1200 grade silicon carbide paper, then ultrasonically cleaned for ten minutes first in methanol and finally in deionized water, and immediately put into the electrochemical cell. A rotating disc assembly was used at a rotation rate of 23.3 Hz in all experiments except for $E_{corr}$ and EIS measurements.

The potential profile used in potentiostatic polarization and EIS experiments is shown in Figure 2.3 in Chapter 2. The electrode was first cathodically cleaned at $-1$ V for one hour to reduce any residual air-formed oxide; then the potential was raised in 0.1 V increments from $-1$ V to the anodic limit (0.1 V or 0.9 V) and then stepped back to $-0.9$ V (negative scan) in the same stages. The potential was held at each setting for one hour (two hours for EIS experiments). The last recorded current value after one hour was taken as the steady-state value and used to plot the polarization curve. Experiments were performed at 30 ºC, 50 ºC, 70 ºC and 90 ºC.

The potential profile used in CV experiments is shown in Figure 2.4 in Chapter 2. After a period of cathodic cleaning, the potential was scanned to a specific film-growth potential at 5 mV•s⁻¹, held at this value (between $-0.6$ V and 0.6 V) for one hour to allow film growth, and then scanned to $-1$ V (forward scan) and back to the film-growth potential (reverse scan) at 5 mV•s⁻¹.
4.3 Results and Discussion

4.3.1 Corrosion Potential ($E_{corr}$) Measurements

Figure 4.1 shows $E_{corr}$ measurements for Alloy C22 as a function of time in aerated and deaerated 5 mol dm$^{-3}$ NaCl solutions at room temperature (22 ºC). In aerated solution, $E_{corr}$ rises rapidly (in a few minutes) to a steady-state value $\sim -0.15$ V. By contrast, in deaerated solution, $E_{corr}$ first increases rapidly and then slowly rises to $\sim -0.35$ V after 24 hours, indicating a slower film formation process than in aerated solution. Even after 24 hours a final steady-state $E_{corr}$ is not achieved in deaerated solution, indicating a slow, on-going oxidation of the surface.

![Figure 4.1 Corrosion potentials ($E_{corr}$) measured in deaerated and aerated 5 M NaCl solutions at room temperature (22 ºC).](image)

Since natural corrosion is a short-circuited electrochemical process (Chapter 2), both
anodic and cathodic reactions occur simultaneously on the electrode surface. The cathodic reactions which drive the corrosion process in aerated and deaerated solutions are O₂ reduction and H₂O reduction, respectively. If O₂ reduction on Alloy C22 proceeds via two consecutive two-electron transfer steps, as proposed by Rogers et al. [1] and Macdonald [2],

\[ \text{O}_2 + 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2 + 2\text{OH}^- \quad E_{\text{SHE}} = -0.13 \text{ V} \quad (4.1) \]

\[ \text{H}_2\text{O}_2 + 2\text{e}^- \rightarrow 2\text{OH}^- \quad (4.2) \]

the equilibrium potential for the first step can be calculated from the Nernst equation,

\[ (E_{\text{SHE}}^\circ)_{\text{H}_2\text{O}_2/\text{O}_2} = 0.70 - 0.0592 \text{ pH} - 0.0295 \log [\text{H}_2\text{O}_2] + 0.0295 \log p_{\text{O}_2} \quad (25 \, ^\circ\text{C}) \quad (4.3) \]

where \( p_{\text{O}_2} \) is the partial pressure of O₂. Assuming \( p_{\text{O}_2} \) is equal to one atmosphere for an O₂-purged solution, the \( E_{\text{Ag/AgCl}}^\circ \) value for a pH 7 solution at 25 °C can be calculated from the relationship

\[ (E_{\text{Ag/AgCl}}^\circ)_{\text{H}_2\text{O}_2/\text{O}_2} = 0.087 - 0.0295 \log [\text{H}_2\text{O}_2] \quad (4.4) \]

Assuming the concentration of H₂O₂ is small (i.e., < 10⁻³ M), then \( (E_{\text{Ag/AgCl}}^\circ)_{\text{H}_2\text{O}_2/\text{O}_2} \) is > 0.18 V. Similarly, for a direct four-electron O₂ reduction pathway

\[ \text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad E_{\text{SHE}}^\circ = -0.401 \text{ V} \quad (4.5) \]

the equilibrium potential can be calculated from the relationship

\[ (E_{\text{SHE}}^\circ)_{\text{OH}^-/\text{O}_2} = 1.229 + 0.0148 \log p_{\text{O}_2} - 0.0592 \text{ pH} \quad (25 \, ^\circ\text{C}) \quad (4.6) \]

When \( p_{\text{O}_2} = 1 \text{ atm}, \text{pH} = 7, \)
For H₂O reduction,

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2 \quad \quad E_{\text{SHE}}^e = -0.828 \text{ V} \quad (4.7) \]

and the equilibrium potential is given by

\[ (E_{\text{SHE}})^{e}_{\text{H}_2/\text{H}_2\text{O}} = -0.0296 \log p_{\text{H}_2} - 0.0592 \text{ pH} \quad (25 \ ^\circ\text{C}) \quad (4.8) \]

When pH = 7,

\[ (E_{\text{Ag/AgCl}}^e)_{\text{H}_2/\text{H}_2\text{O}} = -0.61 - 0.0296 \log p_{\text{H}_2} \quad (4.9) \]

which, if \( p_{\text{H}_2} \leq 10^{-10} \text{ atm} \), yields \( (E_{\text{Ag/AgCl}}^e)_{\text{H}_2/\text{H}_2\text{O}} \geq -0.31 \text{ V} \).

Since at \( E_{\text{corr}} \) the total anodic current must be equal and opposite in sign to the total cathodic current, \( E_{\text{corr}} \) must lie between the equilibrium potentials of the anodic and cathodic half-reactions:

\[ (E^e)_{\text{anodic}} < E_{\text{corr}} < (E^e)_{\text{cathodic}} \]

When \( E_{\text{corr}} \) (or the applied potential) is lower than the equilibrium potentials calculated above, the cathodic reactions are thermodynamically possible.

A comparison of \( E^e \) values shows both the 4- and 2-electron O₂ reduction pathways exhibit a larger potential driving force for the metal oxidation (corrosion) than H₂O reduction. In aerated solutions, \( E_{\text{corr}} \) is sufficiently positive that only O₂ reduction (either 4- or 2-electron pathway) can support corrosion. However, in deaerated solutions in which only H₂O should be available to support the metal oxidation (corrosion), the on-going steady increase in \( E_{\text{corr}} \) indicates a slow surface oxidation, resulting in an...
improvement in passivity, and possibly attributable to the reduction of traces of dissolved O_2.

4.3.2 Potentiostatic Polarization Experiments

4.3.2.1 Potentiostatic Polarization Curves at 70 °C

Figure 4.2 shows the steady-state polarization curves recorded from potentiostatic experiments after one-hour’s polarization on Alloy C22 in aerated solutions at 70 °C. Three distinct regions, but no active region, were observed: (i) a region where O_2 reduction is observed as a shoulder in the potential range ~ – 0.4 to – 0.8 V and H_2O reduction is observed when E < – 0.7 V; (ii) a passive region, and (iii) a transpassive region. The absence of an active (metal dissolution) region confirms the presence of a passive film from very negative potentials. The passive region is that within which the current density is small (< 1 µA) and independent of applied potential. It covers the range from ~ – 0.2 V to ~ 0.4 V, where the lower limit is defined by the potential at which O_2 reduction becomes undetectable, and the upper limit by the potential at which the current increases due to transpassive oxidation of species in the oxide film.

The currents recorded in the positive direction for O_2 reduction are reproducible. However, when the potential is “scanned” back to the negative limit, the O_2 reduction current observed depends on the anodic potential limit achieved. The O_2 reduction current is larger for an anodic limit of 0.9 V (in the transpassive region) than for one of
Figure 4.2  (a) Steady-state potentiostatic polarization curves recorded on Alloy C22 after one-hour’s polarization in aerated 5 mol•dm$^{-3}$ NaCl (pH 7) at 70 °C at a rotation rate of 23.3 Hz; (b) cathodic O$_2$ and H$_2$O reduction current densities on the negative scans.
0.1 V (in the passive region), Figure 4.2 (b). In fact, the cathodic current densities for both O_2 and H_2O reduction are reduced on the negative scans, due to oxide film formation on the positive scan. The extremely small current observed in the polarization curve recorded from an anodic limit of 0.1 V indicates O_2 reduction is almost completely suppressed by the formation of the passive film. However, when the film-growth potential is extended into the transpassive region, O_2 reduction is revived to a small degree on the apparently re-activated surface.

To separate O_2 reduction from H_2O reduction, the currents measured in potentiostatic polarization curves (anodic limit of 0.9 V) in deaerated and aerated solutions, Figure 4.3 (a), were subtracted to yield the net O_2 reduction current, Figure 4.3 (b). A linear relationship for log (−j) as a function of E is obtained on the positive scan in the potential region − 0.6 V and − 0.2 V, suggesting Tafel behaviour, as illustrated by the green line. The Tafel slope was calculated to be -118±10 mV•decade^{-1} of change in current density. Theoretically, the Tafel slope is given by

$$\beta_e = -\frac{2.303RT}{(1 - \alpha)nF}$$  \hspace{1cm} (4.10)

where n is the number of electrons transferred, F is Faraday’s constant, R is the gas constant, T is the temperature in Kelvin, and α is the transfer or symmetry coefficient, and is generally taken to be 0.5. When the kinetics are controlled by a one-electron transfer process, a Tafel slope of − 136 mV•decade^{-1} would be expected at 70 °C. The
Figure 4.3  (a) Potentiostatic polarization curves recorded on Alloy C22 after one-hour’s polarization in either aerated or deaerated 5 mol·dm⁻³ NaCl (pH 7) at 70 °C at a rotation rate of 23.3 Hz; (b) net O₂ reduction current after subtraction of the current for H₂O reduction recorded in deaerated solution. The green line is a least squares fit to 5 points.
measured value suggests the reaction is controlled by the first electron transfer step, but it is sufficiently different to the theoretical value to suggest an additional influence is present.

After polarization to 0.9 V, the O₂ reduction current is considerably enhanced at low reduction potentials (−0.2 V to −0.5 V) compared to the currents measured on the positive scan at this temperature, Figure 4.3 (b). This suggests either catalysis of the first electron transfer rate-controlling process by the high oxidation states of Mo (or W) (Chapter 3) formed in the transpassive region, or easier electron transfer through the partially destroyed barrier layer of the film, which is not completely repaired on the negative scan. Also, the shape of the polarization curve changes markedly. The logarithmic current as a function of $E$ is not linear as observed on the positive scan, the current reaching a maximum at −0.6 V before decreasing as the potential is further decreased. A likely possibility is that the catalytic states are destroyed by electrochemical reduction as the potential is made more negative. Once the catalytic high oxidation states of Mo (or W) are reduced, O₂ reduction is suppressed on the remaining film.

Only one current plateau with a limiting current density of $\sim 0.63 \text{ mA} \cdot \text{cm}^{-2}$ ($E \leq -0.6 \text{ V}$) was observed on the positive scan for O₂ reduction, consistent with the literature [1]. The theoretical limiting cathodic currents expected for a 2- and a 4-electron process, reactions 4.1 and 4.5, respectively, can be calculated using the Levich equation [3]

$$j_L = 0.620 nFAD^{2/3} \omega^{1/2} v^{-1/6} c^b$$  \hspace{1cm} (2.2)
with the following parameter values: the surface area of the electrode, \( A \), is 0.785 cm\(^2\); the rotation rate of the disk, \( \omega \), is 146.61 radians/s; \( \nu \) (6.367\( \times \)10\(^{-2} \) cm\(^2\)•s\(^{-1} \)) is the kinematic viscosity of the electrolyte solution (5 mol•dm\(^{-3} \) NaCl) obtained from the CRC handbook by assuming a constant viscosity ratio of 1.871 relative to water at the same temperature [4-6]; and \( D \) (2.98\( \times \)10\(^{-5} \) cm\(^2\)•s\(^{-1} \)) is the diffusion coefficient of O\(_2\) in the electrolyte, and can be calculated using the Stokes-Einstein equation and experimentally measured parameter values in water [6-8],

\[
\frac{D \nu}{T} = \frac{k'}{6\pi r} = \text{constant} \tag{4.11}
\]

where \( T \) is absolute temperature; \( k' \) is the Boltzmann constant; and \( r \) is the radius of the solute molecule. The bulk concentration of O\(_2\), \( c^b \), can be calculated to be 1.432\( \times \)10\(^{-7} \) mol•cm\(^{-3} \) using the following equation to predict O\(_2\) solubility in an electrolyte solution [9]

\[
\frac{\left( c_{aq} \right)_{l}}{P_{O2}} = K \left( 1 + \kappa \gamma \right)^{-h} \tag{4.12}
\]

where \( \left( c_{aq} \right)_{l} \) (mol•cm\(^{-3} \)) is the concentration of O\(_2\) in the electrolyte; \( P_{O2} \) (atm) is the partial pressure of O\(_2\), corrected for the vapor pressure of water at the same temperature; \( c_i \) (5 mol•dm\(^{-3} \)) is the concentration of electrolyte; \( \kappa \), \( \gamma \) and \( h \) are empirical modeling parameters used to define the effect of inorganic solutes on O\(_2\) solubility, with values 0.076, 1.01 and 4.224 for NaCl, respectively; and \( K \) is the equilibrium constant for the phase equilibrium between dissolved O\(_2\) in water and gas phase O\(_2\), given by
\[ K = \exp \left( \frac{0.046T^2 + 203.35T \ln \left( \frac{T}{298} \right) - (299.378 + 0.092T)(T - 298) - 20.591 \times 10^4}{8.3144T} \right) \]  

(4.13)

The calculated theoretical limiting current densities for a 2- and a 4-electron process for O₂ reduction are 0.46 and 0.92 mA•cm⁻², respectively. Comparison to the experimental limiting current density of 0.63 mA•cm⁻² on the positive scan, measured on a cathodically-cleaned surface, suggests O₂ reduction on Alloy C22 does not proceed via either a 2- or a 4-electron process, but possibly by a mixture of both. Alternatively, the reaction is a 4-electron process, but partially suppressed on the defective oxide present on the surface. The maximum current of 0.14 mA•cm⁻² observed at – 0.6 V on the negative scan indicates O₂ reduction is significantly limited on the transpassively re-activated surface, making it impossible to determine whether O₂ is a fully (4-electron) or a partially (2-electron) process on these surfaces.

If the limiting current density of 0.63 mA•cm⁻² on the positive scan is taken as approaching diffusion-control, and O₂ reduction proceeds through a series 2 step pathway, as suggested by the literature [1,2], the reaction rate can be expressed as

\[ rate = \frac{j}{nF} = \frac{D}{\delta} (c_b - c_s) \]  

(4.14)

whereas in the diffusion controlled region (\( c_s = 0 \)), the rate becomes

\[ rate = \frac{j_L}{nF} = \frac{Dc_b}{\delta} \]  

(4.15)
where $j$ and $j_L$ are the current density and limiting current density, respectively; $\delta$ is the thickness of the diffusion layer; And $c_b$ and $c_s$ are the concentrations of O$_2$ in the bulk solution and at the surface, respectively. Combining 4.13 and 4.14, the following relationship can be obtained

$$\frac{j_L - j}{nF} = \frac{Dc_s}{\delta}$$  \hspace{1cm} (4.16)

On the other hand, by considering the rate of O$_2$ reduction on the alloy surface to have a first order dependence on O$_2$ concentration [10], the reaction rate can also be expressed as

$$rate = \frac{j}{nF} = kc_s$$  \hspace{1cm} (4.17)

where $k$ is the rate constant, and can be calculated using the following expression obtained by rearranging equations 4.15, 4.16 and 4.17, and using an $n$ value of 2.

$$k = \frac{j_L \times j}{nF(j_L - j)c_b}$$  \hspace{1cm} (4.18)

The calculated rate constants as a function of potential are shown in Figure 4.4. A linear Tafel relationship between $\log k$ and $E$ is observed, suggesting a pure charge transfer process occurring on the surface on the positive scan according to the theoretical Tafel relationship between rate constant and applied potential.

$$\log(k) = \log(k_0) - \frac{anF}{2.303RT}(E - E^\circ)$$  \hspace{1cm} (4.19)

where $k_0$ is the standard rate constant, and $E^\circ$ is the equilibrium potential.

### 4.3.2.2 Effect of Temperature on Potentiostatic Polarization Curves

Similar potentiostatic polarization measurements were made in deaerated and aerated
Figure 4.4  Rate constants for O₂ reduction calculated on Alloy C22 for the positive scan of the polarization curve in 5 mol•dm⁻³ NaCl (pH 7) at 70 °C at a rotation rate of 23.3 Hz.

solutions at temperatures of 30 °C, 50 °C and 90 °C. Figure 4.5 shows the steady-state polarization curves in deaerated (a) and aerated solutions (b) at these temperatures, and Figure 4.6 shows the net O₂ reduction currents corrected for H₂O reduction as a function of potential. Consistent with the literature [1], only one limiting current plateau is observed at all temperatures for the positive scans. Figure 4.6 shows that, on the positive scan, temperature has little effect on the limiting current densities for O₂ reduction from 30 to 70 °C, but the limiting current density decreases significantly at 90 °C. On the negative scan, the limiting current density increases with temperature over the range from 30 to 70 °C, but again, decreases with a further increase to 90 °C.
Figure 4.5 Potentiostatic polarization curves recorded on Alloy C22 in deaerated (a) and aerated (b) 5 mol\textperiodcentered dm\textsuperscript{-3} NaCl (pH 7) at various temperatures at a rotation rate of 23.3 Hz. The two vertical lines indicate the range of the passive region.
Figure 4.6  Net O₂ reduction currents recorded on Alloy C22 on the positive (a) and negative (b) scans as a function of potential at various temperatures. The anodic limit in the positive scan was 0.9 V (Figure 4.5).
The observed limiting current densities and theoretically-calculated diffusion limited values (obtained using the Levich equation (2.2)), as well as the parameters used in the calculation, are listed in Table 4.1. A 2-electron O₂ reduction process could be assumed to occur, as suggested by Rogers et al. [1]. For T ≤ 70 °C, on the positive scan, the experimentally observed limiting currents are generally larger than the diffusion limiting values for a 2-electron process, but less than the limiting currents for a 4-electron process, suggesting some reduction of H₂O₂ to H₂O is also occurring. However, on the negative scan, the observed limiting currents are much lower than the calculated limiting values. These observations suggest O₂ reduction on cathodically cleaned Alloy C22 may proceed primarily by a 2-electron process, but probably also involves some further reduction

**Table 4.1**  O₂ limiting current densities in 5 mol•dm⁻³ NaCl at various temperatures assuming a 2-electron reduction process.

