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The Influence of Alloying Elements on The Crevice Corrosion Behaviour of 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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THE INFLUENCE OF ALLOYING ELEMENTS ON THE Crevice Corrosion Behaviour of Ni-Cr-Mo Alloys
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by

Nafiseh Ebrahimi

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

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Abstract

To enhance its corrosion resistance in aggressive media, Ni is alloyed with various amounts of Cr and Mo along with small amounts of other alloying elements such as W, Cu, and Fe. While the resulting alloys (known as Ni superalloys) show excellent passive behaviour, the function of individual alloying elements in resisting localized corrosion processes, in particular crevice corrosion is not fully understood. This study focuses on the electrochemistry and corrosion of a series of Ni-Cr-Mo (W) alloys with various Cr and Mo contents. Several electrochemical and surface characterization techniques were used to investigate the role of major alloying elements on maintaining passivity and protecting the alloy under crevice corrosion conditions.

To initiate crevice corrosion, either galvanostatic or galvanodynamic polarization was used. Using these techniques to apply an electrochemical current the cathodic reaction on the counter electrode is controlled simulating the cathodic reaction needed to drive the anodic crevice corrosion reaction. A comparison of the crevice corrosion behaviour, controlled galvanostatically, of C22 (Ni-22Cr-13Mo-3W), BC1 (Ni-16Cr-22Mo) and C625 (Ni-21Cr-9Mo) in 5 M NaCl solution at 150°C shows that crevice initiation is mainly controlled by the Cr content of the alloy while both Cr and Mo (Mo + W) synergistically determine the crevice activation rate. Once the crevice is activated, the corrosion damage propagation profile is dominantly influenced by the Mo (Mo + W) content of the alloy and also by the applied current. Higher currents and a higher Mo + W content lead to shallower and more laterally distributed corrosion damage. A series of weight change measurements on BC1, galvanostatically crevice corroded to a constant applied charge, show that internal proton reduction plays a key role in supporting active alloy dissolution, with more than 50% of the corrosion damage supported by this reaction. The results indicate that the alloy resists initiation of crevice corrosion, but once initiation has occurred it can continue to propagate spontaneously.

The properties of the oxide films anodically formed on the alloys were investigated before and after a period of dissolution at pH 7 and 9 using electrochemical impedance spectroscopy (EIS), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). The purpose of these experiments was to determine the properties of the passive film formed on
the alloy after transpassive dissolution. While Cr is the main element in maintaining passivity, the corrosion resistance of the reformed passive film after transpassive break down is enhanced mainly by Mo.

Investigation of the crevice corrosion damage morphology beneath corrosion products, showed intergranular corrosion initiated preferentially on high energy random grain boundaries. Transmission electron microscopy (TEM) and electron energy loss spectroscopy (EELS) analyses of grain boundaries showed needle shaped inclusions enriched in oxygen and depleted in nickel were present on these boundaries but not on the dominant \( \Sigma 3 \) boundaries.

**Keywords**

Ni-Cr-Mo alloys, Crevice corrosion, Molybdenum, Galvanodynamic polarization, Grain boundary, Cathodic reaction.
Co-Authorship Statement

I have been the primary investigator and writer of all chapters with some help from following people:

Chapter 3: P. Jakupi assisted with crevice experimental design, J.J. Noël and D.W. Shoesmith with editing.

Chapter 4: J.J. Noël helped with analyses of results and editing, M.A. Rodrigues with galvanodynamic polarization measurements, D.W. Shoesmith helped with editing.

Chapter 5: D. W. Shoesmith assisted with editing.

Chapter 6: P. Jakupi and I. Barker assisted with EBSD analyses, A. Korinek performed TEM analyses, D. Moser and D.W. Shoesmith assisted with editing.
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This thesis is dedicated to my biggest fan,

my best friend and

my life partner…

Arash Imani
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<td>a</td>
<td>Activity</td>
</tr>
<tr>
<td>α</td>
<td>Transfer coefficient</td>
</tr>
<tr>
<td>ADC</td>
<td>Analogue to digital converter</td>
</tr>
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<td>Annular dark-field imaging</td>
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<td>Breakdown potential (V)</td>
</tr>
<tr>
<td>E_B</td>
<td>Binding energy (eV)</td>
</tr>
<tr>
<td>EBSD</td>
<td>Electron backscatter diffraction technique</td>
</tr>
<tr>
<td>E_C</td>
<td>Crevice electrode potential (V)</td>
</tr>
<tr>
<td>(E_C)_{SS}</td>
<td>Steady state crevice electrode potential (V)</td>
</tr>
<tr>
<td>E_{CORR}</td>
<td>Corrosion potential (V)</td>
</tr>
<tr>
<td>E_{Crev}</td>
<td>Crevice breakdown potential (V)</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>E_e</td>
<td>Equilibrium potential (V)</td>
</tr>
<tr>
<td>EELS</td>
<td>Electron energy loss spectrometer</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical impedance spectroscopy</td>
</tr>
<tr>
<td>E_K</td>
<td>Kinetic energy (J)</td>
</tr>
<tr>
<td>E_p</td>
<td>Planar electrode potential (V)</td>
</tr>
<tr>
<td>E_{Pass}</td>
<td>Passivation potential (V)</td>
</tr>
<tr>
<td>E_R</td>
<td>Repassivation potential (V)</td>
</tr>
<tr>
<td>E_{R,Crev}</td>
<td>Crevice repassivation potential (V)</td>
</tr>
<tr>
<td>\eta</td>
<td>Over potential (V)</td>
</tr>
<tr>
<td>F</td>
<td>Faraday’s constant (96,487 C.mol(^{-1}))</td>
</tr>
<tr>
<td>FCC</td>
<td>Face center cubic</td>
</tr>
<tr>
<td>FIB</td>
<td>Focused ion beam</td>
</tr>
<tr>
<td>GBE</td>
<td>Grain boundary engineering (J)</td>
</tr>
<tr>
<td>\Delta G</td>
<td>Gibbs free energy change (J)</td>
</tr>
<tr>
<td>H^+</td>
<td>Proton</td>
</tr>
<tr>
<td>I</td>
<td>Absolute current (A)</td>
</tr>
<tr>
<td>i</td>
<td>Current density (A.cm(^{-2}))</td>
</tr>
<tr>
<td>I_a</td>
<td>Anodic current (A)</td>
</tr>
<tr>
<td>I_c</td>
<td>Cathodic current (A)</td>
</tr>
<tr>
<td>I_C</td>
<td>Current flowing between crevice and counter electrode (A)</td>
</tr>
<tr>
<td>I_{CORR}</td>
<td>Corrosion current (A)</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively-coupled plasma mass spectrometry</td>
</tr>
<tr>
<td>i_{Crit}</td>
<td>Critical passivating current density (A.cm(^{-2}))</td>
</tr>
<tr>
<td>i_{Final}</td>
<td>Final current density (A.cm(^{-2}))</td>
</tr>
<tr>
<td>I_0</td>
<td>Exchange current (A)</td>
</tr>
<tr>
<td>i_{Pass}</td>
<td>Passive current density (A.cm(^{-2}))</td>
</tr>
<tr>
<td>IPF</td>
<td>Inverse pole figure</td>
</tr>
<tr>
<td>IR</td>
<td>Ohmic potential drop (V)</td>
</tr>
<tr>
<td>K_{sp}</td>
<td>Solubility product (mol.L(^{-1}))</td>