<table>
<thead>
<tr>
<th>T</th>
<th>C₀₂</th>
<th>D</th>
<th>ν</th>
<th>jₑ(cal.)</th>
<th>jₑ(exp, pos.)</th>
<th>jₑ(exp, neg.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>°C</td>
<td>10⁻⁷ mol•cm⁻³</td>
<td>10⁻⁵ cm•s⁻¹</td>
<td>10⁻³ cm•s⁻¹</td>
<td>mA•cm²</td>
<td>mA•cm²</td>
<td>mA•cm²</td>
</tr>
<tr>
<td>30</td>
<td>2.85</td>
<td>1.33</td>
<td>12.58</td>
<td>0.48</td>
<td>0.52</td>
<td>0.0069</td>
</tr>
<tr>
<td>50</td>
<td>2.07</td>
<td>2.08</td>
<td>8.62</td>
<td>0.50</td>
<td>0.71</td>
<td>0.028</td>
</tr>
<tr>
<td>70</td>
<td>1.43</td>
<td>2.98</td>
<td>6.37</td>
<td>0.46</td>
<td>0.63</td>
<td>0.14</td>
</tr>
<tr>
<td>90</td>
<td>0.606</td>
<td>4.06</td>
<td>4.96</td>
<td>0.25</td>
<td>0.026</td>
<td>0.058</td>
</tr>
</tbody>
</table>
process. The much lower limiting currents observed on the negative scans indicate that the kinetics of O₂ reduction are suppressed by the formation of the oxide film and only partially revived by an excursion into the transpassive region. The temperature dependence of the limiting current on the negative scan, for \( T \leq 70 \, ^\circ\text{C} \), indicates that O₂ reduction is temperature-dependent on the transpassively re-activated surface, and this would be consistent with a catalyzed electrochemical process. At 90 \(^\circ\text{C}\), the experimentally obtained limiting currents on both the positive and negative scans are much lower than the calculated values. For the positive scan, the observed limiting current is 10 times less than the calculated diffusion-controlled current. This could be attributed to rapid passive film formation at this temperature. Compared to the currents at lower temperatures, the suppressed currents at 90 \(^\circ\text{C}\) suggest the passive film formation is accelerated at high temperatures. For the negative scan, the observed limiting current is two times larger than the value on the positive scan. This can be attributed to the existence of catalytic states (high oxidation states of Mo (or W), Chapter 3) formed in the transpassive region. The decrease in O₂ reduction current when the temperature is increased to 90 \(^\circ\text{C}\) is only marginal and could be accounted for by the decrease in O₂ concentration counterbalanced by the increase in the diffusion coefficient.

In the potential region of \(-0.6\) V to \(-0.2\) V, the linear logarithmic increase in current with potential on the positive scan indicates that interfacial charge transfer is the
rate-controlling process, although there are insufficient data points to attempt a Tafel analysis.

4.3.2.3 EIS Measurements at 70 °C

An EIS measurement was performed after each 2-hour potentiostatic polarization experiment starting from a potential of –1 V (Figure 2.3) in both aerated and deaerated stagnant solutions over the temperature range of 30-90 °C. Figure 4.7 shows the Nyquist (a) and Bode plots (b and c) measured at selected potentials on the positive scan of the polarization curve at 70 °C in aerated 5 mol•dm⁻³ NaCl, and Figure 4.8 shows spectra measured on the following negative scan: the solid lines represent fits to the spectra as discussed below. While only the data recorded in the low frequency range can be seen in the Nyquist plot, the Bode plots exhibit the full range of frequency information. Over the potential range –0.9 V to ~0.1 V, the low-frequency impedance magnitude $|Z|$ increases with increasing potential (Figure 4.7 (b)). When the potential is further increased over the potential range up to 0.9 V, the impedance decreases gradually with potential to ~250 Ω•cm². These changes in impedance magnitude with potential are consistent with the polarization data discussed above.

The phase angle ($\theta$) vs frequency curves (Figure 4.7 (c)), show only one maximum at the lowest and highest potentials (~0.8 V and 0.7 V) suggesting the presence of only one time constant, but two maxima at other potentials, indicating the existence of two time
(a) $Z''$ (Ω$^*$cm$^2$)

(b) $|Z|$ (Ω$^*$cm$^2$)
Figure 4.7 Impedance spectra recorded on Alloy C22 in aerated 5 mol•dm$^{-3}$ NaCl at 70 °C at selected potentials applied on the positive scan of the polarization curve from –1 V: (a) Nyquist and (b and c) Bode plots. The lines are for fits of these spectra to one or other of the equivalent circuits shown in Figure 4.9.

Constants. The maximum phase angle for all potentials was $< -90^\circ$, indicating that the films are not fully capacitive. This is particularly noticeable at the most positive potential (0.7 V). The maximum in the frequency range, $10^1$ to $10^3$ Hz, is most likely attributable to an interfacial charge-transfer process at the barrier layer/outer layer (solution) interface [11]. The impedance response at low frequencies is attributed to dielectric processes within the barrier layer of the passive film.

Even though similar Nyquist and Bode plots and trends with potential were observed on
the negative scan (Figure 4.8), significant differences exist between the two sets of spectra. In the transpassive region ($E > 0.3$ V), the low-frequency impedance magnitude $|Z|$ is larger on the negative scan than that on the positive scan. While in the passive region, based on visual inspection of the spectra, there appears to be little difference between spectra recorded on both scans. In the near-passive ($E \leq -0.5$ V) region, the impedance magnitude $|Z|$ decreases (compared to the positive scan), suggesting the barrier layer destroyed on the positive scan is not completely repaired on the negative scan, consistent with the enhanced O$_2$ reduction currents observed in this region, Figure 4.3 (b). At the negative potential end ($E < -0.6$ V), the impedance magnitude $|Z|$ is larger than that on the positive scan again, consistent with the suppressed O$_2$ reduction currents in this region shown in Figure 4.3 (b).
Figure 4.8  Impedance spectra recorded on Alloy C22 in aerated 5 M NaCl at 70 °C at selected potentials applied on the negative scan of the polarization curve from – 1 V: (a) Nyquist and (b and c) Bode plots. The lines are for fits of these spectra to one or two of the equivalent circuits shown in Figure 4.9.
The variation in the phase angle ($\theta$) with potential on the negative scan is more noticeable. The phase angle increases as the film-growth potential decreases from 0.8 V to $\sim$ 0.1 V, and then decreases as the film-growth potential is further decreased to $-0.9$ V, especially at low frequencies. Also, even though the phase angle ($\theta$) vs log(frequency) curves (Figure 4.8 (c)) only show one maximum at the highest potentials ($E > 0.6$ V) on the negative scan, two maxima are observed at other potentials, indicating the existence of two time constants.

Figure 4.9 shows the electrical equivalent circuits which adequately fitted the impedance spectra. For the positive scan, spectra recorded at the cathodic and the anodic ends of the potential range ($E < -0.5$ V, and $E > 0.6$ V) were fitted to a one time constant equivalent circuit since only one maximum between $10^1$ to $10^3$ Hz was observed in the phase angle plot at these potentials. This impedance response represents charge transfer at the

![Figure 4.9](image)

**Figure 4.9** Electrical equivalent circuits used to fit impedance spectra on Alloy C22 at 70 °C. The circuits consist of a solution resistance ($R_s$), a charge transfer resistance ($R_1$) and capacitance (CPE$_1$) combination for the occurrence of electrochemical reactions, at the barrier layer /outer layer (solution) interface (a); and an additional parallel barrier layer resistance ($R_b$) and capacitance (CPE$_b$) (b).
oxide/solution interface as mentioned above. At negative potentials it will be charge transfer to $O_2$ leading to its reduction. However, at positive potentials it is attributed to the creation of transpassive states once the barrier layer is destroyed. Spectra exhibiting two maxima in the phase angle plot were fitted to the equivalent circuit shown in Figure 4.9 (b), the second time constant being attributed to the properties of the passive film which change with potential. All spectra recorded on the negative scan were fitted to two time constants, except for the potentials at the anodic end ($E > 0.6$ V). The fitted spectra are shown as solid lines in Figure 4.7 and Figure 4.8 (a) through (c). In all cases, acceptable agreement between experimental and fitted data was achieved.

In the electrical equivalent circuits, the constant phase elements, CPE, are introduced in place of pure capacitors to account for the distribution of the time constants as described in Chapter 2. The fitted CPE exponents, $n$, are $> 0.8$ for all applied potentials except for the cathodic (only on the negative scan) and the anodic ends of the potential range. In these potential range, these low $n$ values can be attributed to the presence of large oxidation states for many cations at positive potentials, and a high density of film defects at negative potentials, both of which lead to the extremely large capacitances. Despite these deviations in $n$ at extreme potentials, the CPEs are taken to represent the capacitances.

The parameter values obtained from the fitted spectra are shown in Figure 4.10 and Figure 4.11 where the polarization resistance ($R_p$) is the sum of the charge-transfer
Figure 4.10  Variation of resistance (R₁ and R₂) with applied potential on Alloy C22 in aerated 5 mol•dm⁻³ NaCl at 70 ºC during a potentiostatic polarization experiment (a) on the positive scan; (b) on the negative scan.
Figure 4.11  Variation of capacitance ($\text{CPE}_1$ and $\text{CPE}_b$) with applied potential on Alloy C22 in aerated 5 mol•dm$^{-3}$ NaCl at 70 °C during a potentiostatic polarization experiment (a) on the positive scan; (b) on the negative scan.
resistance (R₁) and the barrier layer resistance (R₉). Inspection of Figure 4.10 shows a number of features, especially when comparing the resistance values obtained on the positive and negative scans. On the positive scan, for \( E < -0.4 \text{V} \), Rᵱ is dominated by R₁, consistent with R₁ being the charge transfer resistance for the O₂ reduction reaction. Although no film resistance is measured in this potential region (since only a single time constant circuit is used to fit the spectra), it is clear that it is \( \leq R₁ \) for \( E < -0.4 \text{V} \). For higher potentials, R₉ increases rapidly with potential as the passive film thickens and becomes less defective. Throughout the passive region R₁ varies only slightly as R₉ increases. Since the current for O₂ reduction becomes negligible in this region, it is likely that R₁ represents the charge transfer process across the alloy oxide interface; i.e. cation/oxygen vacancy injection into the passive film.

For \( E > 0.3 \text{V} \), Rᵱ begins to decrease markedly with potential, accompanied by a decrease in R₁. Since Rᵱ is dominated by R₉, this decrease, as previously discussed [12], can be attributed to defect injection into the barrier layer. As discussed above, for \( E \geq 0.6 \text{V} \) it is likely that R₁, which then dominates Rᵱ, can be attributed to charge transfer processes producing highly charged Mo and W species in the transpassive layer on the alloy surface as observed in Chapter 3.

On the negative scan, the polarization resistance, Rᵱ, is larger than on the positive scan in the transpassive region (\( E > 0.3 \text{V} \)), consistent with the presence of a transpassive layer which thickened on the positive scan at higher potentials. Previous experiments showed
this to be a highly oxidized Mo (W) film (Chapter 3). However, while the value of $R_p$, dominated by the film resistance, achieves an equally high value in the potential range 0.1 to 0.3 V to that observed on the positive scan, its more rapid decrease as the potential is decreased (compared to values recorded on the positive scan) clearly indicates that the highly resistive properties of the barrier layer are not fully recovered after the excursion deep into the transpassive region. Consequently, the very high value of $R_p$ in the range 0.1 V to 0.3 V can be taken to represent a combination of the resistance of the partially reformed barrier layer and the thicker transpassively formed outer layer.

The rapidly decreased $R_p$ at $E < 0.1$ V on the negative scan, dominated by $R_b$ (now considered to be the resistance of an incompletely reformed passive layer covered with a thicker outer Mo(VI)/W(VI) oxide), achieves a minimum at $-0.6$ V. This is the region within which enhanced $O_2$ reduction currents are observed, Figure 4.3 (b), and attributed to catalysis by these high oxidation states of Mo and W. As the potential is further decreased, $R_p$ increases slightly and the $O_2$ reduction current decreases (Figure 4.3 (b)), consistent with the partial destruction of these catalytic states.

Accepting that the CPE values represent capacitances, the capacitance of the passive film (CPE$_b$) decreases markedly on increasing the potential through the passive potential region, Figure 4.11. This is consistent with expectations for the growth and defect annealing of a passive film. The capacitance associated with the oxide/solution interface (CPE$_i$) remains effectively constant from -0.9 V, when the dominant interfacial process
is O₂ reduction on a highly defective oxide to ~ 0.2 V, beyond which the injection of
cation defects leads to destruction of the passive barrier layer. The value of the
capacitance, ~100 µF cm⁻² is not inconsistent with a predominantly double layer
capacitance. At more positive potentials, this capacitance, associated with charge transfer
processes within the film, increases markedly as would be expected for the generation of
a defective surface film containing multiple cations with high oxidation states.

On the negative scan the film capacitance (CPEₜ), effectively retraces the behaviour
observed on the positive scan down to ~ −0.2 V, consistent with the partial regeneration
of the barrier layer indicated by the film resistance values. By contrast the capacitance
associated with charge transfer processes (CPEᵢ) is considerably larger on the negative
scan, especially for potentials < −0.2 V, when the cathodic reduction of O₂ becomes
possible. The very large values at negative potentials support the claim that the surface is
covered with a highly defective surface layer containing Mo(VI)/W(VI) states. The slight
decrease in both capacitances at E < −0.6 V, which coincides with the decrease in O₂
reduction current, Figure 4.3 (b), would then be consistent with the electrochemical
destruction of these Mo(VI)/W(VI) oxidation states.

A similar set of measurements was conducted in deaerated solution. Figure 4.12 shows a
comparison of Rₚ (R₁ + Rₜ) on Alloy C22 as a function of potential in deaerated and
aerated solutions at 70 °C. There is a clear difference in behaviour especially for
potentials ≤ −0.1 V, when the presence of an electron acceptor in solution (O₂) leads to
Figure 4.12  Comparison of Rp on Alloy C22 as a function of potential in deaerated and aerated 5 mol·dm$^{-3}$ NaCl at 70 °C (a) on the positive scan; (b) on the negative scan.
charge transfer across the oxide/solution interface and a lower value of $R_p$. On the positive going scan in deaerated solutions, the plateau in $R_p$ between $-0.6$ and $-0.4$ V suggests a change in film properties may occur in this region leading to a more rapid development of the passive layer at potentials more positive than $-0.4$ V. This potential region coincides with that within which $O_2$ reduction is observed, Figure 4.5 (b) and Figure 4.6 (a), and beyond which it is suppressed. For potentials $> 0.3$ V, $R_p$ can be up to one order of magnitude lower in aerated compared to deaerated solutions, suggesting that chemical oxidation may play a role in determining the properties of the transpassive layer.

On the negative scan $R_p$ values are effectively identical under aerated and deaerated conditions until the potential is $\leq -0.1$ V, when measurable $O_2$ reduction currents are obtained once the potential is more negative than this value, Figure 4.6.

### 4.3.2.4 Temperature Dependence of EIS Measurements

Similar EIS measurements were carried out at 30 ºC and 90 ºC in both deaerated and aerated solutions. Figure 4.13 and Figure 4.14 show the $R_p$ values obtained as a function of potential in deaerated and aerated solutions, respectively. In deaerated solutions on the positive scan (Figur 4.13), the behaviour as a function of temperature changes only marginally with temperature. The general trend with potential does not change with temperature, similar features being observed at all three temperatures, although slightly
Figure 4.13  Effect of temperature on $R_p$ on Alloy C22 as a function of potential in deaerated 5 mol\,dm$^{-3}$ NaCl during a potentiostatic polarization experiment. (a) positive scans; (b) negative scans.
Figure 4.14  Effect of temperature on $R_p$ on Alloy C22 as a function of potential in aerated 5 mol•dm$^{-3}$ NaCl during a potentiostatic polarization experiment.  
(a) positive scans; (b) negative scans.
lower $R_p$ values are obtained at all potentials as the temperature increases. XPS and ToF-SIMS analyses (Chapter 3) show that the oxide film thickens with temperature but may be more defective since larger amounts of Mo(IV)Mo(V) are retained in the inner barrier layer. These two compensating trends could account for the relatively small drop in $R_p$ ($\sim R_b$ in this potential range) with temperature. The largest difference in $R_p$ with temperature is observed for $E < -0.6$ V where the $R_p$ values are up to an order of magnitude lower at the higher temperatures. This observation is consistent with the clear temperature dependence of the steady-state currents in deaerated solutions shown in Figure 4.5 (a).

By contrast, the behaviour on the negative scan exhibits considerable variation with temperature, the value of $R_p$ being lower in both the passive region and the cathodic region ($E < -0.3$ V). Throughout the passive region (0.2 V to $\sim$ -0.4 V) the $R_p$ values ($\sim R_b$) are up to $10^2$ times lower at 90 °C than at 30 °C, indicating that the barrier layer becomes less readily reformed as the temperature is increased. As observed on the positive scan the kink between $-0.4$ V and $-0.6$ V is clearly visible at all temperatures. Also the increased $R_p$ at the cathodic end ($E < -0.7$ V) at all temperatures compared to the positive scan is consistent with the suppressed H$_2$O reduction currents observed on the negative scan, Figure 4.5 (a).

As observed in deaerated solutions, the general behaviour of $R_p$ in aerated solutions (Figure 4.14) as a function of potential is the same at all three temperatures. In the
passive region, the \( R_p \) (~ \( R_b \)) values are up to one order of magnitude lower at the two higher temperatures but, in all cases, approach or exceed \( 10^6 \ \Omega \cdot \text{cm}^2 \). The onset of passivity (for \( E > -0.3 \ \text{V} \)) is considerably more rapid at 30 °C and 90 °C than at 70 °C, although it is not clear whether this is a meaningful (or reproducible) difference. There is a very clear difference in \( R_p \) values with temperature in the transpassive region (\( E > 0.4 \ \text{V} \)). In this region \( R_p \) is dominated by charge transfer processes such as the generation of oxidized Cr and Mo (W) states. Since these differences are not observed in deaerated solutions, they can be attributed to an influence of \( \text{O}_2 \) on the transpassive behaviour. The \( R_p \) value does not show any significant temperature dependence in the \( \text{O}_2 \) reduction region (\( E < -0.1 \ \text{V} \)). The lack of temperature dependence for \( R_p \) could explain the absence of any temperature dependence for \( \text{O}_2 \) reduction currents measured in this potential range, Figure 4.5 (b), supporting the claim that the \( \text{O}_2 \) reduction currents are controlled primarily by the properties of the oxides.

Another parameter obtained from EIS spectra, \( \text{CPE}_b \), is shown in Figure 4.15 and Figure 4.16 for deaerated and aerated solutions, respectively. The \( \text{CPE}_b \) at all temperatures initially decreases with applied potential and reaches a minimum value in the passive region, as expected for a film growth/defect (metal interstitials and/or oxygen vacancies) annealing process according to the point defect model (PDM) for passive films on metals and alloys [13, 14]. At high potentials the increase in \( \text{CPE}_b \) is consistent with the injection of cation vacancies into the film. A similar variation of film capacitance with potential is
Figure 4.15 Effect of temperature on CPE\textsubscript{b} on Alloy C22 as a function of potential in deaerated 5 mol dm\textsuperscript{-3} NaCl during a potentiostatic polarization experiment. (a) positive scans; (b) negative scans.
Figure 4.16  Effect of temperature on CPE$_b$ on Alloy C22 as a function of potential in aerated 5 mol•dm$^{-3}$ NaCl during a potentiostatic polarization experiment.

(a) positive scans; (b) negative scans.
observed on the reverse scans.

Consistent with the relatively small variations in $R_p$ with temperature on the positive scan in deaerated solution (Figure 4.13), the variations in capacitance are relatively small being generally slightly larger at 90 °C compared to the two lower temperatures. The general increase in capacitance at 90 °C can be attributed to the presence of a more defective passive film at this higher temperature, as indicated in XPS and ToF-SIMS measurements (Chapter 3). As expected on the negative scan, based on the significantly lower $R_p$ values observed as the temperature increases, there is a very significant increase in capacitance with temperature. This confirms that once the barrier layer is transpassively destroyed its reformation on the negative scan becomes progressively more difficult as the temperature is increased.

In aerated solution, these $R_p$ and capacitance values suggest that it should become progressively easier to support O$_2$ reduction at more positive potentials as the temperature increases. However, for films not transpassively destroyed, based on Figure 4.14 (a) and Figure 4.16 (a), the sudden jump in $R_p$ and drop in capacitance that occurs around – 0.1 to – 0.2 V irrespective of temperature, indicate that a potential more negative than this is required to sustain a cathodic O$_2$ reduction current, despite the increase in defectiveness with temperature indicating an increased electrical conductivity of the film. It is worth noting that this is the potential established at the crevice mouth in galvanostatically-driven crevice propagation experiments [15]. This observation of a
temperature-independent threshold for the onset of O$_2$ reduction supports the claim that the kinetics of this reaction is determined by film properties and how they change with potential.