</tr>
<tr>
<td>LPR</td>
<td>Linear polarization resistance</td>
</tr>
<tr>
<td>\lambda</td>
<td>Wavelength (m)</td>
</tr>
<tr>
<td>m</td>
<td>Mass (g)</td>
</tr>
<tr>
<td>MCB</td>
<td>Mass and charge balance</td>
</tr>
<tr>
<td>M</td>
<td>Molar mass (g.mol(^{-1}))</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>NHE</td>
<td>Normal hydrogen electrode</td>
</tr>
<tr>
<td>μ</td>
<td>Chemical potential (J.mol(^{-1}))</td>
</tr>
<tr>
<td>μ°</td>
<td>Standard chemical potential (J.mol(^{-1}))</td>
</tr>
<tr>
<td>n</td>
<td>Number of electrons exchanged in an electrochemical reaction</td>
</tr>
<tr>
<td>ω</td>
<td>Angular frequency (rad.s(^{-1}))</td>
</tr>
<tr>
<td>PD-GS-PD</td>
<td>Potentiostatic-galvanostatic-potentiodynamic</td>
</tr>
<tr>
<td>PDM</td>
<td>Point defect model</td>
</tr>
<tr>
<td>PD-PS-PD</td>
<td>Potentiodynamic-galvanostatic-potentiodynamic</td>
</tr>
<tr>
<td>PREN</td>
<td>Pitting resistance equivalent number</td>
</tr>
<tr>
<td>QA</td>
<td>Applied charge (C)</td>
</tr>
<tr>
<td>QV</td>
<td>Equivalent charge calculated from volume of material loss (C)</td>
</tr>
<tr>
<td>QW</td>
<td>Equivalent charge calculated from the weight change (C)</td>
</tr>
<tr>
<td>R</td>
<td>Universal gas constant (8.3121 J.K(^{-1}).mol(^{-1}))</td>
</tr>
<tr>
<td>R</td>
<td>Resistance (Ω)</td>
</tr>
<tr>
<td>R(_{CT})</td>
<td>Charge transfer resistance (Ω)</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>R(_{f})</td>
<td>Film resistance (Ω)</td>
</tr>
<tr>
<td>R(_{s})</td>
<td>Solution resistance (Ω)</td>
</tr>
<tr>
<td>ρ</td>
<td>Density (g.cm(^{-3}))</td>
</tr>
<tr>
<td>SCE</td>
<td>Standard calomel electrode</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary electrons</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SHE</td>
<td>Standard hydrogen electrode</td>
</tr>
<tr>
<td>SSW</td>
<td>Surface science western</td>
</tr>
<tr>
<td>STEM</td>
<td>Scanning transmission electron microscopy</td>
</tr>
<tr>
<td>t</td>
<td>Time (s)</td>
</tr>
<tr>
<td>((θ))</td>
<td>Phase angle</td>
</tr>
<tr>
<td>Δθ</td>
<td>Misorientation</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>Time of flight secondary ion mass spectrometry</td>
</tr>
<tr>
<td>T(_{Prot})</td>
<td>Protection temperature (°C)</td>
</tr>
<tr>
<td>ν</td>
<td>Stoichiometric coefficient</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>W</td>
<td>Weight change (g)</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>wt.%</td>
<td>Weight percent</td>
</tr>
<tr>
<td>X_{Max}</td>
<td>Location of most severe attack within the creviced region (m)</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction spectroscopy</td>
</tr>
<tr>
<td>Z</td>
<td>Impedance (Ω)</td>
</tr>
<tr>
<td>Z'</td>
<td>Real impedance (Ω)</td>
</tr>
<tr>
<td>Z''</td>
<td>Imaginary impedance (Ω)</td>
</tr>
<tr>
<td></td>
<td>Magnitude of impedance (Ω)</td>
</tr>
<tr>
<td>Z_{RA}</td>
<td>Zero resistance ammeter</td>
</tr>
</tbody>
</table>
Chapter 1

1 Introduction

1.1 Project Motivation

Since the beginning of the Industrial Revolution, corrosion has been an on-going concern for many industries and a considerable scientific and engineering effort has, and is being expended to find workable solutions to the many corrosion problems encountered. Extensive industrial effort has been invested in the design of nickel superalloys able to resist corrosion in aggressive media. This is generally achieved by alloying Ni with various amounts of Cr and Mo along with small amounts of other alloying elements such as W, Cu, and Fe. While the properties of the oxides which protect these alloys generally enforce good passive corrosion behaviour, the function of individual alloying elements in resisting localized corrosion processes, in particular pitting and crevice corrosion, is not fully understood, and optimization of alloy composition to resist corrosion not yet been achieved.

While localized corrosion processes rely on the inertness of passive oxide films to prevent their initiation, it is often extremely difficult to be fully assured that initiation will not be attempted. Consequently, the response of alloying elements once a passive film is breached is important in controlling propagation and inducing repassivation. As will be discussed in more detail below and throughout this thesis, Cr is the primary alloying element maintaining passivity [1,2] while Mo tends to limit the accumulation of corrosion damage once localized corrosion has initiated [3].

The mode of damage accumulation was found to be highly dependent on the grain boundary properties of the alloys with grain-boundaries with coincide lattice points (Σ) being more resistant to corrosion [4], but the reasons for this enhanced corrosion resistance was not resolved.
In this study, three commercial Ni-Cr-Mo (W) alloys with different compositions, Table 1-1, were investigated. The primary motivation for this project was to determine the key compositional and microstructural features controlling the accumulation and distribution of corrosion damage, thereby offering guidance for the optimization of alloy composition for corrosion resistance.

Table 1-1: Alloy chemical compositions (wt.%).

<table>
<thead>
<tr>
<th>Alloy/Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>C22</td>
<td>56</td>
<td>22</td>
<td>13</td>
<td>3</td>
<td>3</td>
<td>2.5</td>
<td>0.01</td>
<td>0.5</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>BC1</td>
<td>62</td>
<td>15</td>
<td>22</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>0.01</td>
<td>0.25</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>C625</td>
<td>62</td>
<td>21</td>
<td>9</td>
<td>-</td>
<td>5</td>
<td>1</td>
<td>0.10</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

1.2 Ni-Cr-Mo Alloys

Ni can be easily alloyed with a variety of other metals such as Cr, Mo, Fe, Cu and W to form many binary and ternary Ni based alloys. These alloys are designed to handle a wide range of corrosive and high temperature environments encountered in the chemical processing, petrochemical, oil and gas, energy conversion and many other industries [5]. Since these alloys are heavily alloyed and their fabrication requires specific thermomechanical processing, they are more expensive than stainless steels and only used when these steels fail to meet the required criteria. Figure 1.1 shows the ternary diagram for composition of some commercially available Ni-Cr-Mo alloys.
1.2.1 Role of Nickel

Ni has a Face Center Cubic (FCC) structure with a high solubility for alloying elements in solid solution without the formation of intermetallic particles. The Ni matrix possesses excellent ductility, malleability, and formability for a range of alloys [7]. From a corrosion perspective, Ni is more noble than Fe and less noble than Cu [7] with excellent resistance to caustic and mild reducing environments but not oxidizing media [8].

1.2.2 Role of Chromium

Cr is added to Ni and Fe alloys to provide corrosion resistance in oxidizing media, such as nitric acid and at higher temperatures [9]. Cr has a low metal-metal bond strength and a high heat of oxygen adsorption, leading to breakage of Cr-Cr bonds by the formation of Cr-O bonds and the formation of a Cr-O-Cr network [10]. The Cr₂O₃ oxide formed is stable and insoluble and protects the underlying metal from dissolution. However, a minimum of 11 wt.% Cr is required to provide significant enhancement of corrosion resistance.
properties [11]. However, while higher Cr content leads to lower corrosion rates and a wide passive range, a too high Cr content causes brittleness and a degradation in mechanical properties [12].

### 1.2.3 Role of Molybdenum

Addition of Mo to Cr alloys improves their high temperature and creep strength, and improves corrosion resistance in hot reducing media (such as HCl-containing environments) [7]. A synergistic effect of Mo and Cr in resisting corrosion is well-known for both Ni-based and stainless steel alloys [12,13]. However, Mo is moderately expensive and a higher Mo content increases the hardness of an alloy making machining more difficult.

### 1.2.4 Microstructure of Ni-Cr-Mo Alloys

Solution heat treating is the most common processing operation applied to Ni-Cr-Mo alloys. In this heat treatment, the alloy is heated up to a temperature (1095-1205°C) to stabilize one or more elements in solid solution. The alloy is then cooled rapidly to hold these constituents in solution [14]. After this treatment, the microstructure generally consists of a single phase matrix with essentially clean grain boundaries (Figure 1.2). Mill annealing and stress relief annealing are other finishing treatments often applied to these alloys.