### 4.3.3 Potentiostatic Film-growth Followed by Cyclic Voltammetry

After oxide film growth at constant potentials for 1 hour, the potential was potentiodynamically scanned from the film growth potential to the cathodic limit of -1 V (forward scan) and back (reverse scan) at a scan rate of 5 mV•s$^{-1}$. As described in Chapter 2, the forward scan shows the influence of the film on the O$_2$ and H$_2$O reduction reactions, and the reverse scan determines whether any changes occurred in the oxide film during the forward scan.

Figure 4.17 shows a series of CVs recorded after potentiostatic film-growth in aerated and deaerated 5 mol•dm$^{-3}$ NaCl at 70 ºC. The currents are shown offset to illustrate the differences. In aerated solutions, the currents remain negative but reversible current-potential behaviour is observed for oxidation at – 0.6 and – 0.4 V, suggesting O$_2$ reduction current remains on the defective oxide film but no film reduction process occurred on the forward scan and was reoxidized on the subsequent reverse scan. The reversible current-potential behaviour and no O$_2$ reduction wave are observed for oxidation in the passive region (up to 0 V) suggesting the O$_2$ reduction current is completely suppressed on the oxide film grown at these potentials on the forward scan,
Figure 4.17  CV scans recorded on Alloy C22 at various film-growth potentials in aerated (a) and deaerated (b) 5 mol•dm⁻³ NaCl at 70 °C at a rotation rate of 23.3 Hz. The currents are shown offset by 1 mA•cm⁻².
consistent with the potentiostatic polarization experiments and EIS results in section 4.3.2 in this chapter. The absence of any hysteresis or visible reoxidation current on the reverse scan suggests no change in the film.

After anodic oxidation at 0.2 V, a slight reduction current is observed on the forward scan but not on the reverse scan. This slight reduction current could be due to O\textsubscript{2} reduction on a slightly transpassively activated surface since the EIS results (Figure 4.10 and 4.14) show that this is approximately the threshold potential above which defect injection into the oxide commences. As previously demonstrated by Jakupi et al. [12], this is the potential beyond which crevice initiation can occur.

After polarization in the transpassive region (0.4 V and 0.6 V), a very distinct O\textsubscript{2} reduction current is observed on the forward scan, and the value of the current density in the plateau region observed is greater after polarization at 0.6 V than at 0.4 V. This is consistent with the claim above that O\textsubscript{2} reduction is catalyzed on the oxidized Mo and W states, produced in the transpassive region. The higher O\textsubscript{2} reduction current observed after polarization at 0.6 V (compared to 0.4 V) would then reflect a more complete surface coverage with these states. This is consistent with the observation (Figure 3.2) that oxidation in the transpassive region does not occur uniformly on the electrode surface making an increase in density of catalytic states with increased potential likely. The lower O\textsubscript{2} reduction current on the reverse scan can be attributed to the reduction (at least partial) of these states at more cathodic potentials and a film reoxidation process. It
is also worth noting that this reduction process leads to a depression of the current at the most negative potentials (–1 V).

A similar series of experiments conducted in deaerated solutions, Figure 4.17 (b), show that transformations in the oxide film also occur in this series of experiments. After oxidation at potentials of –0.2 V or greater a film reoxidation process is observed on the reverse scan suggesting that the passive oxide film was not irreversibly formed after the initial potentiostatic oxidation. This is supported by the EIS data, Figure 4.12 and 4.13, which show that the maximum barrier layer resistance is not achieved until a potential $\geq$ – 0.2 V is achieved.

That the above proposed mechanism of passivation may be operative is supported by the observation that after anodic oxidation at 0 V and a scan to –1 V no reoxidation process is observed on the reverse scan. However, polarization at 0.2 V (the threshold of the transpassive region) and 0.4 V/0.6 V leads to a reoxidation process which is more marked the more positive the anodic potential applied. Also the reoxidation peak transforms from an apparently single peak at $\sim$ – 0.5 V to a broader, apparently double peak covering the potential range –0.7 to –0.3 V. This range coincides with the plateau region observed in the polarization resistance plots, Figures 4.13 and 4.14. Even when this plateau is not observed, Figure 4.10, the positive limit of this range coincides with the complete establishment of the passive region, and the disappearance of an O$_2$ reduction current.
These observations clearly show that the reduction of $O_2$ on the alloy surface is coupled to transformations in the oxide film. There are also two additional features worth noting in Figure 4.18. (i) The current at the negative potential limit of $-1$ V is greater in aerated than in deaerated solutions. (ii) After potentiostatic treatment in the transpassive region the current at the cathodic limit ($-1$ V) is significantly suppressed irrespective if whether $O_2$ is present or not; i.e., the cathodic reduction of the film formed in the transpassive region leads to a catalytically less active film than the original defective film present at lower potentials.

4.4 Summary and Conclusions

Various electrochemical techniques, including $E_{corr}$ measurements, potentiostatic polarization, EIS and potentiostatic film-growth followed by CV experiments, were employed to investigate the kinetics of $O_2$ reduction on oxide-covered Alloy C22 in 5 mol•dm$^{-3}$ NaCl solutions up to 90 ºC. The $E_{corr}$ at 70 ºC in aerated solution achieves a steady-state value $\sim -0.15$ V after 24 hours, whereas in deaerated solution, the value is $\sim -0.35$ V but still increasing. While corrosion in deaerated solutions should be supported by $H_2O$ reduction, the on-going increase in $E_{corr}$ can be attributed to the presence of traces of dissolved $O_2$.

Potentiostatic polarization curves recorded by increasing the applied potential from $-1$ V yield a logarithmic current-potential plot for $O_2$ reduction with a slope of $-118\pm10$
mV•decade⁻¹ of change in current density, suggesting the reaction is controlled by the first electron transfer step. A limiting current density of 0.63 mA•cm⁻² is observed at $E < –0.6$ V suggests O₂ reduction on Alloy C22 may proceed primarily by a 2-electron process.

The O₂ reduction current determined depends on the preoxidation potential. When the electrode is preoxidized in the passive region (0.1 V), O₂ reduction is almost completely suppressed by the passive film. However, when the preoxidation potential is extended into the transpassive region, O₂ reduction is revived to a small degree on the apparently re-activated surface. After potentiostatic preoxidation at 0.9 V, the net O₂ reduction current is considerably enhanced at low potentials (–0.2 V to –0.5 V), suggesting catalysis of the O₂ reduction reaction by the high oxidation states of Mo (or W) (Chapter 3) formed in the transpassive region. The O₂ reduction current reaches a maximum at –0.6 V before decreasing as the potential is further decreased. A possibility is that the catalytic states are destroyed by electrochemical reduction as the potential is made more negative. Once the catalytic high oxidation states of Mo (or W) are reduced, O₂ reduction is suppressed on the remaining film.

EIS measurements show that the polarization resistance ($R_p$) is dominated by the charge transfer resistance for the O₂ reduction reaction for $E < –0.4$ V. As the potential is made increasingly more positive, the barrier layer resistance increases rapidly with potential as the passive film thickens and becomes less defective and reaches a maximum in the
passive region (– 0.3 V ≤ E ≤ 0.3 V). For E > 0.3 V, R_p begins to decrease markedly with potential due to the injection of cation defect into the barrier layer. For E ≥ 0.6 V the polarization resistance again becomes dominated by the charge transfer process producing highly charged Cr, Mo and W species in the transpassive layer on the alloy surface. The capacitance of the passive film decreases markedly on increasing the potential through the passive potential region, and at more positive potentials, increases markedly with the generation of the defective transpassive film containing multiple cations with high oxidation states.

After polarizing the potential at a series of increasingly positive potentials up to 0.9 V, EIS spectra were recorded at a series of increasingly negative values. The polarization resistance again achieves high values in the potential range 0.1 to 0.3 V, but more rapidly decreases at E < 0.1 V (compared to values recorded on increasing the potential). This indicates that the resistive properties of the barrier layer are not fully recovered after an excursion deep into the transpassive region. As a consequence an enhanced O_2 reduction current is observed in this potential region. The R_p achieves a minimum at -0.6 V and increases slightly as the potential is further decreased, leading to a decrease in O_2 reduction current at more negative potentials. This can be attributed to the reduction of the catalytic Mo(VI)/W(VI) states formed in the transpassive region.

With increasing temperature, the O_2 reduction current recorded at increasingly positive potentials shows no dependence on temperature from 30 to 70 ºC, but the current
decreases significantly at 90 °C. This decrease is attributed to an increase in film thickness with temperature accompanied by the temperature-enhanced dissolution of the potentially catalytic Mo(VI)/W(VI) states from the film. After potentiostatic polarization up to 0.9 V, the O₂ reduction current recorded at increasingly negative potentials increases with temperature over the range from 30 to 70 °C, indicating that O₂ reduction is thermally activated on the transpassively re-activated surface, but again decreases at 90 °C. This decrease is marginal and could be accounted for by the decrease in O₂ concentration at high temperatures.

EIS measurements made at a series of increasing potentials show only slight differences in polarization resistance and film capacitance values, except at potentials < -0.6 V when the passive film is highly defective allowing the H₂O reduction current to be thermally activated. When the spectra are recorded at a series of decreasing potentials after polarization in the transpassive region, the polarization resistance becomes significantly lower with an increase in temperature. This decrease is primarily due to a decrease in passive film resistance, as it becomes increasing difficult to reform the passive film at higher temperatures.

EIS measurements show that, irrespective of temperature in aerated solution, a potential ≤ –0.15 V is required to sustain a cathodic O₂ reduction current. This potential threshold (~ –0.15 V) for the onset of O₂ reduction is not particularly dependent on temperature.
Cyclic voltammetric experiments conducted on surfaces pre-oxidized at various potentials at 70 ºC show the O₂ reduction current is completely suppressed on the oxide film grown at potentials < 0 V, which is consistent with potentiostatic polarization experiments and EIS results. After oxidation at potentials > 0.2 V, a very distinct O₂ reduction current is observed, the current density increasing as the preoxidation potential is increased. This is consistent with the claim that O₂ reduction is catalyzed on oxidized Mo and W states produced in the transpassive region.

The CVs conducted in deaerated solutions show that transformations in oxide film properties also occur. After oxidation at potentials up to 0 V, no apparent film reoxidation process is observed in a voltammetric scan to – 1 V and back. However polarization at 0.2 V (the threshold of the transpassive region) and 0.4 V/0.6 V leads to a reoxidation process which is more marked the more positive the anodic potential applied. Also the reoxidation peak transforms from an apparently single peak to a broader, apparently double peak. These observations confirm that the reduction of O₂ on the alloy surface is coupled to transformations in the oxide film.

4.5 References


Chapter 5

Exploring the Film Transformations on Alloy C22

5.1 Introduction

In chapter 4, various electrochemical techniques were employed to investigate the kinetics of O\textsubscript{2} reduction on oxide-covered Alloy C22. Cyclic voltammetric (CV) experiments demonstrated that the kinetics of O\textsubscript{2} reduction strongly depend on the pre-oxidation potential, and, hence, on the composition of the oxide. When the oxide film was grown at high potentials in the transpassive region, O\textsubscript{2} reduction was revived by catalysis on the Mo(VI)/W(VI) oxidation states created in this region. The properties of the passive film and its influence on O\textsubscript{2} reduction kinetics was found to be influenced by redox transformations in the oxide film. To identify these redox transformations, a series of CV experiments were performed in deaerated 5 mol\(\text{•}\text{dm}^{-3}\) NaCl solutions over the temperature range of 30-90 °C. The potential was scanned to various cathodic limits and XPS was employed to explore the film transformations. CV experiments were also conducted on pure Ni, Cr and Mo to help identify the film transformations on Alloy C22.

5.2 Experimental Details

Similar experimental procedures and techniques for electrode preparation to those described in Chapter 4 were employed. The general potential profile used in most cyclic
voltammetry (CV) experiments is shown in Figure 2.4. Preoxidation potentials used for Alloy C 22 ranged from – 0.6 V to 0.6 V to cover the cathodic, passive and transpassive regions. Experiments were performed over the temperature range from 30 °C to 90 °C. In multiple preoxidation–CV experiments (potential profile shown in Figure 5.1), the following electrochemical sequence was performed. After cathodic cleaning at –1 V for 1 hour, the electrode was preoxidized at 0.6 V for 1 hour. Then a CV scan was run from the preoxidation potential (0.6 V) to a cathodic limit (– 0.83 V) and back 3 times (3 cycles), at a scan rate of 5 mV•s⁻¹. On completion of this procedure (period 1), the electrode was again oxidized at 0.6 V for 1 hour, followed by CV scans over the same potential range and at the same scan rate (period 2). This sequence was repeated for 4 periods. During this procedure the electrode was rotated at a constant rate of 23.3 Hz.

XPS was used to investigate the film transformation processes, and the potential-time profile used in these experiments is displayed in Figure 5.2. The electrode was pre-oxidized at 0.6 V for 1h at room temperature before removal for XPS analysis, point 1. In a subsequent experiment, after preoxidation at 0.6 V, the electrode potential was scanned from 0.6 V to – 1 V and back to 0.6 V and then analyzed by XPS, point 6. In additional experiments, the potential was stopped at selected values within the scan and removed for XPS analyses (point 2: – 0.6 V; point 3: – 0.78 V; point 4: – 1 V and point 5: – 0.1 V). The purpose of these experiments is to analyze the variations in film composition during the CV scan. A new electrode was used in each experiment. To avoid
Figure 5.1  The experimental potential sequence used for multiple preoxidation-CV experiments.

Figure 5.2  Potential-time profile used to identify film transformation processes using XPS.
air exposure, electrochemical experiments were performed in an Ar-purged glove box and the samples were sealed in a specifically designed container to facilitate transfer from the glove box to a glove box attached to the introduction chamber to the XPS.

High purity Ni, Cr and Mo metals (≥ 99.9 %) were also studied to identify film transformations. Electrodes were prepared using the procedure described for C22. Polarization scans were performed from the corrosion potential to potentials in the transpassive region for these pure metals at a scan rate of 0.1667 mV•s⁻¹ in deaerated solutions. Preoxidation potentials were then selected from these scans and additional CV experiments performed after preoxidation.

5.3 Results and Discussion

5.3.1 Film Transformations on Alloy C22

5.3.1.1 Potentiostatic Preoxidation Currents at Various Temperatures

Figure 5.3 shows the final positive current densities as a function of applied potential after a one hour film-growth on Alloy C22 in deaerated solutions. Over the temperature range from 30 ºC to 90 ºC, the steady-state current densities are independent of applied potential in the passive region (−0.2 V to 0.2 V), and increase with increasing potential in the transpassive region (E > 0.2 V). The current increases by just over an order of magnitude over this temperature range. The low current densities are consistent with the
Figure 5.3  Potentiostatic current densities as a function of applied potential measured on Alloy C22 in deaerated 5 mol•dm\(^{-3}\) NaCl solutions (1 hour) over the temperature range 30 °C to 90 °C.

high polarization resistances (~ 10\(^6\) Ω•cm\(^2\)) measured in the passive region and the decreasing polarization resistance with increasing potential in the transpassive region in Chapter 4. The relatively small increase in steady-state current with temperature is also in agreement with the slight decrease in polarization resistance with increasing temperature, Chapter 4.

5.3.1.2  \textit{CV Scans to } -1 \textit{ V after Potentiostatic Preoxidation at Various Temperatures}

After oxide film growth at a constant preoxidation potential, the potential was scanned
from this preoxidation value to the cathodic limit of – 1 V (forward scan) and back (reverse scan) at a scan rate of 5 mV s\(^{-1}\) in deaerated solutions at various temperatures. In the absence of dissolved O\(_2\), the film transformations in the oxide can be observed. Figure 5.4 displays a series of CV scans recorded on Alloy C22 after preoxidation at various potentials in deaerated 5 mol\(\cdot\)dm\(^{-3}\) NaCl at 30 °C. The currents are shown offset to illustrate the differences. While there is no indication of any reduction process on the forward scans from the preoxidation potential to –1 V, the reverse scans show that film reduction did occur, leading to a reoxidation process over the potential range of – 0.6 V to

![Figure 5.4](image)

**Figure 5.4** CV scans recorded on Alloy C22 at various film growth potentials in deaerated 5 mol\(\cdot\)dm\(^{-3}\) NaCl at 30 °C. The currents are shown offset by 0.25 mA\(\cdot\)cm\(^{-2}\).
– 0.2 V on the reverse scans. This process becomes observable once the preoxidation potential is increased to \( \geq -0.2 \) V, Figure 5.4. The size of the reoxidation peak increases with the film growth potential, and becomes significantly larger once the film growth potential is increased into the transpassive region.

The growth in the size of the reoxidation peak with film-growth potential is consistent with the EIS results in Chapter 4 which showed that significant changes occurred in the film at transpassive potentials and that these changes were not fully reversed on scanning the potential to the cathodic limit. Additionally the film grown in the transpassive region became thicker as the oxidation potential was made more positive within the transpassive region. Previous XPS studies [1] showed that at potentials in the transpassive region the Cr(III) barrier layer is destroyed and high oxidation states of Mo and W (Mo(VI)/W(VI)) accumulate on the electrode surface. The O\(_2\) reduction studies described in Chapter 4 suggest these Mo(VI)/W(VI) states are partially reduced on the scan to the cathodic limit. The presence of a reoxidation peak after preoxidation in the potential range – 0.2 V to 0.2 V followed by a cathodic scan can not, however, be attributed to the transpassive film breakdown and the need to reoxidize partially reduced Mo(VI)/W(VI) states. Previous studies [1] showed that oxidation in this potential region leads primarily to the development of the Cr(III) barrier layer. This suggests that the reoxidation process is the reformation of this barrier layer after its partial reduction on the scan to – 1 V. Thus, the reoxidation peak observed in the potential range – 0.5 V to – 0.2 V can most likely be
attributed to the reformation of the Cr(III) barrier layer and, after preoxidation at a sufficiently positive potential, reoxidation of the reduced Mo/W states.

Figure 5.5 shows the CV scans recorded at various temperatures after preoxidation at –0.6 V (a), 0 V (b) and 0.6 V (c). A dependence on temperature of the film transformations is clearly observed. As indicated by the EIS studies described in Chapter 4, a potential of –0.6 V is in the “prepassive” region where the passive layer is not fully formed (at least after 1 to 2 hours of anodic oxidation). After oxidation at this potential H$_2$O reduction is readily sustained on the cathodic scan and the rate increases markedly with temperature. At all temperatures up to 70 ºC no reoxidation current is observed. At 90 ºC, a very shallow reoxidation current occurs suggesting some film reduction on the cathodic scan at this temperature.
Figure 5.5 CV scans recorded on Alloy C22 at various temperatures after preoxidation at various film growth potentials in deaerated 5 mol•dm⁻³ NaCl: (a) – 0.6 V; (b) 0 V; (c) 0.6 V. The currents are shown offset by 0.5 mA•cm⁻² for (b) and (c).
After preoxidation at 0 V in the passive region, Figure 5.5 (b), no obvious reduction process is observed on the forward scan to – 1 V but a reoxidation process is observed on the reverse scan, and becomes more prominent with temperature. This process occurs in the potential range – 0.55 V to – 0.3 V as observed in Figure 5.4. Preoxidation at 0 V leads to a fully-formed Cr(III) passive oxide layer as indicated by EIS measurements, Figure 4.13, and demonstrated by XPS [1]. Consequently, the reoxidation process can be attributed to the reformation of the barrier layer which becomes more readily reducible on the forward scan as the temperature is increased.

After preoxidation at 0.6 V, a very clear cathodic reduction process, distributed over the potential range – 0.2 to – 0.7 V, becomes observable at higher temperatures. As demonstrated in Chapter 4, it is within this range that the O₂ reduction process is initially catalyzed but eventually suppressed, Figure 4.3 and 4.6. This coincidence supports the claim that the reduction process involved is that of Mo(VI)/W(VI) to lower oxidation states. As a consequence of this reduction a new reoxidation process is observed around – 0.6 V on the reverse scan. The growth in the size of this reoxidation peak with temperature indicates that the preoxidation at 0.6 V produced a thicker oxide film containing more reducible species at high temperatures, which is demonstrated by ToF-SIMS and XPS analyses on Alloy C 2000 in Chapter 3.
5.3.1.3  CV Scans to Various Cathodic Limits after Preoxidation at 50°C

To investigate the observed film transformations further, an additional series of preoxidation-CV experiments were performed. After preoxidation at either 0.6 V or –0.2 V for 1h, the potential was scanned from the preoxidation potential to various cathodic limits (forward scan) and back (reverse scan). Figure 5.6 shows examples of CV scans to various cathodic limits after preoxidation at 0.6 V for 1 hour in deaerated solutions at 50°C. When the potential was scanned from 0.6 V to – 0.6 V, two reduction peaks, C1 and C2, are observed before the onset of H₂O reduction (Figure 5.6 (a)). While the origin of reduction peak C1 is not immediately obvious, the reduction peak C2 can be tentatively assigned to the reduction of the transpassively formed Mo(VI)/W(VI) states which lead to the catalysis of O₂ reduction in aerated solutions, Figure 4.3 and 4.6. However, if the cathodic limit is confined to – 0.6 V only a very shallow reoxidation process is observed on the reverse scan.

Extending the cathodic limit to – 0.8 V leads to a substantial reoxidation peak A1 (Figure 5.6 (b)) in the potential range where a reoxidation current was observed after preoxidation in the transpassive region, Figure 5.5 (c). Another substantial reoxidation peak A2 is observed, superimposed upon A1, (Figure 5.6 (d)), when the cathodic limit was extended to more negative potentials than – 0.85 V. This peak occurs in the same potential range within which it was claimed above that reformation of the Cr(III) barrier layer was occurring. However, when the cathodic limit is between – 0.8 V and – 0.85 V,
(a) Graph showing current density ($j$) vs. potential ($E$) for different potentials at $-0.6$ V.

(b) Graph showing current density ($j$) vs. potential ($E$) for different potentials at $-0.8$ V.
Figure 5.6  Examples of CV scans after potentiostatic preoxidation at 0.6 V to various cathodic limits (a) – 0.6 V; (b) – 0.8 V; (c) – 0.83 V; (d) – 0.85 V in deaerated solutions at 50 ºC.
the reoxidation peak A1 is observed on the first CV cycle and reoxidation peak A2 on the second cycle (Figure 5.6 (c)). Additionally, on the second CV cycle, the two reduction peaks C1 and C2 observed on the first cycle are absent, since the potential is only at very positive potentials for a short time prior to the second cycle. These observations support the claim that the reactions C1, C2 and A1 are related to the transformations of transpassive species (in high oxidation states) whereas A2 can be attributed to reformation of the Cr(III) barrier layer. A complete set of CV scans to various cathodic limits after preoxidation at 0.6 V for 1 hour are displayed in Figure 5.7. This sequence clearly demonstrates that the reduction process C2, leads to the reoxidation process A1.

**Figure 5.7** CV scans to various cathodic limits after preoxidation at 0.6 V for 1 hour in deaerated 5 mol·dm$^{-3}$ NaCl at 50 ºC.
while reduction at more negative potentials \((E \leq -0.85 \text{ V})\) leads to the reoxidation process A2.

Since the two reduction peaks C1 and C2 are not observed on the second CV cycle when only a short time is spent at very positive potentials, a further set of multiple preoxidation \((0.6 \text{ V, 1 hour})\)-CV (to \(-0.83 \text{ V and back}\)) experiments were performed, using the potential profile shown in Figure 5.1. For the first period, the two reduction peaks, C1 and C2, and a reoxidation peak, A1, were observed on the first CV cycle. However, on the second and third voltammetric cycles of period 1 neither reduction peak but both reoxidation peaks, A1 and A2, were observed, Figure 5.8 (a), as observed previously and shown in Figure 5.6 (c). During period 2, the two reduction peaks, C1 and C2, and the reoxidation peak, A1, were observed on the first CV cycle, similar to period 1, but neither of the reduction peaks nor the reoxidation peak, A2, were observed on the second and third CV cycles, Figure 5.8 (b). A similar result was obtained over periods 3 and 4.

These observations confirm that the transformations C1, C2 and A1 can be attributed to the reduction and reoxidation of transpassive states as suggested above. The absence of reoxidation peak A2 during the second and later periods, suggesting the reduction/reformation of the Cr(III) barrier layer is not so readily achieved under the thickening outer layer of transpassive states. This would be consistent with the considerably larger anodic currents observed in the transpassive region in period 2, Figure 5.8 (b).
Figure 5.8 CV scans obtained in periods 1 and 2 (Figure 5.1) during a multiple preoxidation (0.6 V, 1 hour)-CV (to −0.83 V and back) experiments in deaerated 5 mol•dm⁻³ NaCl at 50 ºC.
When the preoxidation potential was set at $-0.2 \text{ V}$ (in the passive region), and the potential was scanned from this potential to various cathodic limits and back, the only film transformation observed is the reoxidation peak A2, providing the cathodic limit is more negative than $-0.75 \text{ V}$, Figure 5.9. The EIS data in Chapter 4 shows this potential is not sufficiently positive for the formation of high oxidation states of Cr, Mo and W, confirming that the reoxidation peak A2 is due to reformation of the Cr(III) barrier layer. The figure also shows that the reduction of a fully formed Cr(III) barrier layer requires a cathodic potential $<-0.7 \text{ V}$ to $-0.75 \text{ V}$. Since passive film reduction will involve the

![Figure 5.9 CV scans to various cathodic limits after preoxidation at $-0.2 \text{ V}$ on Alloy C22 in deaerated solutions at 50 °C.](image-url)
The reduction of Cr(III), Ni(II), and the lower oxidation states of Mo and W, the reoxidation process must involve one or more of these oxidation steps. The requirement for a potential $< -0.7$ V to reduce the passive film and render it conductive, is consistent with the polarization data (Figure 4.5 (a)) which show that a potential more negative than this is required to support H$_2$O reduction.

These experiments indicate that the two reduction peaks C1 and C2 and the first reoxidation peak A1 are associated with the reduction and reoxidation of transpassively formed Cr(VI), Mo(VI) and W(VI)) oxidation states, whereas the reduction occurring at the cathodic limit ($< -0.7$ V), which leads to the second reoxidation peak A2, is associated primarily with redox transformations in the passive oxide involving Ni/Ni(II), Cr/Cr(III) and the lower oxidation states of Mo and W. Using equilibrium potential values calculated with the Nernst equation for various redox reactions (and assuming ranges of soluble species concentrations), Table 5.1, the shallow peak C1 can be attributed to the reduction of Cr(VI) to Cr(III) within the transpassively formed film. The shallowness of this process is to be expected since most of Cr(VI) will have dissolved out of the film.

The larger more negative reduction peak, C2, can be attributed to the reduction of Mo(VI) to Mo (IV), with the latter oxidation state being further reduced at the cathodic limit ($E < -0.7$ V) and reoxidized on the reverse scan, producing peak A1. The relatively large size of C2 to C1 is not unexpected, since the high oxidation states of Mo are retained within the film after transpassive oxidation (demonstrated by XPS in Chapter 3). These Mo(VI)
Table 5.1  Calculated equilibrium potentials for possible film transformation reactions on Alloy C22 at pH 7.

<table>
<thead>
<tr>
<th>Transformation reactions</th>
<th>Equilibrium potentials (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CrO}_4^{2-} + 4\text{H}_2\text{O} + 3e^- = \text{Cr(OH)}_3 + 5\text{OH}^- )</td>
<td>&lt; 0.32 (([\text{CrO}_4^{2-}] &lt; 10^{-5} \text{ mol}\cdot\text{dm}^{-3}))</td>
</tr>
<tr>
<td>( \text{Cr(OH)}_3 + 3e^- = \text{Cr} + 3\text{OH}^- )</td>
<td>– 1.08</td>
</tr>
<tr>
<td>( \text{Ni(OH)}_2 + 2e^- = \text{Ni} + 2\text{OH}^- )</td>
<td>– 0.47</td>
</tr>
<tr>
<td>( \text{MoO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- = \text{MoO}_2 + 4\text{OH}^- )</td>
<td>&lt; – 0.16 (([\text{MoO}_4^{2-}] &lt; 10^{-5} \text{ mol}\cdot\text{dm}^{-3}))</td>
</tr>
<tr>
<td>( \text{WO}_4^{2-} + 2\text{H}_2\text{O} + 2e^- = \text{WO}_2 + 4\text{OH}^- )</td>
<td>&lt; – 0.72 (([\text{WO}_4^{2-}] &lt; 10^{-5} \text{ mol}\cdot\text{dm}^{-3}))</td>
</tr>
<tr>
<td>( \text{MoO}_2 + 2\text{H}_2\text{O} + 4e^- = \text{Mo} + 4\text{OH}^- )</td>
<td>– 0.73</td>
</tr>
<tr>
<td>( \text{WO}_2 + 2\text{H}_2\text{O} + 4e^- = \text{W} + 4\text{OH}^- )</td>
<td>– 0.73</td>
</tr>
</tbody>
</table>

states are not fully reduced even at potentials as low as – 0.6 V. The reoxidation peak A2, due to reformation of the Cr(III) barrier layer, will involve oxidation of the alloy substrate and possibly also reduced Mo states in the cathodically reduced oxide. Although no reduction/reoxidation reactions for W have been included, they are likely to accompany the similar reactions of Mo.

5.3.1.4 Investigation of Film Transformations by XPS

In an attempt to analytically validate the nature of the transformations within the film, XPS was employed to trace the changes in redox states during a CV scan. The potential-time profile adopted prior to XPS analyses is shown in Figure 5.2, and outlined in section 5.2. Figure 5.10 shows the variations in surface composition calculated from
XPS survey spectra during a CV scan. After oxidation at 0.6 V followed by scanning the potential to −0.6 V and −0.78 V (XPS analysis points 1, 2 and 3), the content of Mo and W slightly decreases and as a consequence the content of Ni increases slightly. This is consistent with the above assignments for the reduction of Mo(VI)/W(VI). When the potential was scanned to −1 V and back to 0.6 V (XPS analysis points 4, 5 and 6), a significant decrease in Ni content and slight increase in Mo/W contents in the surface are accompanied by an increase in Cr. This indicates that the reduction at the cathodic limit (−1 V) and following reoxidation processes lead to the decrease in Ni and increase in Cr
content expected when the Cr(III) barrier layer is reformed. The minor changes in relative concentrations of Mo and W confirm that, while their oxidation states may change as a consequence of voltammetric scanning, they are retained within the film.

The high-resolution spectra for Ni 2p in Figure 5.11(a) show that the peak intensity for Ni(II) dramatically decreases and the metal content corresponding increases when the potential was scanned to the negative potential limit. And the fitting results in Figure 5.11(b) show that this decrease in Ni(II) can be attributed to a decrease in Ni(OH)₂. This suggests that the reduction of Ni(OH)₂ is a major feature of the reduction process leading to the reoxidation peak A2. As mentioned above, when the potential was scanned to – 1 V and then back to more positive values, the relative Ni content in the film decreases, Figure 5.10, suggesting Ni(OH)₂ reduction/dissolution during the reformation of the barrier layer. However, the high Ni metal content may suggest a rougher, less uniformly distributed oxide film is formed. The properties of this film have not been investigated in any significant detail.

5.3.2 CV Scans on Pure Metals

In an attempt to further justify the peak assignments described above, polarization curves were measured on pure Ni, Cr and Mo in deaerated solutions at room temperature (22 ºC) starting from the corrosion potential measured right after immersion after 10 min cathodic cleaning at – 1 V, Figure 5.12. Examination of these polarization curves shows
Figure 5.11 The variation in high-resolution spectra and fitting results for Ni species in the surface of Alloy C22 during a CV scan after preoxidation at 0.6 V.
that Cr has the widest passive region from \(-0.7\) V to \(0.2\) V with a rather low passive current density in the range of \(\mu\text{A}\cdot\text{cm}^{-2}\) in \(5\ \text{mol}\cdot\text{dm}^{-3}\) NaCl. By contrast, Mo has the narrowest passive region from \(-0.2\) V to \(-0.1\) V with a considerably larger passive current density \(~0.02\ mA\cdot\text{cm}^{-2}\). The passive region of Ni ranges from \(-0.4\) V to \(-0.2\) V with a similar passive current density to that observed on Mo. Based on this information, the Ni electrode was preoxidized at \(0\) V and then the potential scanned to \(-1\) V and back to \(0\) V, Figure 5.13. Ni exhibits a rather large cathodic current \(~1.8\ mA\cdot\text{cm}^{-2}\) at \(-1\) V and a reoxidation peak in the potential range between \(-0.35\) V and \(-0.55\) V which is within the potential range in which the reoxidation peak A2 is observed on Alloy C22. This observation supports the claim that the reoxidation peak, A2, on Alloy C22 involves Ni
Figure 5.13 CV scans on pure Ni, Cr and Mo to –1 V after preoxidation at a potential in the transpassive region for the individual metals (Ni: 0 V, Cr: 0.6 V, Mo: 0.1 V). A CV from 0.6 V to –0.83 V recorded on Alloy C22 after preoxidation at 0.6 V is included for comparison.

oxidation. It is possible this Ni was produced on Alloy C22 by Ni(OH)\textsubscript{2} reduction on the forward cathodic scan. This could explain the unexpectedly large Ni metal content observed by XPS at potentials in the reverse (reoxidation) scan.

A similar preoxidation-CV scan on Cr (after preoxidation at 0.6 V) shows very little cathodic or anodic activity indicating that while Cr(III) may be reduced or oxidized during the redox transformations on Alloy C22, it is not particularly redox active. For Mo, preoxidation was performed at 0.1 V and then the potential scanned to –1 V and back to
A wide reduction band between – 0.4 V and – 0.8 V was observed on the forward scan and a reoxidation peak at ~ – 0.7 V on the reverse scan. The potentials at which these processes occur are comparable to those at which the reduction peak C2 and reoxidation peak A1 occur on Alloy C22, supporting the claim that these transformations primarily involve Mo redox processes.

5.4 Summary and Conclusions

In this chapter, a series of CV experiments were performed on Alloy C 22 in deaerated 5 mol•dm⁻³ NaCl solutions over the temperature range of 30 to 90 ºC to explore the film reduction-reoxidation processes described in Chapter 4. XPS and CV scans on pure Ni, Cr and Mo metals were also performed to help identify individual film transformations on Alloy C 22.

The steady-state current densities, recorded potentiostatically in the passive and transpassive regions, are in the range of µA•cm⁻², and independent of potential in the passive region between – 0.2 V and 0.2 V, but increase with potential in the transpassive region (E > 0.2 V). Both passive and transpassive currents show only a slight dependence on temperature, consistent with the changes in polarization resistance discussed in Chapter 4. After preoxidation, CVs were recorded from the preoxidation potential to – 1 V (forward scan) and back (reverse scan). Preoxidation at a potential more positive than – 0.2 V leads to a reoxidation peak on the reverse scan, the size of which increases with
preoxidation potential and temperature, indicating the presence of a thicker film. The XPS and ToF-SIMS analyses presented in Chapter 3 indicate this process can be attributed to the reoxidation of Mo/W states formed transpassively and reduced on the cathodic scan.

To determine the potential conditions under which film transformations occurred, the electrode was preoxidized at 0.6 V at 50 ºC, and the potential then scanned from this preoxidation potential to various cathodic limits (forward scan) and back (reverse scan). Two reduction peaks were observed at ~ 0.1 V and ~ – 0.4 V and attributed to the reduction of Cr(VI) and Mo(VI)/W (VI) states, respectively. Depending on the preoxidation potential and the limit of the cathodic scan, two reoxidation peaks were observed. The first reoxidation peak (~ – 0.6 V to ~ – 0.45 V) is attributed to the reoxidation of Mo/W states, and the second reoxidation peak (~ – 0.45 V to ~ – 0.3 V) to the reformation of passive film. These assignments are supported by calculated equilibrium potentials and XPS measurements. The XPS measurements also indicate that the anodic peak associated with reformation of the barrier layer involved the reoxidation of Ni, deposited by reduction of Ni(OH)₂ on the cathodic scan.

CV scans on pure Ni, Cr and Mo to -1 V after preoxidation at a potential in the transpassive region show film transformations similar to those obtained on Alloy C22.

5.5 References

Chapter 6

Effect of Alloying Elements on the Kinetics of O₂ Reduction on Ni-Cr-Mo Alloys

6.1 Introduction

In chapter 4, various electrochemical techniques were employed to investigate the kinetics of O₂ reduction on oxide-covered Alloy C22. Potentiostatic polarization and cyclic voltammetric experiments demonstrate that the kinetics of O₂ reduction depend on the properties of the oxide film. O₂ reduction was completely suppressed by the oxide film grown in the passive region, but revived to a small degree on a transpassively activated surface. On a transpassively activated surface at 0.9 V, the O₂ reduction current recorded at increasingly negative potentials increases with temperature over the range from 30 to 70 °C, but decreases at 90 °C due to a decrease in dissolved O₂ concentration. EIS measurements show that the polarization resistance reaches a maximum in the passive region (–0.3 V ≤ E ≤ 0.3 V) and decreases in the transpassive region (E > 0.3 V) due to the oxidative ejection of cations from the barrier layer of the oxide film. The polarization resistance also decreases with increasing temperature, consistent with the dependence of the polarization data on potential and temperature.

In this chapter, the kinetics of O₂ reduction were investigated on other oxide-covered Ni-Cr-Mo Alloys in 5 mol•dm⁻³ NaCl solutions at 70 °C using similar potentiostatic
polarization, CV and EIS measurements. This allows us to study the effect of alloying elements in the materials on the kinetics of O₂ reduction.

6.2 Experimental Details

A series of Ni-Cr-Mo alloys (Alloy C22, C2000, C276, C4 and 625) with the compositions shown in Table 1.1, Chapter 1, were studied. SEM micrographs were obtained with a Leo 1540 FIB/SEM with CrossBeam (Zeiss) and EDX system (Oxford Instruments) and a Hitachi S-4500 field emission SEM equipped with an EDAX™ EDX system. The microstructures of the alloys were obtained from SEM micrographs after etching. During etching, due to differences in the chemical composition of the phases and their dissolution rate in the etchant, structural components of an alloy are revealed by a preferential attack or staining of the various constituents. The etchant used was a mixture of 5 g of oxalic acid and 95 mL of HCl (reagent grade) and a detailed description of the etching process can be found in reference [1]. The same electrode preparation and potential profiles described in Chapter 4 were used in potentiostatic polarization, EIS and CV experiments.

6.3 Results and Discussion

6.3.1 SEM Micrographs of Ni-Cr-Mo Alloys

Figure 6.1 displays the SEM micrographs showing the microstructure of each alloy after etching. The micrograph shows that the grain size varies with alloy composition. For C4
the grain size is rather large (> 300 µm). The grains in C22 and C2000 are smaller at ~150 µm, while the grains in C276 are generally in the range of 50-100 µm. The smallest grain size, ~ 30µm, was observed for Alloy 625. EDX examinations of the white, light grey, dark grey and black areas detected no clear difference in elemental composition.

After oxidation at 0 V for 24 hours, the SEM micrographs in Figure 6.2 show that a uniform film covered the surface of each alloy. The dark or light color locations can be attributed to the deposition of either polishing residue or dried salt from the electrolyte. The alloy microstructure is almost visible indicating the surface oxide films are very thin. The thickness of the passive film on Ni-Cr-Mo alloys has been determined to be a few nanometers (generally less than 5 nm) [2].
Figure 6.2  SEM micrographs of the passive surfaces on 5 Ni-Cr-Mo alloys anodically oxidized at 0 V.