![Microstructure of Ni-Cr-Mo Alloys](image)

**Figure 1.2**: Microstructure of the BC1 alloy showing large grains and annealing twin grain boundaries [15].
1.3 Introduction to Aqueous Corrosion

1.3.1 Thermodynamics of Corrosion

For a general reversible reaction, e.g.,

\[ aA + bB \rightleftharpoons cC + dD \]  \hspace{1cm} (1-1)

thermodynamics dictates it will only occur if the Gibbs free energy (\( \Delta G \)) of the overall reaction is < 0.

\[ \Delta G = \sum_i v_i \mu_i (\text{reactant}) - \sum_i v_i \mu_i (\text{product}) \]  \hspace{1cm} (1-2)

where \( \mu_i \) is the chemical potential of the reactants and products, and \( v_i \) is the stoichiometric coefficient. The \( \mu \) of an element \( (i) \) is a function of its activity \( (\alpha) \):

\[ \mu_i = \mu_i^\circ + RT \ln \alpha_i \]  \hspace{1cm} (1-3)

where \( R \) is the gas constant (8.314 J/K·mol), \( T \) is temperature, and \( \mu_i^\circ \) is the standard chemical potential of element \( i \).

Substituting equation 1-3 in 1-2 leads to

\[ \Delta G = c\mu_c^\circ + d\mu_d^\circ - a\mu_A^\circ - b\mu_B^\circ + RT \ln \left( \frac{\alpha_c^\circ \alpha_D^d}{\alpha_B^b \alpha_A^a} \right) \]  \hspace{1cm} (1-4)

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{\alpha_c^\circ \alpha_D^d}{\alpha_B^b \alpha_A^a} \right) \]  \hspace{1cm} (1-5)
For an electrochemical reaction $\Delta G$ is defined by equation (1-6)

$$\Delta G = -nFE$$

(1-6)

where $n$ is the number of electrons involved in the reaction, $F$ is Faraday’s constant (96490 Coul.mol$^{-1}$) and $E^e$ is the equilibrium electrode potential.

Using equation 1-5, equation 1-6 can be rewritten as,

$$E^e = E^o - \frac{RT}{nF} \ln \left( \frac{\alpha_C^{\alpha_d}}{\alpha_D^{\beta_d} \alpha_A^{\alpha_a}} \right)$$

(1-7)

which is the Nernst equation that defines the equilibrium potential of a reversible reaction under non-standard conditions.

Corrosion is an electrochemical reaction that involves the coupling of one or more oxidation and reduction half reactions involving a solid phase (usually a metal) and an oxidizing environment [16],

$$M \rightarrow M^{n+} + n \text{ e}^-$$

(1-8)

$$\text{Ox} + n \text{ e}^- \rightarrow \text{Red}$$

(1-9)

where M represents the metal. The Nernst equations for these two half reactions are

$$E^{e}_{M^{n+}/M} = E^{o}_{M^{n+}/M} - \frac{RT}{nF} \ln \left( \frac{1}{\alpha_{M^{n+}}} \right)$$

(1-10)
\[ E_{\text{Ox/Red}}^{e} = E_{\text{Ox/Red}}^{\circ} - \frac{RT}{nF} \ln \left( \frac{\alpha_{\text{Red}}}{\alpha_{\text{Ox}}} \right) \] (1-11)

, which is the sum of the two half-reactions. The corrosion reaction can only occur if \( E_{\text{Ox/Red}} > E_{\text{M/M}^n} \).

By calculating the Nernst equations for all the possible electrochemical half reactions and the chemical complexation and solubility equilibria for a metal in a specific aqueous environment at 25°C a plot of potential vs pH, known as a Pourbaix diagram, can be constructed [17]. Such a diagram summarizes the chemical compounds and solution soluble species which are thermodynamically stable at each potential and pH.

Figure 1.3 shows the Pourbaix diagram for the Ni/H₂O system at different Ni²⁺ activities and 25°C.