6.3.2 Corrosion Potential Measurements

Figure 6.3 shows the corrosion potentials \( E_{\text{corr}} \) for 5 alloys measured as a function of time in aerated and deaerated 5 mol\(\cdot\)dm\(^{-3}\) NaCl at room temperature (22 °C). In aerated solutions, the \( E_{\text{corr}} \) for all 5 alloys rises rapidly to ~ – 0.25 V in a few minutes, and then more gradually increases to ~ – 0.15 V after 24 hours. For Alloy C4 the increase in \( E_{\text{corr}} \) to this final value is significantly slower. In deaerated solutions, the rates of increase in \( E_{\text{corr}} \) vary with the final potentials in the range between – 0.45 V and – 0.35 V after 24 hours. With the exception of C4, for which \( E_{\text{corr}} \) rises rapidly to the eventual steady-state value, \( E_{\text{corr}} \) for the alloys exhibits two stages: (i) a period between ~ – 0.65 V and ~ – 0.5
Figure 6.3  Corrosion potential ($E_{corr}$) measurements for 5 Ni-Cr-Mo alloys in aerated (a) and deaerated (b) 5 mol•dm$^{-3}$ NaCl at pH 7 at room temperature (22 ºC).
V over which the potential increases steadily; (ii) a second stage at \( \geq -0.5 \) V when \( E_{\text{corr}} \) achieves a slightly erratic steady-state. No meaningful correlation exists between the time to reach the second stage and the composition of the alloy. This suggests that the variations in, and rate of rise of, \( E_{\text{corr}} \), reflect differences in trace O\(_2\) concentration in the exposure solutions. The presence of potential oscillations in \( E_{\text{corr}} \) indicates a non-uniform passivation process, which may be partially due to coverage by H\(_2\) gas produced from H\(_2\)O reduction. No clear differences in \( E_{\text{corr}} \) between the 5 studied alloys were observed in 5 mol\( \cdot \)dm\(^{-3}\) NaCl at neutral pH.

### 6.3.3 Potentiostatic Polarization Experiments

Figure 6.4 displays the potentiostatic polarization curves recorded on the alloys up to an anodic limit of 0.1 V and back to \(-0.9\) V in aerated 5 mol\( \cdot \)dm\(^{-3}\) NaCl solutions at 70 °C. A much larger cathodic current for both O\(_2\) reduction, observed as a shoulder in the potential range \(~-0.6\) to \(-0.8\) V, and H\(_2\)O reduction, at \( E < -0.7 \) V, was observed on the positive compared to the negative scan for all alloys, indicating that O\(_2\) reduction is significantly suppressed by the films grown in the passive region on all the alloys. The O\(_2\) reduction currents on Alloy C2000 and C22 are smaller on the positive scan than those on Alloy C276, 625 and C4. These differences may be attributed to the difference in alloy composition, Table 1.1 in Chapter 1. Alloy C22 and C2000 contain the highest Cr and Mo (W) contents and it is likely that oxide growth occurs more readily on these alloys, thereby suppressing O\(_2\) reduction. On the negative scan the differences in O\(_2\) reduction
Figure 6.4  Potentiostatic polarization curves recorded up to, and back from, 0.1 V on 5 Ni-Cr-Mo alloys in aerated 5 mol•dm$^{-3}$ NaCl at 70 ºC.

currents for the alloys are not as readily apparent although the current for C4 seems anomalously low at – 0.9 V.

The log current-potential plots in Figure 6.5 are able to better distinguish the differences in current at low values. Figure 6.5 (a) shows that the currents on the positive scan decrease substantially for $E > -0.5$ V; i.e., over the potential range within which the passive film becomes fully developed, Figure 4.13. No clear correlation between the currents measured and the Cr+Mo (W) content of the alloys was observed, although it is noted that the O$_2$ reduction current on C22 (Ni22Cr13Mo3W) is considerably lower than
Figure 6.5  Steady-state cathodic current densities recorded on Ni-Cr-Mo alloys in aerated 5 mol•dm$^{-3}$ NaCl at 70 ºC; (a) positive scan to 0.1 V, (b) negative scan from 0.1 V.
that for C4 (Ni16Cr16Mo). The slopes measured over the range – 0.2 V to – 0.5 V are ~ 70 mV•decade⁻¹ of change in current density. This value is considerably lower than the value of 136 mV•decade⁻¹ expected for charge transfer to O₂ controlled by the first electron transfer at this temperature (70 ºC) (α is taken 0.5). One possibility is that this could indicate catalysis of the electron transfer step on the defective oxide film present. However, the impedance studies described in Chapter 4, Figures 4.12 and 4.13, show that the oxide film resistance on alloys such as C22 changes significantly through this region. This would suggest that the steep slope in the log(− j)-E plot is caused by changes in the properties of the surface oxide film throughout this potential range.

The slopes recorded on the negative scan, Figure 6.5 (b) are considerably larger at > 200 mV•decade⁻¹ consistent with the suppression of O₂ reduction by passive oxide formation. The currents measured on C22 and C2000 are considerably lower than those measured on 625 and C4. These differences may be attributed to the more complete development of the passive film on C22 and C2000. The SR-XPS, AR-XPS, and ToF-SIMS results in Chapter 3 and previously published results [3] indicate that this can be attributed to the segregation of Cr/Ni and Mo (W) in the oxide films on these alloys. This leads to a well-developed passive oxide with an outer Mo (W) rich layer over a well developed Cr barrier layer. By contrast the alloys containing lower amounts of Cr and/or Mo (W), 625 and C4, do not develop such a clearly segregated surface layer. Alloy C276 exhibits behaviour intermediate between these two extremes.
When the anodic limit of the potentiostatic polarization was extended into the transpassive region (0.9 V), Alloy 625 and C4 initiated localized corrosion before the transpassive region was reached. Figure 6.6 shows the potentiostatic polarization curves recorded for the remaining 3 Ni-Cr-Mo alloys in aerated 5 mol•dm\(^{-3}\) NaCl solutions at 70 °C. On the positive scan, the O\(_2\) reduction currents on Alloy C22 and C2000 are considerably smaller than on C276, as observed in the experiment presented in Figure 6.4, confirming the reproducibility of this observation and supporting the claim that the passive film is more readily formed on the higher Cr/Mo (W)-containing alloys. After reactivation in the transpassive region (0.9 V), the O\(_2\) reduction currents recorded at

![Potentiostatic polarization curves](image)

**Figure 6.6** Potentiostatic polarization curves recorded up to, and back from, 0.9 V on Ni-Cr-Mo alloys in aerated 5 mol•dm\(^{-3}\) NaCl at 70 °C.
increasingly negative potentials, Figure 6.7, are up to an order of magnitude higher than those observed after preoxidation in the passive region, Figure 6.5. In addition, the slope decreases from $> 200$ to $\sim 140$ mV•decade$^{-1}$; i.e., approaches the expected Tafel value assuming rate control by the first electron transfer. This is consistent with the observation that transpassively activated surfaces are better able to support $O_2$ reduction as observed for Alloy C22 in Chapter 4. Also, a limiting current density of $\sim 0.1$ mA•cm$^{-2}$ was observed on these alloys at $E < -0.6$ V. While these observations can be attributed to the presence of higher oxidation states of Cr and Mo (W) on the surface created during

![Figure 6.7](image.png)

**Figure 6.7** Steady-state cathodic current densities as a function of potential recorded at progressively more negative polarization to $-0.9$ V on Ni-Cr-Mo alloys in aerated $5$ mol•dm$^{-3}$ NaCl at $70$ °C.
transpassive oxidation, there is no correlation between the currents observed and the Mo content of the alloy.

Examination of the potentiostatic polarization curves in Figure 6.7 shows that the \( \text{O}_2 \) reduction current on C2000 in the potential region – 0.2 V to – 0.5 V is smaller than that on C276 and C22. The different \( \text{O}_2 \) reduction kinetics on C2000 may be attributed to the accumulation of Cu on the outer surface as demonstrated analytically in Chapter 3. It is noted in Chapter 4 that the kinetics of \( \text{O}_2 \) reduction are catalyzed by the high oxidation states of Mo (W) created by transpassive oxidation, but this catalysis appears to be suppressed by the accumulation of Cu on the outer surface on Alloy C2000. It is also possible that the accumulation of Cu on the surface leads to the high transpassive dissolution current on C2000, Figure 6.6.

Figure 6.7 also shows that Alloy C2000 exhibited 2 limiting current stages whereas only one plateau was observed on Alloy C22 and C276, the latter of which is consistent with the literature [3]. Two stages for \( \text{O}_2 \) reduction may indicate that two consecutive two-electron transfer processes involving the intermediate production of hydrogen peroxide occur on a transpassively activated, and partially Cu-covered, Alloy C2000 surface.

6.3.4 Potentiostatic Film Growth and Following Cyclic Voltammetric (CV) Experiments
6.3.4.1 Potentiostatic Film Growth at 70 °C

Figure 6.8 shows log-log plots of current transients recorded on the 5 alloys at an applied potential of 0 V in aerated 5 mol•dm\(^{-3}\) NaCl at 70 °C. These alloys exhibit similar film growth kinetics in 5 mol•dm\(^{-3}\) NaCl, and reach quite small current densities in the range of \(\mu\text{A}\cdot\text{cm}^{-2}\) as expected for the growth of passive films. As Wagner has pointed out [4], film growth on Ni-Cr-Mo alloys involves a continuous transition from an initially thin film to a thicker film during which diffusion of ions and electrons would occur yielding parabolic oxidation kinetics with the general expression [5]

\[ i = at^{-b} \]  

(6.1)

![Log-log plots of current transients recorded on Ni-Cr-Mo alloys at 0 V in aerated 5 mol•dm\(^{-3}\) NaCl at 70 °C.](image)

Figure 6.8 Log-log plots of current transients recorded on Ni-Cr-Mo alloys at 0 V in aerated 5 mol•dm\(^{-3}\) NaCl at 70 °C.
where $0.5 \leq b \leq 1$. The rate of the reaction is, therefore, inversely proportional to the oxide thickness. Figure 6.8 indicates film-growth is initially fast with a slope of ~ 0.1 but eventually slower with slopes varying from – 0.56 on Alloy C4 to – 0.97 on Alloy C22. The increased current at the end of the one-hour film growth period on Alloy 625 indicates the onset of localized corrosion at the electrode-resin junction.

Figure 6.9 shows the final current density as a function of applied potential after one-hour of anodic oxidation in both aerated and deaerated solutions. The 5 studied alloys have similar passive currents, but behave differently in the transpassive region. Alloy 625 and

![Figure 6.9](image)

**Figure 6.9** Final current densities as a function of potential recorded on Ni-Cr-Mo alloys after polarization for 1 hour in aerated and deaerated 5 mol·dm$^{-3}$ NaCl at 70 °C.
C4 initiated localized corrosion before the transpassive region was reached, which may be attributable to their low Mo (W) content. The other 3 alloys remain passive to higher potentials. Consistent with the potentiostatic polarization data in Figure 6.6, the Cu-containing Alloy C2000 exhibits higher transpassive currents than the W-containing Alloy C22 and C276 with similar Cr and/or Mo contents. This observation supports the claim that the higher oxidation states of Mo (W) are retained in the outer regions of the film and stabilized as MoO$_4^{2-}$/WO$_4^{2-}$ by the high electric field. The stabilized MoO$_4^{2-}$/WO$_4^{2-}$ is claimed to give the outer regions of the oxide a cation selective character [6] which discriminates against the incorporation of Cl$^-$ into the passive film, thereby increasing its resistance to breakdown and the initiation of localized corrosion [2]. The extremely high anodic current observed on Alloy C2000 in deaerated solution may suggest the initiation of localized corrosion at the electrode-resin junction.

6.3.4.2 CV Scans after Potentiostatic Film Growth at 70 °C

After oxide film growth at a constant preoxidation potential, the potential was scanned from this preoxidation value to the cathodic limit of – 1 V (forward scan) and back (reverse scan) at a scan rate of 5 mV•s$^{-1}$, to examine the stability of the oxide film and to determine O$_2$ reduction currents. As described in Chapter 2 and Chapter 4, the forward scan shows the influence of the film on the O$_2$ and H$_2$O reduction reactions, and the reverse scan determines whether any changes occurred by reduction of the oxide film during the forward scan.
Figure 6.10 (a) and (b) display a series of CVs recorded on 5 Ni-Cr-Mo alloys after preoxidation at 0 V in aerated and deaerated 5 mol•dm\(^{-3}\) NaCl solution for 1 hour at 70 \(^\circ\)C, respectively. The currents are shown offset to illustrate the differences. Alloy 625 exhibits an effectively reversible O\(_2\) reduction wave in the potential range between \(-0.4\) V and \(-0.8\) V. For C4, passive film growth leads to a suppression of the O\(_2\) current on the scan to \(-1\) V but the current is revived on the reverse scan. For the other alloys containing both high Cr and high Mo (W) contents, the current on the reverse scan is very similar to that on the forward scan, with no clear O\(_2\) reduction current being observed. For C276 a small reoxidation peak is observed on the reverse scan but no such peak is observed for C22 and C2000. This reoxidation peak on Alloy C276 is in the potential range between \(-0.55\) and \(-0.35\) V, and can be attributed to the reformation of the passive film by the oxidation of Ni which formed by Ni(OH)\(_2\) reduction on the forward cathodic scan, as discussed in Chapter 5. The absence of any O\(_2\) reduction current or oxide reformation process on the high Cr and Mo (W) alloys (C2000, C22) indicates that the passive films formed at 0 V on these alloys are not easily reduced at negative potentials.

In deaerated solutions reversible current-potential behavior was observed on all 5 alloys, Figure 6.10 (b), indicating the oxide films grown at 0 V are stable in oxygen-free solutions and not reduced when the cathodic potential limit was reached. The absence of any reduction/reoxidation processes after film growth at 0 V suggests the oxides on all these alloys are similar. However, the behaviour when O\(_2\) is present indicates they are
Figure 6.10  CV scans recorded on 5 Ni-Cr-Mo alloys after preoxidation at 0 V for 1 hour in aerated (a) and deaerated (b) 5 mol•dm$^{-3}$ NaCl at 70 °C. The currents are shown offset by 1 mA•cm$^{-2}$. 
not. Only Alloy 625, and to a lesser degree C4, exhibit an O₂ reduction current after preoxidation. This indicates that the oxides on these alloys are able to sustain electron transfer to dissolved O₂ whereas the oxides on the other alloys are not. It is worth noting that these are also the two alloys which initiate and propagate localized corrosion, Figure 6.9.

When the preoxidation potential is in the transpassive region, significant differences between the alloys in both surface reactivity and their ability to support O₂ reduction was observed, Figure 6.11. Alloy 625 exhibits a high anodic current at preoxidation potentials as low as 0.2 V, and a large current for the combination of O₂ reduction and film reduction in the potential range between – 0.8 V to – 0.4 V when the potential was scanned to – 1 V. For C4 the anodic current is considerably smaller after preoxidation at this potential, and a much smaller O₂ reduction/film reduction current is observed when the potential was scanned to – 1 V. For the other 3 alloys preoxidation was performed at 0.6 V; i.e., in the transpassive region. Only a small O₂ reduction/film reduction current was observed on the forward scan for C276 and C2000 while a well-defined O₂ reduction wave was observed on Alloy C22.

Under deaerated conditions, Figure 6.11 (b), Alloy 625 exhibits a large film reduction current on the scan to – 1 V in the potential range between – 0.8 V to – 0.4 V, indicating that the majority of the reduction current observed in the presence of O₂, Figure 6.11(a), is due to film reduction. This current can be attributed to the reduction of the
Figure 6.11  CV scans recorded on 5 Ni-Cr-Mo alloys after preoxidation at 0.6 V or 0.2 V for 1 hour in aerated (a) and deaerated (b) 5 mol•dm$^{-3}$ NaCl at 70 °C. The currents are shown offset by 1 mA•cm$^{-2}$. 
transpassively formed Mo(VI) states as discussed in Chapter 5. By contrast, no
significant anodic current was observed for C4 at 0.2 V and, hence, only a very small
film reduction current was observed on scanning the potential to – 1 V, leading to a very
minor reoxidation current, Figure 6.11 (b). For the remaining 3 alloys preoxidized at 0.6
V, while no significant reduction process was observed, the observation of a reoxidation
current on the reverse scan confirms some film reduction process did occur as the
negative potential limit was approached. This is consistent with the observations in
Chapters 4 and 5. The size and location of the reoxidation peak depends on the extent of
transpassive activation, Figure 6.11 (b), indicating that the need for reoxidation is due
primarily to the reduction of the film formed in the transpassive region, as discussed in
Chapter 5.

This variation in resistance to localized corrosion and ability to support O2 reduction
among the alloys indicates that alloys with low Cr + Mo (W) content are more
susceptible to localized corrosion and more easily support O2 reduction, especially after
preoxidation at high potentials. This observation is consistent with the modified pitting
resistance equivalent number (PRE') [7], which expresses the benefit of selected alloying
elements in solid solution and is indicative of the relative corrosion resistance, as well as
the results of Scully et al. [8] on Alloy 625 and C22. The calculated values for pitting
resistance equivalent number (PREN) and PRE’ for the studied Ni-Cr-Mo alloys are
listed in Table 6.1. From Figure 6.10 and 6.11, it can be concluded that the PRE’ number,
Table 6.1  Calculated values for pitting resistance equivalency numbers (PREN) and modified pitting resistance equivalency numbers (PRE') for Ni-Cr-Mo alloys [7].

<table>
<thead>
<tr>
<th></th>
<th>625</th>
<th>C4</th>
<th>C22</th>
<th>C2000</th>
<th>C276</th>
</tr>
</thead>
<tbody>
<tr>
<td>PREN</td>
<td>50.7</td>
<td>68.8</td>
<td>64.9</td>
<td>75.8</td>
<td>68.8</td>
</tr>
<tr>
<td>PRE'</td>
<td>50.7</td>
<td>68.8</td>
<td>74.8</td>
<td>75.8</td>
<td>82.0</td>
</tr>
</tbody>
</table>

Note:  
PREN = wt%Cr + 3.3wt%Mo + 16wt%N;  
PRE' = wt%Cr + 3.3wt%(Mo + W) + 30wt%N.

in which the W content is taken into account, agrees most clearly with a clear distinction between two sets of alloys 625/C4 and C22/C2000/C276, and with the observations that film breakdown readily occurs on Alloy 625 and C22 but not on the other 3 alloys. It is also worth noting that this susceptibility to film breakdown correlates with the ability of alloys to sustain O₂ reduction. Alloy 625 has the lowest PRE' number and initiated localized corrosion at $E > 0$ V. It is also more able to support the O₂ reduction than other alloys. C4 exhibited a slightly better resistance to localized corrosion than 625 and a lower but still observable O₂ reduction current, with slightly higher PRE' number. For the remaining 3 alloys, C22 has lower PREN and PRE’ numbers than C2000 and C276, and a well-defined O₂ reduction wave was observed on Alloy C22 while only small O₂ reduction/film reduction currents were observed on the forward scan for C276 and C2000.
6.3.5  *Electrochemical Impedance Spectroscopy (EIS) Measurements at 70 °C*

EIS measurements were performed after 2 hours of potentiostatic oxidation at a series of potentials over the range – 0.9 V to an anodic limit (which depended on the specific alloy) and back in stagnant deaerated 5 mol•dm\(^{-3}\) NaCl solutions at 70 °C (the potential profile used is illustrated in Figure 2.3). As discussed in Chapter 4, a one or two time constant model (Figure 4.9) representing oxide film and/or interfacial charge transfer processes at the film/solution interface was used to fit the spectra.