For the Ni metal dissolution reaction,

\[ \text{Ni} \Leftrightarrow \text{Ni}^{2+} + 2e^- \] (1-12)

the Nernst equation is given by

\[ E_{\text{Ni/Ni}^{2+}}^{e} = E_{\text{Ni/Ni}^{2+}}^{\circ} + \frac{RT}{2F} \ln \alpha_{\text{Ni}^{2+}} \] (1-13)

Using known values for the constants yields

\[ E_{\text{Ni/Ni}^{2+}}^{e} = -0.25 + 0.03 \log \alpha_{\text{Ni}^{2+}} \] (1-14)

For a constant Ni²⁺ activity, the equation 1-12 yields by a horizontal line in a Pourbaix diagram (9 in Figure 1.3). Dissolution of Ni is only thermodynamically possible at
potentials above this line making corrosion possible, as indicated in the figure. Below
this line metallic Ni is stable and immune to corrosion (also indicated in the figure).

Figure 1.3: Pourbaix diagram for the Ni-H₂O system at 25°C for various values of log αNi²⁺ [17].

Ni can also react with water to yield an oxide,

\[
\text{Ni} + \text{H}_2\text{O} \rightleftharpoons \text{NiO} + 2\text{H}^+ + 2\text{e}^- \tag{1-15}
\]

for which the Nernst equation, can be written as

\[
E_{\text{Ni/Ni}^{2+}}^\circ = E_{\text{Ni/NiO}}^\circ + \frac{RT}{2F} \ln \left( \frac{\alpha_{\text{NiO}} \alpha_{\text{H}^+}^2}{\alpha_{\text{Ni}}} \right) \tag{1-16}
\]
with the activity of the oxide being taken as 1. Converting $\alpha_{H^+}$ to pH yields

$$E_{Ni/Ni^{2+}}^e = -0.11 - 0.059 \text{ pH}$$  \hspace{1cm} (1-17)

The $E^e$ for the reaction (1-15) is a linear function of pH and represented by a diagonal line in the Pourbaix diagram, Figure 1.3. Below this line is the immunity region (Ni metallic is stable) and above it the NiO can form. Within this last region NiO is stable and the metal is potentially passive (as indicated in Figure 1.3). Whether or not passivation is actually achieved will depend on the properties of the oxide.

The boundary between the passive and corrosion regions will be determined by the equilibrium between the oxide and the Ni$^{2+}$ species; i.e. the solubility equilibrium,

$$\text{Ni}^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{NiO} + 2\text{H}^+$$  \hspace{1cm} (1-18)

This reaction is independent of potential and determined by the solubility product ($K_{sp}$),

$$K_{sp} = \frac{\alpha_{H^+}^2}{\alpha_{Ni^{2+}}}$$  \hspace{1cm} (1-19)

for a constant activity of Ni$^{2+}$, equation (1-19) will be a vertical line at the pH at which equilibrium is established.

In all Pourbaix diagrams, two lines encompassing the stability region for H$_2$O can be drawn (dashed lines (a) and (b) on Figure 1.3) for the oxidation and reduction reactions involving water,

$$2\text{H}_2\text{O} + 2\text{e}^- \rightleftharpoons \text{H}_2 + 2\text{OH}^-$$  \hspace{1cm} (1-20)
Both reactions are potential and pH dependent with a slope of -0.059. At potentials between these two lines, H₂O is thermodynamically stable. The relative positions of the equilibrium lines for metal (e.g. lines 9, 2 and 10) with respect to lines (a) and (b) indicate whether corrosion on a metal can couple to the reduction of H₂O.

The simplified Pourbaix diagrams for the main elements in the alloys in this study (Ni, Cr, Mo and W), are presented in Figure 1.4 and show that passivation by one oxide or more is possible over a wide range of potentials and pH values. However, one should remember these diagrams are generated for the metals in pure H₂O and at 25°C while many service conditions for these Ni-Cr-Mo alloys involve high temperatures in environments containing aggressive ions such as Cl⁻ and S²⁻.

Figure 1.4: Simplified Pourbaix diagrams for Ni, Cr, Mo and W at 25°C and for log \( a_{\text{M}^{\text{m+}}} \) = - 6 showing the passivation, immunity and corrosion regions. The dashed lines show the stability limits for H₂O [17].
The $E^\circ$ values will vary with temperature and the presence of ions depending on their reactions with the metals and dissolved cations. While these diagrams provide insight on thermodynamics of the system under study, they contain none of the kinetic information required to understand alloy behaviour in a corrosive environment.