Figure 6.12 shows the fitted passive film resistance (\(R_b\)) and CPE values obtained on the above 5 alloys. The CPEs were taken to represent capacitances since the CPE exponent was > 0.8 in all cases. On polarization in stages to 0.1 V on Alloy C4, \(R_b\) increases rapidly with potential for \(E \leq \) – 0.3 V to reach a maximum value in the passive region (–0.3V < \(E\) ≤ 0.1 V). This is accompanied by a decrease in capacitance indicating an increase in passive film thickness accompanied by a decrease in its defectiveness, as observed on Alloy C22 in Figures 4.10 and 4.11 in Chapter 4. For this alloy, polarization at more positive potentials leads to the initiation of crevice corrosion at the electrode/resin boundary. On the negative scan, \(R_b\) and capacitance show similar variations with potential to those observed on the positive scan, but \(R_b\) increases and the capacitance decreases slightly compared to the values on the positive scan. This indicates that the film becomes less defective and possibly also thickens on the negative scan after
(c) 

Rb ($\Omega \cdot \text{cm}^2$) vs. $E$ (Volt vs. Sat. Ag/AgCl)

(d) 

CPE$_b$ (F cm$^{-2}$) vs. $E$ (Volt vs. Sat. Ag/AgCl)
Figure 6.12 Variation of passive film resistance ($R_b$) and CPE with potential on Ni-Cr-Mo alloys obtained from EIS spectra measured in deaerated 5 mol·dm$^{-3}$ NaCl at 70 ºC after 2 hours of potentiostatic oxidation at each potential.

By comparison, Alloy C276 was polarized to 0.5 V on the positive scan. Similar variations in $R_b$ and capacitance to those observed for C4 were obtained. For potentials more positive than 0.2 V, $R_b$ decreases and the capacitance increases as observed in Chapter 4 for Alloy C22. On the negative scan it is noted that $R_b$ is slightly higher than on the positive scan at all potentials down to – 0.6 V. This is accompanied by a retraceable capacitance, the values on the positive and negative scans being effectively
identical. This suggests that, for this alloy, the defects injected into the oxide as the potential is increased above 0.2 V on the positive scan can be annealed out on the subsequent negative scan; i.e., oxidation at potentials up to ~ 0.2 V does not lead to an irreversible transpassive degradation of the oxide film. Despite the decrease of ~ one order of magnitude in $R_b$ over the range – 0.1 V to – 0.4 V, $R_b$ remains $> 10^5 \, \Omega \cdot \text{cm}^2$, consistent with the absence of any $O_2$ reduction current in the voltammetric scan in Figure 6.11.

Despite its susceptibility to the initiation of localized corrosion, it was possible to polarize Alloy 625 up to 0.9 V. It is likely that this can be attributed to the slow step-by-step oxidation as the potential was increased on the positive scan. The resistance and capacitance for the oxide film were plotted only up to, and back from, 0.6 V in Figure 6.12, since the charge transfer process at the oxide/solution interface dominates the EIS spectra beyond that potential. After transpassive oxidation at such a high potential, $R_b$ measured on the negative scan decreases significantly for $E < 0.2$ V accompanied by a significant increase in capacitance. As discussed in Chapter 4 for Alloy C22, this indicates an irreversible change in film properties due to polarization at such positive transpassive potentials.

Similar behaviour is observed for Alloy C22 and C2000, although the irreversible changes on C2000 are not so clear. As discussed above, and in Chapter 4 for Alloy C22, this irreversible transformation of the film, and the creation of oxidized Mo/W states
which accompanies it, accounts for the revival of the O₂ reduction current on the negative scan. The less well-defined degradation of the passive film on C2000 is unexpected considering this alloy exhibits the largest anodic current in the transpassive region, Figure 6.6. It is likely that this can be attributed to the presence of Cu, shown to accumulate in the surface of this alloy after oxidation in the passive and transpassive region, Chapter 3. The slightly different O₂ reduction behaviour on this alloy compared to C22 and C276 may reflect this influence of a surface Cu layer. Presently, the influence of Cu is not fully understood.

A comparison of the polarization resistance (Rₚ, the sum of charge-transfer resistance and film resistance) and film capacitance for the alloys is shown in Figure 6.13 and Figure 6.14, respectively. All the alloys exhibit similar resistance and capacitance values as a function of potential on the positive scan, with the possible exception of C4 which exhibits a slightly lower resistance in the passive region (–0.3 V to 0.3 V). Rₚ initially increases and the capacitance decreases with increasing potential. The high Rₚ (~ 10⁶ Ω·cm²) and low capacitance (~ 10⁻⁵ F·cm⁻²) values achieved in the potential range from –0.3 V to 0.3 V, indicate that the differences in alloy composition have little influence on the properties of the passive oxide. The Rₚ and capacitance values are consistent with the small passive currents shown in Figure 6.9 and the reproducible current-potential behavior observed in the CV experiments (Figure 6.10). For those alloys which could be polarized into the transpassive region, almost identical decreases in Rₚ with potential are
Figure 6.13  Comparison of $R_p$ values measured on Ni-Cr-Mo alloys as a function of potential in deaerated 5 mol•dm$^{-3}$ NaCl solutions at 70 ºC after 2 hours of potentiostatic oxidation at each potential: (a) positive scans; (b) negative scans.
Figure 6.14  Comparison of film capacitance values measured on Ni-Cr-Mo alloys as a function of potential in deaerated 5 mol•dm\(^{-3}\) NaCl at 70 °C after 2 hours of potentiostatic oxidation at each potential: (a) positive scans; (b) negative scans.
observed. The decreased resistance and increased capacitance at high potentials are consistent with the increased transpassive currents observed in Figure 6.9 and the increased surface reactivity in CV experiments (Figure 6.10). It should be noted that the capacitance observed for C2000 at positive potentials is significantly larger than for the other two alloys.

However, there are clear differences in the $R_p$ and capacitance values obtained on the negative scan. The $R_p$ values for Alloy 625 and C22 are lower and the capacitance values higher (especially Alloy 625) than for the other alloys in the potential range 0.2 V to –0.5V. On both of these alloys a current for O$_2$ reduction is sustainable, Figure 6.11(a). By comparison, the value of $R_p$ recorded on C2000 is significantly higher in this potential range and the O$_2$ reduction current correspondingly lower, Figure 6.11(a). These observations may suggest that Cu in C2000 plays a role in the film repair process on this alloy. Whether or not this is related to the high PREN and PRE' values for this alloy remains to be studied. $R_p$ for C276 and C4 do not show a similar decrease over the potential range 0.2 V to –0.5 V, but this can be attributed to the fact that neither of these alloys was polarized to very positive potentials on the positive scan.

The similar $R_p$ and capacitance values observed on the positive scan for all the Ni-Cr-Mo alloys indicate similar barrier layer properties. According to the point defect model (PDM) for passive films on metal and alloys[9, 10] and literature [11], the barrier layer of the passive film on Ni-Cr-Mo alloys grown in the passive region is dominated by oxygen
vacancies and/or cation interstitials. And the passive film is composed of NiO and mainly Cr$_2$O$_3$ (Chapter 3) which is generally considered as the barrier layer and the dominant contributor to the polarization resistance. The similar $R_p$ values for all 5 Ni-Cr-Mo alloys also indicate that the outer regions of the oxide film contribute little to the polarization resistance. However, other properties of the outer regions of the oxide film such as composition and distribution of species must be different since the 5 alloys exhibited different susceptibilities to O$_2$ reduction and surface reactivity. These differences in the properties of the outer regions of the film must depend on the alloying composition.

### 6.4 Summary and Conclusions

The kinetics of O$_2$ reduction on 5 Ni-Cr-Mo alloys with various Cr, Mo, W and Cu contents were investigated. Various electrochemical techniques including corrosion potential measurements, potentiostatic polarization curves and EIS measurements, and preoxidation followed by CV experiments were employed to investigate the effect of the alloying elements on the kinetics of O$_2$ reduction in 5 mol•dm$^{-3}$ NaCl solutions at 70 °C.

There is a significant difference in the grain size for the studied 5 Ni-Cr-Mo alloys. It ranges from ~ 30 µm for Alloy 625 to > 300 µm for C4. The grains in C22 and C2000 are of intermediate size, ~ 150 µm, while the grains in C276 are generally in the range 50 to 100 µm. After oxidation at 0 V, the passive films on all alloys exhibited uniform oxidized surfaces irrespective of the difference in grain size.
When freshly polished and cathodically cleaned electrodes were immersed in 5 mol\(\cdot\)dm\(^{-3}\) NaCl at room temperature (22 °C) for 24 hours, they showed similar corrosion potential behaviour in both aerated (\(~ – 0.15 \text{ V}\) ) and deaerated (\(~ – 0.35 \text{ V}\) ) solutions. For all alloys, \(E_{\text{corr}}\) was located in the passive region and no significant influence of alloying composition was observed.

When freshly polished and cleaned electrodes were oxidized at progressively positive potentials from – 1 V at 70 °C, \(\text{O}_2\) reduction was not completely suppressed by the defective oxide film until potentials > – 0.2 V were reached. The \(\text{O}_2\) reduction currents observed in the potential range – 0.8 V to – 0.5 V on Alloy C2000 and C22 were smaller than those on Alloy C276, 625 and C4. This may be due to the high Cr and Mo contents in Alloy C22 and C2000. When the positive potential limit is in the passive region (0.1V), \(\text{O}_2\) reduction currents observed on the negative scans on all alloys were significantly suppressed by the growth of the passive film. When the positive potential limit was extended to 0.9 V (transpassive region), Alloy C2000 exhibited an extremely high transpassive current, but the revived \(\text{O}_2\) reduction currents observed on the negative scan is smaller than those on Alloy C22 and C276. This may be due to the presence of Cu, which perhaps suppresses the catalytic activity of the higher oxidation states of Mo (W) produced in the transpassive oxidation for \(\text{O}_2\) reduction.

Cyclic voltammetric experiments were conducted on these alloys preoxidized at potentials in the passive (0 V) and transpassive (0.6 V) regions in aerated and deaerated
solutions at 70 °C. The alloys exhibited similar passive currents but different transpassive currents. After preoxidation at 0 V, no significant O₂ reduction currents were observed on the forward CV scans, and no obvious film reduction-reoxidation processes confirming the formation of stable passive films on all the alloys. However, after preoxidation at 0.6 V in the transpassive region (Alloy 625 and C4 were only preoxidized at 0.2 V to avoid the initiation of localized corrosion), the kinetics of O₂ reduction and the nature of film transformation processes varied between alloys. Alloy 625 showed a significant reduction current on the forward CV scan, and a comparison of the currents observed in aerated and deaerated solutions indicate this is primarily due to reduction of oxidized surface states. No significant reduction currents were observed on C276 and C4. Both C22 and C2000 exhibited O₂ reduction currents although the current was very low on C2000 possibly due to the presence of Cu on the transpassively oxidized surface. As discussed in Chapter 4, the more substantial O₂ reduction current observed on Alloy C22 can be attributed to the presence of transpassively formed high oxidation states of Mo and W.

EIS measurements were performed to understand the difference in interfacial properties between alloys. The polarization resistance (Rₚ) values initially increased and capacitance decreased with increasing potential for all alloys. The high Rₚ values and low capacitance values achieved in the potential range from – 0.3 V to 0.3 V show that stable passive oxide films were formed on all the alloys. As the potential was extended into the
transpassive region \((E > 0.3 \text{ V})\), the values of \(R_p\) decreased and capacitance increased for all the alloys, due to defect ejection into the barrier layer leading to its destruction.

However, after transpassive oxidation significant differences between the alloys were observed on polarizing to negative potentials. The \(R_p\) values on Alloys 625 and C22 were lower and the capacitances higher (especially for Alloy 625) than other alloys in the potential range 0.2 V to –0.5 V in which \(O_2\) reduction occurs. This decrease was clearly dependent on whether the alloy had been polarized to very positive potentials in the transpassive region. For those alloys (C276 and C4) not polarized in this manner, this decrease in \(R_p\) was not observed. This decrease in \(R_p\) was a prerequisite for the observation of a current for \(O_2\) reduction. The one exception to this rule is C2000. Despite polarizing to very positive potentials, the decrease in \(R_p\) values in the range –0.2V to –0.5 V was minor and the corresponding \(O_2\) reduction current small.

6.5 References


Chapter 7

The Mechanism of O₂ Reduction on Oxide-Covered Ti Alloys

7.1 Introduction

In previous chapters, the kinetics of O₂ reduction was studied on oxide-covered Ni-Cr-Mo (W) alloys in 5 mol•dm⁻³ neutral NaCl solutions. The effect of potential, temperature and alloying elements on the kinetics of O₂ reduction on Ni-Cr-Mo (W) alloys were investigated and discussed. The properties of the oxide films present on the surfaces of the alloys were also investigated by ToF-SIMS, XPS, and EIS in an attempt to define the kinetics and the film transformations observed on these alloys. Generally, in the passive region, the alloys exhibited an extremely high polarization resistance (~ 10⁶ Ω•cm²) and O₂ reduction was completely suppressed on the passive film. However, when the alloys were polarized at high potentials in the transpassive region, the electrode surface was activated by the injection of cation vacancies into the film, resulting in a significant decrease in the polarization resistance of the interface between electrode and solution. This led to a partial revival of O₂ reduction on returning the potential to negative values.

Also, other results on the Ni-Cr-Mo(W) alloys show that the initiation and propagation of crevice corrosion is extremely difficult to induce, even in high temperature, extremely saline solutions [1]. However, providing Ti is not alloyed with Pd/Ni/Mo, electrochemical
inducement is not required for crevice corrosion to occur [2]. Both laboratory studies and industrial experience show that providing the temperature is \( \geq 70 \, ^\circ\text{C} \), crevice corrosion will initiate and propagate on commercially pure Ti (Ti Grade 2, Ti-2). The composition of the three Ti alloys (Ti-2, Ti-7 and Ti-12) used in this study are given in Table 7.1.

<table>
<thead>
<tr>
<th>Table 1.1</th>
<th>Chemical compositions of Ti alloys studied (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni</td>
</tr>
<tr>
<td>Ti-2</td>
<td>0.11</td>
</tr>
<tr>
<td>Ti-7</td>
<td>0.18</td>
</tr>
<tr>
<td>Ti-12</td>
<td>0.79</td>
</tr>
</tbody>
</table>

Ti and its alloys also exhibit excellent corrosion resistance and have been proposed as candidate materials for nuclear waste containers for the deep geological disposal of high-level nuclear waste in Canada, Finland and Sweden [3, 4]. The corrosion resistance of Ti in aggressive environments is due to the presence of an inert oxide on the metal/alloy surface, which is spontaneously and rapidly formed and protective over a wide range of conditions, as illustrated by the Pourbaix diagram, Figure 7.1 [5]. In previous studies, crevice corrosion and hydrogen-induced cracking (HIC) were shown to be the only potential failure processes under deep geologic repository conditions [6-8].

Figure 7.2 illustrates the mechanism of crevice corrosion on Ti metal. Crevice corrosion occurs when a metallic surface is in close proximity to another surface. The tight geometry of the crevice results in limited mass transport between the occluded region
Figure 7.1 Pourbaix diagram for the Ti- H₂O system, at 25 °C [5]. The dashed lines (a) and (b) bracket the stability region for water.

(inside the crevice) and the bulk solution (outside the crevice). Surface oxidation and dissolution within the crevice consumes the limited amount of dissolved oxygen in the
Figure 7.2  Schematic illustration of the mechanism of crevice corrosion on Ti.

occluded region [9]. The dissolved metal cations hydrolyze to produce acidity within the crevice and Cl⁻ ions migrate from the bulk solution into the crevice to neutralize the excess positive charge produced by this process. This leads to the formation of an aggressive acidic saline solution, which rapidly destroys the protective oxide film on the metal surface within the creviced region. As a consequence, the potential within the crevice becomes negative relative to that of the exposed surface. As shown in the figure, both the reduction of protons within the crevice and the reduction of O₂ on the oxide-covered surface outside the crevice can support metal dissolution within the crevice. Proton reduction leads to the absorption of hydrogen into the metal and the formation of surface hydrides (TiHₓ), a process important in determining the corrosion
Since crevice corrosion of Ti must involve O\textsubscript{2} reduction, this means that the oxide outside the crevice must be able to sustain O\textsubscript{2} reduction at a rate able to support a substantial propagation rate. The oxide film (TiO\textsubscript{2}) on Ti is a stable n-type semiconductor with a 3 eV band gap [10], and an electron transfer through the oxide film to support O\textsubscript{2} reduction on the oxide should be very slow. There are two possible processes that could facilitate electron transfer through the oxide thereby allowing O\textsubscript{2} reduction. The first mechanism is oxide reduction to produce a defective Ti(III)-containing oxide/oxyhydroxide (7.1). A threshold potential (~ – 0.6 V) is required for the redox transformation occurring in the oxide [2]. The second possibility is that O\textsubscript{2} reduction could occur at intermetallic sites (TiFe\textsubscript{x}) covered by more defective and conductive oxide, which have been shown to be activated for electron transfer [11], at potentials more positive than – 0.6 V [2]. These intermetallics generally lie along the \(\alpha\)-Ti grain boundaries, and their number and size depends on the nature and amount of alloying additions and the concentration of Fe impurity [12].

To explore the mechanism of O\textsubscript{2} reduction on Ti alloys, a series of electrochemical experiments including \(E_{corr}\) measurements and potentiostatic film-growth followed by CV experiments were employed to study the effect of temperature, potential and alloying...
elements on the kinetics of O₂ reduction on three Ti alloys. Techniques such as SEM, ToF-SIMS, XPS, SECM and dynamic SIMS were used to characterize the properties of the oxide film.

7.2 Experimental Details

Similar electrochemical procedures to those used in Chapter 6 were adopted. One small change in procedure is that some of the Ti electrodes were left overnight in air for 20 hours after polishing (up to 1200 grade silicon carbide paper), and then used without cathodic cleaning at – 1.2 V to avoid hydride formation.

Prior to SECM measurements and surface analyses including SEM, XPS, ToF-SIMS, and dynamic SIMS, the surface of the freshly polished Ti-2 was wet-polished up to 0.05 µm as described in Chapter 3.

To determine the location and extent of hydride formation, a Ti-2 specimen was corroded in 5 mol⋅dm⁻³ NaCl in deuterium oxide (D₂O, Isotope D, 99.9%) at pH 12 for 132 hours in an Ar-purged glove box after wet-polishing. This experiment was conducted in D₂O in order to facilitate the identification of any deuterides (TiDₓ) formed using ToF-SIMS and Dynamic SIMS analyses. The motivation for increasing the pH to 12 in this experiment was to increase the solubility of TiO₂ (Figure 7.1). It is expected that the oxide-covered titanium surface will be less passive at higher pH and thus the intermetallic sites and potentially the areas above the α-Ti grains will become more active for D₂O reduction,
leading to the adsorption of deuterium into the alloy and the formation of TiD_x.

SECM measurements were used to investigate lateral variations in surface reactivity between the α-Ti grains and the intermetallic precipitates. SECM was performed on a well-polished Ti-2 specimen in 0.1 mol•dm⁻³ NaCl electrolyte containing 0.93 mmol•dm⁻³ ferrocenemethanol (Fc) as a redox mediator. The measurements were made in the constant distance mode (6 µm) and the tip feedback current recorded as a function of lateral position to produce the SECM images. As mentioned in Chapter 2, a disk-shaped ultramicroelectrode (UME) with a radius of 5 µm made of carbon and insulated in a glass sheath was used as the SECM probe (tip). The UME tip was biased at 0.4 V to achieve diffusion controlled oxidation of Fc to Fc⁺ on the tip, while the Ti-2 substrate electrode was cathodically polarized at various potentials.

SEM micrographs were obtained with a Leo 1540 FIB/SEM with Crossbeam (Zeiss) to examine the surface morphology. XPS and ToF-SIMS analyses were employed to characterize the composition of the oxide film, and the depth profiles of the oxides and possible deuterides and intermetallic particles in the film, respectively. In a similar manner to ToF-SIMS, Dynamic SIMS (D-SIMS) provides elemental and isotopic analysis of the oxide surface. However, in the D-SIMS mode a high density, DC primary ion beam current is used to provide sputter rates typically in the range 0.5-5 nm•s⁻¹. By using a more energetic primary ion beam, particles in the sample surface were rapidly sputtered and ejected from the sample surface as neutral species or ions and mass
analyzed in a magnetic sector mass spectrometer. By rastering the primary ion beam across the surface, a distribution map of elements and isotopes in the analyzed region of the sample was obtained. A Cameca IMS-3f SIMS instrument equipped with a Cs\(^+\) ion source was used to obtain the distribution of elements in the oxide film on Ti-2 and to determine the locations of intermetallic precipitates and deuterides. The detection range of this technique can be extended from matrix element levels down to trace element levels in the ppb range.

### 7.3 Results and Discussion

#### 7.3.1 Investigation of the Localized Reactivity of Ti-2 by SECM

SECM can provide in situ electrochemical information at a high spatial resolution (micrometer scale), making it a powerful technique to determine the localized reactivity of intermetallic precipitates in the passive oxide film on Ti-2 alloys. Figure 7.3 shows SECM images recorded on a well-polished Ti-2 electrode at various applied potentials. The color indicates the UME tip current according to the scale shown alongside the image. In images recorded at applied potentials of \(-0.1\) and \(-0.3\) V, no high current spots (active spots) were observed. The variation in color from one end to the other end of the images is due to the sample tilt in the Z direction. However, when \(E \leq -0.4\) V, active spots start to appear. Further decreases in applied potential cause a growth in the size and an increase in the number of these active spots. At \(-0.7\) V, a larger surface area and more
Figure 7.3  SECM images (160 µm×160 µm) recorded on a well-polished Ti-2 specimen at various applied potentials. The distance between the tip and the Ti-2 sample was set 6 µm, and the radius of the tip is 5 µm.
the active spots are activated suggesting that the activation of local spots is accompanied by onset of $\alpha$-Ti oxide reduction. In addition, the scale bars for the SECM images show the tip feedback current gradually increases as the applied potential is decreased, suggesting a more general reduction of the oxide on $\alpha$-Ti grains, as well as the detection of locally active locations.

According to the literature [11, 13, 14], the active locations observed in the SECM images, are associated with the presence of Fe-containing intermetallic precipitates on the grain boundaries. Using these data, a grain boundary structure map can be generated on the SECM images by interconnecting the active spots in the SECM images as shown for $–0.5$ V in Figure 7.3. These observations support the claim that the oxide on the intermetallic particles is preferentially reduced allowing these locations to act as preferential sites for $O_2$ reduction and hydride formation.

### 7.3.2 Photomicrograph and SEM Micrographs of FreshlyPolished and Corroded Ti-2

Figure 7.4 displays a photomicrograph showing the microstructure of the Ti-2 alloy used in these experiments [15]. The sample surface was prepared for photomicrography by careful polishing and etching. The grains in Ti-2 are generally in the range of 20 ~ 50 $\mu$m, consistent with the scale of the grain structure pattern generated in the SECM images, Figure 7.3. Ikeda et al. [16] pointed out that the grain size in Ti materials is related to the purity of the material, and decreases with increasing iron impurity and alloying element
Figure 7.4 Photomicrograph showing the microstructure of Ti-2 alloy [15].

levels.

Figure 7.5 and Figure 7.6 show the SEM micrographs of a freshly polished and a corroded Ti-2 specimen in 5 mol•dm$^{-3}$ NaCl in D$_2$O solution (pH 12) in an Ar-purged glove box for 132 hours, respectively. During the corrosion process, $E_{corr}$ reached a final value of $\sim -1$ V, Figure 7.7. Inspection of the micrographs shows a few light colored strips along the $\alpha$-grain boundaries in the freshly polished specimen, indicating the presence of intermetallic precipitates, consistent with published literature [11, 14]. These locations become more visible after corrosion suggesting they are more susceptible to corrosion than the $\alpha$-Ti grains, in good agreement with the SECM measurements. These observations support the claim that the Fe-containing intermetallics along grain boundaries exhibit a higher reactivity than the $\alpha$-Ti grains, and hence could serve as
preferential sites for O$_2$ reduction and hydride formation.

**Figure 7.5** SEM micrograph of a freshly polished Ti-2 specimen.

**Figure 7.6** SEM micrograph of a Ti-2 specimen corroded in 5 mol•dm$^{-3}$ NaCl in D$_2$O solution at pH 12 for 132 hours.
Figure 7.7  $E_{corr}$ of Ti-2 as a function of time in 5 mol•dm$^{-3}$ NaCl in D$_2$O at pH 12.

The experiment was conducted in an Ar-purged glove box.

7.3.3 Surface Analyses by XPS, ToF-SIMS and D-SIMS

7.3.3.1 XPS Analyses

XPS analysis was performed on both the freshly polished and the corroded Ti-2 specimens to determine the surface composition. In both of the survey spectra, strong signals for Ti and O are detected, but no Fe signal is observed due to the low content of Fe in the alloy (Table 7.1). The Ti 2p high-resolution XPS spectra are fitted by the parameters outlined by Biesinger et al. [17]. Both of the Ti 2p spectra are found to be dominated by Ti(IV) (~ 80%), Figure 7.8. Since the $E_{corr}$ for the corroded specimen (Figure 7.7) is extremely negative it would be expected to contain a higher amount of
reduced Ti oxidation states (Ti(III) rather than Ti(IV)). However, since reoxidation of the surface could have occurred on exposure to air during the transport of the sample from the electrochemical cell to the XPS analysis chamber, this composition can not be considered definitive.

Figure 7.8 High-resolution XPS spectrum of the Ti 2p region recorded on Ti-2 corroded in 5 mol•dm$^{-3}$ NaCl in D$_2$O at pH 12 for 132 hours.

7.3.3.2 ToF-SIMS Analyses

ToF-SIMS analyses were undertaken to determine whether or not deuterium was incorporated into the Ti-2 surface to form TiD$_x$ during corrosion. Figure 7.9 shows the $^2$H(D)$^-$ ToF-SIMS spectra obtained on both as-polished and corroded Ti-2 in 5 mol•dm$^{-3}$
Figure 7.9  $^2\text{H(D)}^-$ ToF-SIMS spectra obtained on as-polished Ti-2 and Ti-2 corroded in 5 mol•dm$^{-3}$ NaCl in D$_2$O for 132 hours.

NaCl in D$_2$O. The overall intensity of the $^2\text{H(D)}^-$ peak measured on the corroded specimen is double the intensity of $^2\text{H(D)}^-$ peak measured on the as-polished specimen, in which the $^2\text{H(D)}^-$ peak can be attributed to the natural isotope abundance of $^2\text{H(D)}$. The calculated $^2\text{H(D)}^-$ to H$^-$ area ratio on the corroded specimen almost doubled. This significant increase in $^2\text{H(D)}^-$ indicates the incorporation of deuterium into the Ti-2 surface and the formation of TiD$_x$ at the extremely negative corrosion potential achieved, Figure 7.7.

Figure 7.10 shows the depth profiles obtained for Ti$^-$, TiO$_2^-$ and Fe$^-$ recorded on both the as-polished and corroded Ti-2 specimens. As expected, the intensity of TiO$_2^-$ decreases
Figure 7.10  Depth profiles obtained by ToF-SIMS for Ti\(^{\text{+}}\), TiO\(_2\)\(^{-}\) and Fe\(^{-}\) recorded on the as-polished Ti-2 specimen and the Ti-2 corroded in 5 mol\( \text{dm}^{-3} \) NaCl in D\(_2\)O solution at pH 12 for 132 hours.
with sputtering time and that of Ti\(^-\) increases on both specimens, indicating the presence of a thin surface layer of TiO\(_2\). The TiO\(_2^-\) to Ti\(^-\), \(^2\)H(D)\(^-\) to H\(^-\) and Fe\(^-\) to Ti\(^-\) intensity ratios as a function of sputtering time were determined based on the depth profiles on both the as-polished and corroded Ti-2 specimens, Figure 7.11. The significantly lower TiO\(_2^-\) to Ti\(^-\) intensity ratio obtained at short sputtering times on the corroded specimen compared to the as-polished specimen, indicates the loss of TiO\(_2\) from the surface after corrosion. Similarly, the higher \(^2\)H(D)\(^-\) to H\(^-\) intensity ratio at short sputtering times, Figure 7.11, for the corroded sample compared to the as-polished sample confirms the incorporation of deuterium into the surface. In addition, the strongly enhanced Fe\(^-\) to Ti\(^-\) intensity ratio on the corroded sample is consistent with the SEM evidence and indicates the exposure of the TiFe\(_x\) intermetallic particles by corrosion. Although these results suggest the formation of deuterides occurs at intermetallic sites, this remains to be clearly demonstrated.

![Graph](image-url)
Figure 7.11  TiO$_2^-$ to Ti$^-$, $^2$H(D)$^-$ to H$^-$ and Fe$^-$ to Ti$^-$ intensity ratios as a function of sputtering time obtained by ToF-SIMS on the as-polished Ti-2 specimen and the Ti-2 specimen corroded in 5 mol·dm$^{-3}$ NaCl in D$_2$O solution at pH 12 for 132 hours.
7.3.3.3 Dynamic-SIMS (D-SIMS) Analyses

D-SIMS was used to obtain maps showing the distribution of elements in the oxide film in an attempt to determine the locations of the intermetallic precipitates and TiD$_x$ on the corroded surface. Figures 7.12 to 7.15 show the elemental distribution maps for Ti, O, H, D and Fe on both the as-polished and the corroded Ti-2 samples at various sputtering times. The light color locations in these images show the enhancement of the signal at these sites.

Before sputtering (Figure 7.12) or after 0.5 minutes of sputtering (Figure 7.13), the images for Ti, H, D and Fe obtained on the corroded sample show evidence for localized accumulation compared to the as-polished sample, for which the signals of deuterium and hydrogen may come from the absorption from the atmosphere during the sample preparation and/or from the D-SIMS analysis chamber. The correlation of the maps for Ti, D and H indicates the locations of TiD$_x$, and the non-uniform image for Fe indicates the locations of intermetallic particles (TiFe$_x$) in the grain boundaries, consistent with the SEM observations. However, whether or not there is a correlation between the locations of deuterides and intermetallic particles in the corroded sample is inconclusive. The locations of deuterides do not completely correlate with the locations of TiFe$_x$. This may suggest the Fe-containing intermetallic sites are preferentially deuterided but the further formation of deuterides over a long exposure period is not necessarily limited to these sites. A possible mechanism is that the formation of deuterides initiates at intermetallic
Figure 7.12 D-SIMS images (150 µm in diameter) for Ti, O, H, D and Fe recorded on both the as-polished and corroded Ti-2 samples before sputtering.

Figure 7.13 D-SIMS images (150 µm in diameter) for Ti, O, H, D and Fe recorded on both the as-polished and the corroded Ti-2 samples after 0.5 minute of sputtering.
Figure 7.14  D-SIMS images (150 µm in diameter) for Ti, O, H, D and Fe recorded on both the as-polished and the corroded Ti-2 samples after 1 minute of sputtering.

Figure 7.15  D-SIMS images (150 µm in diameter) for Ti, O, H, D and Fe recorded on both the as-polished and the corroded Ti-2 samples after 3 minutes of sputtering.
sites but their growth then continues more generally on the surface with time.

After 3-minute of sputtering, the localized enrichment of deuterium and hydrogen in the images of the corroded sample disappears, consistent with the ToF-SIMS depth profiles showing their accumulation in a corroded surface layer. The correlation between Ti and Fe persists, as expected since intermetallic particles at grain boundaries are not confined to the surface layer.

### 7.3.4 Kinetics of O₂ Reduction on Ti Alloys

#### 7.3.4.1 $E_{\text{corr}}$ Measurements Followed by Cyclic Voltammetry (CV) on Ti-2 on Cathodically-cleaned Surfaces

Figure 7.16 shows the current density-time profiles recorded on Ti-2 in aerated 5 mol•dm⁻³ NaCl (pH 7) at various temperatures during cathodic cleaning at – 1.2 V. The increase in negative current with time indicates that H₂O reduction becomes progressively kinetically easier, especially at higher temperatures. This could be attributed to reduction of the surface oxide, at least locally, and its replacement with Ti hydrides (TiHₓ) during cathodic cleaning. The $E_{\text{corr}}$ measured for 72 hours after cathodic cleaning, Figure 7.17, is generally in the range from – 0.3 V to – 0.15 V. The increase in $E_{\text{corr}}$ with temperature suggests the alloy becomes progressively more passive at higher temperatures. However, as the temperature approaches and exceeds 70 °C, the negative-going transients indicate that the passive film undergoes fracture-repair events.
Figure 7.16  Current density-time profiles recorded on Ti-2 in aerated 5 mol•dm\(^{-3}\) NaCl (pH 7) at various temperatures during cathodic cleaning at –1.2 V.

Figure 7.17  \(E_{\text{corr}}\) measured on Ti-2 in aerated 5 mol•dm\(^{-3}\) NaCl solutions (pH 7) at various temperatures after cathodic cleaning at –1.2 V.
A passive film breakdown/recrystallization process to yield an anatase/rutile phase transformation occurs, and cracks and faults begin to appear in the oxide in this temperature range [2]. This onset of events in $E_{corr}$ measurements is consistent with the observation that crevice corrosion will not initiate on Ti at temperatures lower than ~ 70 ºC [12, 15]. At 90ºC, the establishment of a lower $E_{corr}$ after a number of these fracture-repair events indicates the establishment of a slightly more active surface state. This transition to a lower $E_{corr}$ in the range from – 0.3 V to – 0.4 V is an indication that the $E_{corr}$ response is primarily on a hydrided surface layer [17]. Based on the D-SIMS analyses described above, it is likely that the formation of hydrides takes place at the intermetallic sites while the $\alpha$-grains remain passive.

Following these $E_{corr}$ measurements, the potential was scanned from $E_{corr}$ to – 1.2 V and back, Figure 7.18. The forward scan shows the influence of the TiO$_2$ film on O$_2$ and H$_2$O reductions, and the reverse scan indicates how these reactions are influenced by any changes in the oxide film or other surface features induced during the forward scan. At room temperature (22 ºC), 50 ºC, and 70 ºC, currents for O$_2$ reduction started to appear at ~ – 0.5 V, whereas the O$_2$ reduction initiated at – 0.3 V at 90 ºC. The observation of a current at – 0.5 V to – 0.3 V suggests O$_2$ reduction may have initiated on intermetallic sites (TiFe$_x$) activated in this potential region, based on the SECM results, since TiO$_2$ film reduction is not anticipated at this potential. However, at more negative potentials, it is not possible to determine whether or not O$_2$ reduction is sustained on the intermetallic
Figure 7.18  CVs after $E_{\text{corr}}$ measurements for Ti-2 in aerated 5 mol•dm$^{-3}$ NaCl solutions at pH 7 at various temperatures.

particles or on the reduced oxide surface.

The $O_2$ reduction current at 50 °C is larger than that at room temperature, and the current at both is suppressed on the reverse scan. This indicates a change in the properties of the electrode surface leading to an inhibition of $O_2$ reduction. A possibility is extensive hydride ($TiH_x$) formation at potentials $<-1$ V when the current for $H_2O$ reduction increases, since hydride formation would only be expected at sites where the oxide had been reduced and the metal exposed,

$$Ti + xH_2O + xe^- \rightarrow TiH_x + xOH^-$$  \hspace{1cm} (7.2)
At 70 °C the O₂ reduction current is smaller than that observed at 50 °C, and the value at 90 °C considerably lower than expected if the reaction was straightforwardly activated by temperature. Based on the $E_{corr}$ data at these temperatures, Figure 7.17, it is suspected that the surface, at least at intermetallic sites, was already hydrided. Since these intermetallic sites are conductive, O₂ reduction would be anticipated to occur at these locations. However, the O₂ reduction reaction generally requires catalysis and the low current density observed at 70 °C suggests the reaction is not catalyzed at these locations. The steep increase in current for potentials $\leq -1$ V in Figure 7.18 can be attributed to H₂O reduction, and is likely to lead to more extensive hydride formation initially at intermetallic locations but possibly more generally, as discussed in section 7.3.3.2 and 7.3.3.3. Since O₂ reduction appears to be inhibited on a hydrided surface, this negative potential region was avoided in further experiments, the negative potential limit being confined to – 0.75 V.

**7.3.4.2 Temperature Dependence of O₂ Reduction on Ti-2 Pre-oxidized at 0 V**

To avoid hydride formation and to determine the influence of temperature on O₂ reduction kinetics, a freshly prepared electrode was left overnight after mechanical polishing then potentiostatically oxidized at 0 V in an attempt to produce a consistent oxide-covered surface. This procedure was then followed by a CV from 0 V to – 0.75 V and back. Figure 7.19 shows the effect of temperature on the anodic current recorded at 0 V on Ti-2. The currents are shown offset to illustrate the differences. At short times,
Figure 7.19  Effect of temperature on the anodic growth of TiO$_2$ at 0 V on Ti-2 in neutral aerated 5 mol·dm$^{-3}$ NaCl solutions. The currents at 40 °C, 50 °C, 60 °C, 70 °C, 80 °C and 90 °C are 2, 3, 4, 8, 12, and 15 times larger than the original values, respectively.

region A, the current is partially dependent on the state of the air-oxidized surface present after overnight storage and is difficult to interpret. In the second region, B, the anodic film-growth is shown to be almost independent of temperature. At lower temperatures up to 80 °C, the linear log$i$ - log$t$ relationship is maintained throughout region B, consistent with a field-driven defect migration process leading to oxide film formation [18, 19]. At 90 °C, the current deviates from this linear relationship, due to the fractured oxide [2]
Figure 7.20  CV scans recorded after film-growth at 0 V on Ti-2 as a function of temperature in neutral aerated 5 mol\(\cdot\)dm\(^{-3}\) NaCl solutions (a) linear scale; (b) log scale for the forward scans only.
leading to enhanced anodic oxidation most likely at the locations of intermetallic phases.

Figure 7.20 shows the CV scans recorded after the potentiostatic film-growth at 0 V, and Figure 7.21 displays the O₂ reduction currents measured at –0.75 V at various temperatures. As expected, the current increases with increasing temperature up to 80 °C, but then decreases at 90 °C, most likely due to the reduced O₂ solubility at this temperature. The log $j$ vs. $E$ plot, Figure 7.20 (b), demonstrates that a meaningful current for O₂ reduction is not observed until the potential $\leq -0.35$ V at 25 °C, whereas at higher temperatures the threshold potential at which O₂ reduction begins increases to $\sim -0.1$ V, suggesting O₂ reduction may have initiated on the intermetallic sites (TiFeₓ) since these potentials are not negative enough for the reduction of TiO₂ (equation 7.1). This observation of an apparent threshold is consistent with the results in Figure 7.18. By

![Figure 7.21](image.png)

**Figure 7.21** Effect of temperature on O₂ reduction current at –0.75 V.
limiting the lower potential limit to $-0.75$ V, more reproducible CV scans with less hysteresis are obtained since TiH$_x$ formation at negative potentials is considerably reduced.

7.3.4.3  **Effect of Film-growth Potential and Alloying Elements on O$_2$ Reduction on Ti Alloys**

CV scans after potentiostatic film-growth experiments were also carried out on Ti-7 and Ti-12 in addition to Ti-2, to investigate the effect of alloying elements on O$_2$ reduction kinetics. All three alloys were preoxidized at various potentials in the passive region [14] and the CVs recorded subsequently are shown in Figure 7.22. O$_2$ reduction currents initiate on all 3 alloys at $\sim -0.4$ V, indicating O$_2$ reduction initiates at the intermetallic sites, consistent with the observations above.

Rather low O$_2$ reduction currents are observed on all alloys pre-oxidized at these potentials. For Ti-2 the current density for O$_2$ reduction varies within the range of 0.02 to 0.035 mA•cm$^{-2}$, whereas there is a suppression of the O$_2$ reduction current as the film-growth potential decreases on Ti-12 and Ti-7 with the exception of Ti-7 at the film-growth potential of 0 V. The difference between the three alloys lies in the nature and composition of intermetallic particles on the grain boundaries since an $\alpha$-phase (Ti-2 and Ti-7) or near $\alpha$-phase (Ti-12, the microstructure is shown in Figure 7.23) grain structure is adopted by all three alloys. These intermetallic particles vary in composition.
The figure shows two cyclic voltammetry (CV) plots for Ti-2 and Ti-12. The x-axis represents the electrode potential (E, Volt vs. Sat.Ag/AgCl), and the y-axis represents the current density (j, mA cm$^{-2}$). The plots display various film-growth potentials: 0 V, -0.1 V, -0.2 V, and -0.35 V, indicated by different line colors. The CV plots illustrate the electrochemical behavior of the Ti samples under different potentials.
Figure 7.22  CV scans recorded after film-growth at various potentials on Ti-2, Ti-12 and Ti-7 alloys in neutral aerated 5 mol dm$^{-3}$ NaCl solutions.

Figure 7.23  The photomicrograph showing the microstructure of Ti-12 [15].
from TiFe$_x$ (Ti-2), to TiFe$_x$Pd$_y$ (Ti-7) and TiFe$_x$Ni$_z$Mo$_z$ (Ti-12). The observation that the O$_2$ reduction current on Ti-2 shows only small variations with film growth potential may be attributed to the low number density of intermetallic phases in this alloy. By contrast, the larger amounts of alloying elements and impurities in Ti-7 and especially Ti-12 (a near-α alloy containing significant amounts of β-phase [7]), lead to the variations in surface reactivity to O$_2$ reduction with film-growth potentials. The decreased O$_2$ reduction current with decreasing film-growth potential on Ti-7 and Ti-12 suggests that, despite trying to avoid hydride formation, corrosion of the intermetallic particles leads to surface hydride formation and, thus, the suppression of O$_2$ reduction. It is not clear why the current is suppressed at 0 V on Ti-7. A possible reason is that the TiFe$_x$Pd$_y$ intermetallics are more readily passivated at this more positive potential than the intermetallics in Ti-2 and Ti-12.

Figure 7.24 shows the CV plots for 3 Ti alloys after potentiostatic film-growth at – 0.35 V, a potential close to the $E_{corr}$ recorded on these alloys on a hydrided surface [17] (Figure 7.17). The O$_2$ reduction currents varied only slightly, the currents increasing in the order of Ti-2 > Ti-7 > Ti-12. The oxide over the α-grains is expected to be the same in composition for all three alloys. Thus, these differences in current cannot be attributed to O$_2$ reduction of this oxide layer, indicating the differences are due to differences in O$_2$ reduction at the intermetallic sites. Ti-12 and Ti-7 are expected to have higher contents of intermetallic phases than Ti-2, and, hence, higher O$_2$ reduction currents are expected on
these alloys than on Ti-2. This CV data suggests that more hydride formation covered on the intermetallic sites and suppressed the O₂ reduction on Ti-12 than Ti-7 and Ti-2.

![Figure 7.24](image.jpg)

**Figure 7.24** Comparison of CV scans recorded after film-growth at – 0.35 V on Ti-2, Ti-12 and Ti-7 alloys in neutral aerated 5 mol•dm⁻³ NaCl solutions.

### 7.4 Summary and Conclusions

A series of surface-sensitive techniques such as ToF-SIMS, XPS, SEM, dynamic SIMS and SECM were used to characterize the properties of the oxide film on Ti-2, and various electrochemical experiments including \( E_{corr} \) measurements and potentiostatic film-growth followed by CV experiments were employed to study the effect of temperature, potential and alloying elements on the kinetics of O₂ reduction on 3 Ti alloys.
SECM was used to investigate the local reactivity of intermetallic precipitates in a Ti-2 alloy. Measurements on a well-polished Ti-2 specimen show that high current spots (active spots) start to appear when the applied potential $E$ is $\leq -0.4$ V. Further decrease in potential causes a growth in the size and an increase in the number of these active spots. The literature [11, 13, 14] has demonstrated that these active locations, are associated with the presence of Fe-containing intermetallic precipitates on the grain boundaries in the alloy. These observations indicate that the oxide on the intermetallic particles is preferentially reduced allowing these locations to act as preferential site for $O_2$ and $H_2O$ reductions leading to hydride formation.

While a few light-colored strips along the $\alpha$-grain boundaries, suggesting the presence of intermetallic precipitates (TiFe$_x$), were observed in SEM micrographs recorded on freshly polished sample, many more such sites were exposed after corrosion in 5 mol•dm$^{-3}$ NaCl ($D_2O$, pH 12) solution for 132 hours. XPS analysis indicates the presence of multiple oxidation states for Ti in the surface of corroded Ti-2 with the majority (> 80%) being Ti(IV). An accurate quantitative analysis is not possible since reduced Ti oxidation states (Ti(III)) maybe reoxidized by exposure to air prior to analysis.

ToF-SIMS analyses show a significant decrease in TiO$_2$ to Ti$^-$ intensity ratio at short sputtering times for the corroded sample, compared to the as-polished sample, indicating the loss of TiO$_2$ from the surface during corrosion. In addition, the overall intensity (or area) of $^2$H(D)$^-$ peak in the ToF-SIMS spectra of corroded Ti-2 is double of that peak in
the spectra of as-polished specimen, and the $^2\text{H(D)}^-$ to $\text{H}^-$ intensity ratio at short sputtering times in ToF-SIMS sputtering profiles is greater for the corroded sample than for the as-polished sample. These data indicate incorporation of deuterium into the Ti-2 surface probably due to the formation of deuterides ($\text{TiD}_x$). This was accompanied by an enrichment of Fe-containing intermetallics in the surface, consistent with the SEM evidence. However, D-SIMS experiments could not confirm that the formation of deuterides coincided with the locations of Fe-containing intermetallics.

A series of CV experiments were carried out on Ti-2 at various temperatures after $E_{\text{corr}}$ measurements for 72 hours on cathodically-cleaned surfaces at $-1.2 \, \text{V}$ in 5 mol•dm$^{-3}$ NaCl solution. The $E_{\text{corr}}$ was in the range from $-0.3 \, \text{V}$ to $-0.15 \, \text{V}$, and increased with temperature up to 70 °C before decreasing at 90 °C. The observation of negative-going transients at $T \geq 70 \, \text{°C}$ indicates film breakdown processes most likely at intermetallic sites. Currents for O$_2$ reduction were observed when the potential was more negative than $-0.5 \, \text{V}$ at room temperature (22 °C) and 50 °C, but occurred at more positive potentials at higher temperatures, suggesting O$_2$ reduction on exposed intermetallic sites ($\text{TiFe}_x$). The current for O$_2$ reduction increased up to 50 °C but was inhibited at higher temperatures probably due to hydride ($\text{TiH}_x$) formation.

To avoid the formation of surface hydrides the cathodic cleaning procedure at $-1.2 \, \text{V}$ was dropped and Ti-2 specimens preoxidized at 0 V. Subsequent measurements of O$_2$ reduction current showed they increased with temperature up to 80 °C but decreased at 90
°C. More importantly, O₂ reduction started at higher potentials at higher temperatures, consistent with its occurrence on exposed intermetallic locations.

The effects of alloying elements were studied on Ti-2, Ti-7 and Ti-12. Rather small O₂ reduction currents were observed on all three alloys after preoxidation at the potentials in the passive region. These currents were found to commence on all three alloys at ~ – 0.4 V, indicating the intermetallic sites are the active locations for O₂ reduction. The current density for O₂ reduction on Ti-2 seems not affected by the variations in film-growth potentials in the passive region, whereas there is a suppression of the O₂ reduction current as the film-growth potential decreases on Ti-12 and Ti-7. After potentiostatic film-growth at – 0.35 V, a potential close to the $E_{corr}$ observed on these alloys on a hydried surface layer [17], the O₂ reduction currents increase in the order of Ti-2 > Ti-7 > Ti-12. The slight current differences on the three alloys can be attributed to the varied composition and contents of intermetallic particles on the grain boundaries and the possible coverage by hydrides at intermetallic sites.

7.4 References


Chapter 8

Summary and Future Work

8.1 Summary

The primary objective of this research project is to investigate the influence of the oxide film on Alloy 22, and similar Ni-Cr-Mo alloys, on the kinetics of O₂ reduction. Surface analytical techniques such as XPS, ToF-SIMS, and SEM were employed to investigate the chemical composition and structure of the passive film on 2 Ni-Cr-Mo alloys, Alloy C22 and C2000, as a function of potential, temperature, and pH. The kinetics of O₂ reduction on Ni-Cr-Mo alloys in a range of environments were studied by various electrochemical techniques including the use of rotating disk electrode (RDE), potentiostatic polarization, and CV, to measure the influence of parameters such as potential, temperature, and alloy substrate composition, on the kinetics of O₂ reduction. The interfacial electronic properties were obtained by EIS measurements. To facilitate understanding of the mechanism of O₂ reduction on Ni-Cr-Mo alloys, the influence of the chemical properties of the oxide film on Ti alloys on O₂ reduction were also investigated.

The passive film (0 V vs. sat. Ag/AgCl) on Alloy C22 and C2000 grown in 5 mol·dm⁻³ NaCl is composed of oxides of Ni, Cr, Mo (W) or Cu in various oxidation states as well as hydroxides of Ni, Cr and Cu. The presence of a layered structure in the passive film was demonstrated by XPS and ToF-SIMS, with the outermost surface being enriched in Cu (or Cu oxide) and Mo oxide, the intermediate region dominated by Cr/Ni/Cu hydroxides, and the inner region comprising Cr/Ni oxide. In the transpassive region (0.6 V), the overall film thickness increases, but the transpassive oxidation of Cr(III) to Cr(VI)
in the barrier layer of the film leads to the loss of the Cr$_2$O$_3$-rich inner layer and the destruction of passivity. The relative Cr content in the film increases while that of Ni decreases.

At higher temperatures, the film-growth process is enhanced and the thicknesses of both the outer hydroxide layer and inner oxide layer increase. This is accompanied by a loss of Cr$_2$O$_3$ in the inner layer, an increase in the relative Ni content of the film and a decrease in Cr and Mo contents. With a decrease in pH, a decrease in film thickness, especially in the outer region of the film, and a relative loss in Cr$_2$O$_3$ from the film were observed. In addition, the relative amounts of Mo and Cr in the film are greatly enhanced, while the Ni content decreases.

Potentiostatic polarization and CV measurements on Alloy C22 demonstrated that the kinetics of O$_2$ reduction depends on the properties of the oxide film. When the electrode was preoxidized at potentials in the passive region ($\sim -0.2$ V to 0.3 V), O$_2$ reduction at negative potentials is almost completely suppressed by the passive film. However, when the preoxidation potential was extended into the transpassive region ($E > 0.3$ V), O$_2$ reduction is revived to a small degree on the apparently reactivated surface, i.e., the O$_2$ reduction is catalyzed by the high oxidation states of Mo (or W) formed in the transpassive region. With increasing temperature, the O$_2$ reduction current recorded at increasingly negative potentials increases with temperature over the range from 30 to 70 ºC, indicating that O$_2$ reduction is thermally activated on the transpassively reactivated surface. But the current decreases at 90 ºC, due to the decrease in dissolved O$_2$ concentration at high temperatures.
Film reduction-reoxidation was observed on Alloy C22 in CV experiments in deaerated solutions, and the extent of the film-reoxidation processes increases with preoxidation potential and temperature. When the electrode was preoxidized at 0.6 V at 50 ºC, two reduction peaks attributed to the reduction of Cr(VI) and Mo(VI)/W(VI) states were observed on the cathodic scan, and one or two reoxidation peaks were observed on the subsequent anodic scan depending on the potential limit of the cathodic scan. Based on a series of CV measurements and XPS analyses, the first reoxidation peak (~ – 0.6 V to – 0.45 V) is attributed to the reoxidation of Mo/W states, and the second reoxidation peak (~ – 0.45 V to – 0.3 V) to the reformation of the passive film involving the reoxidation of Ni, deposited by reduction of Ni(OH)₂ on the cathodic scan.

Potentiostatic polarization and CV measurements were also performed on other Ni-Cr-Mo alloys. As observed on Alloy C22, the kinetics of O₂ reduction was almost completely suppressed by the growth of a passive film on the surface, Alloy 625 being an exception. However, when these alloys were transpassively oxidized, the kinetics of O₂ reduction observed on the cathodic scan varied among the alloys. Alloy 625 and C4 are more susceptible to localized corrosion and O₂ reduction. On preoxidation at 0.2 V, Alloy 625 exhibited a high anodic current leading to a large O₂ reduction/film transformation current on the cathodic scan. By contrast, Alloy C4 exhibited only a slight O₂ reduction/film transformation current. The O₂ reduction current was revived on Alloy C22 after preoxidation at 0.6 V, while smaller O₂ reduction currents were observed on Alloy C2000 and C276 after transpassive oxidation up to 0.9 V.

EIS measurements on Ni-Cr-Mo alloys demonstrated that the polarization resistance ($R_p$) on all alloys initially increased while the capacitance decreased with increasing potential,
with extremely high $R_p$ ($\sim 10^6 \, \Omega \cdot \text{cm}^2$) and low capacitance ($\sim 10^{-5} \, \text{F} \cdot \text{cm}^{-2}$) values being observed in the potential range from $\sim -0.2 \, \text{V}$ to $0.3 \, \text{V}$, due to the presence of the passive oxide film. Irrespective of temperature in aerated solution, a potential $\leq -0.15 \, \text{V}$ is required to sustain a cathodic $\text{O}_2$ reduction current. The high resistances and low capacitances of the passive film on these alloys are consistent with the small passive currents and suppressed $\text{O}_2$ reduction currents measured in polarization curves. As the potential was extended into the transpassive region ($E > 0.3 \, \text{V}$), $R_p$ decreased and the capacitance increased with potential for all alloys, due to oxidative ejection of cations from the barrier layer. The decreased resistances and increased capacitances at high potentials are consistent with the increased transpassive currents observed.

When the electrodes were polarized to progressively more negative potentials after polarization up to a positive potential limit of $0.9 \, \text{V}$, differences in $R_p$ and capacitances among the alloys become clear. The $R_p$ values on Alloy 625 and C22 are lower and capacitance higher (especially for Alloy 625) than on Alloy C2000 in the potential range $0.2 \, \text{V}$ to $-0.5 \, \text{V}$, in which $\text{O}_2$ reduction occurs. Also, the $R_p$ values become significantly lower with an increase in temperature. These decreased resistances and increased capacitances are in good agreement with the increased kinetics of $\text{O}_2$ reduction and surface reactivity observed in potentiostatic polarization and CV experiments on these two alloys. The relative low repassivation ability observed on Alloy 625 and C22 compared to C2000, can be attributed to the lower PREN and PRE' values for these two alloys. The better film stability and resistance to $\text{O}_2$ reduction observed on Alloy C2000 may be due to either the high PREN and PRE' value or the presence of Cu, which appears
to suppress the catalytic activity of the higher oxidation states of Mo (W) produced in the transpassive oxidation.

To gain additional insight into the influence of oxide films, the kinetics of O₂ reduction was also studied on Ti alloys. Unlike Ni-Cr-Mo alloys, Ti alloys do not have a uniform structure and secondary phases are commonly formed. SECM measurements show that the Fe-containing intermetallic precipitates exhibited higher reactivity than the α-Ti grains when \( E \) is \( \leq -0.4 \) V. This suggests the oxide on the intermetallic particles can be preferentially reduced allowing these locations to act as preferential sites for O₂ and H₂O reduction, the latter leading to hydride formation. Currents for O₂ reduction were observed on Ti-2 at \( E < -0.5 \) V at room temperature (22 °C) and 50 °C, but at more positive potentials at higher temperatures, suggesting O₂ reduction on exposed intermetallic sites. The hydride formation at negative potentials was shown to suppress O₂ reduction. However, D-SIMS experiments could not confirm that the formation of hydrides coincided with the locations of Fe-containing intermetallics.

### 8.2 Future Work

(1) **Rotating Ring-disk Electrode (RRDE) Measurements to Clarify the O₂ Reduction Kinetics**

The primary use of a RRDE is to detect, on the ring electrode, soluble reaction products created at the disk electrode. In the case of O₂ reduction, it can be used to detect whether hydrogen peroxide is produced as an intermediate in the O₂ reduction process (reaction 1.7 in Chapter 1). Such studies would help confirm the mechanism of O₂ reduction on
oxide-covered Ni-Cr-Mo alloys. The detection of peroxide on a Au ring electrode during O2 reduction has been reported on nickel metal alloy discs, C22 and C276 [1]. Whether or not hydrogen peroxide is produced during O2 reduction on other Ni-Cr-Mo alloys remains to be investigated.

(2) Characterization of the Oxide Film on Other Ni-Cr-Mo Alloys

The surface characterization on Alloy C22 and C2000 by SR-XPS, AR-XPS and ToF-SIMS demonstrated the presence of a layered structure in the passive film on these two alloys, consisting of an inner Cr/Ni oxide barrier layer, and outer layers enhanced in Mo (W, or Cu). However the oxide film stability and kinetics of O2 reduction varied for the 5 alloys studied. Lloyd et al. [2, 3] claimed that thicker oxides with a high-Cr inner layer and a structured elemental distribution can only be grown on alloys with > 20 wt.% Cr, but these studies were limited to acidic solutions (pH 1). Therefore, it is necessary to characterize the composition and structure of the oxide film formed on a wider range of high and low Cr and/or Mo-containing alloys such as Alloy 625 and C276 over a wider pH range, and to determine how this influences the kinetics of O2 reduction.

(3) Determination of the Influence of Cu on Alloy C2000

The chemical state of the Cu layer deposited on the surface of Alloy C2000 is hard to determine by XPS, due to the possibility of Cu(II) reduction to Cu(I) under X-ray exposure, and because the closeness of the binding energies for Cu metal and cuprous oxide make their separation in XPS spectra impossible. However, as described by McIntyre et al. [4], the x-ray induced Auger spectra of Cu metal and cuprous oxide [Cu(L3 M4,5 M4,5)] are significantly different and allow a quantitative characterization of
oxide or metal. In addition, compared to Cu₂O, the Cu (L₃ M₄,5 M₄,5) Auger spectra of 
CuO and Cu(OH)₂ are both shifted to different kinetic energies. Consequently, a 
combination of XPS and Auger electron spectroscopy (AES) could be used to determine 
the oxidation states of Cu on the surface of Alloy C2000.

8.3 References

# Curriculum Vitae

<table>
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</tr>
<tr>
<td>Xiangrong Zhang, Melissa Karsay, Dmitrij Zagidulin, James J. Noël, David W. Shoesmith, poster presentation at Gordon Research Conference (Corrosion - Aqueous), New London, NH, USA, July</td>
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</tr>
</tbody>
</table>
24-30, 2010


Xiangrong Zhang, Dmitrij Zagidulin, James J. Noël, David W. Shoesmith, poster presentation at The 60th Annual Meeting of the International Society of Electrochemistry, Beijing, China, August 16-21, 2009


Xiangrong Zhang, Dmitrij Zagidulin, James J. Noël, David W. Shoesmith, poster presentation at The Electrochemical Society 2008 Fall Symposium, Montréal (Québec), November 8-9, 2008


Publications/Conference Papers:


Cr-Mo (W) Alloys. 29th Annual Canadian Nuclear Society Conference & 32nd CNS/CNA Student Conference, Toronto, Ontario, June 1-4, 2008


L. Zhou and X. Zhang, Determination of CaO, MgO, Al₂O₃ and MnO in iron ores by ICP-AES, Chinese Journal of Analysis Laboratory, 2002, Vol. 21, No.3, 52-54

X. Zhang and X. Liu, Determination of aluminium and manganese in chromium-silicon alloy by ICP-AES, Metallurgical Analysis, 2002, Vol. 22, No.4, 47-48