### 1.3.2 Kinetics of Aqueous Corrosion

There are several ways to measure the rate of a corrosion reaction including weight loss/gain measurements, chemical analyses of the electrolyte, measurement of the rate of production of a gas (such as H$_2$ reaction with H$_2$O), and electrochemical measurements. This section will describe the electrochemical kinetics of corrosion process.

Faraday’s law reflects the mass of metal (alloy) reacted ($m$) to the current ($I$) produced in the corrosion reaction. For a single metal this law is represented by the relationship

$$I_{CORR} = \frac{m \cdot n \cdot F}{t \cdot M} \tag{1-22}$$

where $n$ is the number of equivalent electrons exchanged in the overall corrosion reaction, $M$ is the molar mass (g/mol) and $t$ is the time (s) for which the reaction occurs and $F$ is the Faraday’s constant (96,485 C/mol).

For an alloy containing a number of different alloying elements ($i$), and corroding congruently, the equivalent term ($n/M$) can be determined using the relationship

$$\left(\frac{n}{M}\right)_{eq} = \sum_{i=1} \left(\frac{f_i n_i}{M_i}\right) \tag{1-23}$$

Where $f_i$ is the mass fraction, $n_i$ is the number of electrons exchanged and $M_i$ is the molar mass of the $i^{th}$ alloying element.
Although a weight loss measurement is a fast and easy way to estimate the corrosion rate, it yields no insight into the underlying mechanism of corrosion and the factors controlling the corrosion rate, features that can be studied using electrochemical techniques. For a metal dissolution reaction \( \text{M} \rightleftharpoons \text{M}^{n+} + n \text{e}^- \) at its equilibrium potential \( E^* \), the anodic and cathodic reactions occur at the same rate, which is known as exchange current density \( (i_0) \),

\[
i_a = i_c = i_0
\]

with \( i_a \) and \( i_c \) being the current densities for the forward (anodic) and reverse (cathodic) reactions. When the reaction is polarized away from the equilibrium condition to an over potential, \( \eta \) \( (\eta = E \pm E_{eq}) \), the \( I-E \) relationship is described by the Butler-Volmer (BV) equation,

\[
i = i_a - i_c = i_0 \left[ \exp \left( \frac{\alpha n F \eta}{RT} \right) - \exp \left( \frac{(1 - \alpha)n F \eta}{RT} \right) \right]
\]

in which \( \alpha \) is the charge transfer coefficient, \( R \) is the gas constant, \( T \) is the temperature and \( n \) is the number of exchanged electrons. Figure 1.5 shows a graphical representation of equation (1-25). At small \( \eta \), the net current \( (i) \) is the sum of both \( i_a \) and \( -i_c \). For a sufficiently anodic or cathodic \( \eta \), the net current becomes equal to either \( i_a \) or \( i_c \) and equation 1-25 can be simplified, for example, at high anodic over-potential,

\[
i = i_a = i_0 \left[ \exp \left( \frac{\alpha n F \eta}{RT} \right) \right]
\]
Figure 1.5: Potential-current (Butler-Volmer) relationship for the reaction $M \rightleftharpoons M^{n+} + n \, e^-$. The solid line shows the measurable $I$ and the dashed ones the partial currents for the anodic and cathodic reactions [18].

Taking the log of equation (1-26) yields

$$\log(i_a) = \log(i_0) + \frac{\alpha n F}{RT} \eta$$

(1-27)

A plot of $\log(i)$ vs. $\eta$ yields a line with an intercept of $\log(i_0)$ and a slope given by

$$\beta = \frac{\alpha n F}{RT}$$

(1-28)

This slope is called the Tafel slope and yields the coefficient $\beta$.

In a corrosion reaction, the anodic half of a metal oxidation reaction of $M \rightleftharpoons M^{n+} + n \, e^-$ is coupled to the cathodic half of a redox reaction, $\text{Ox} + n \, e^- \rightleftharpoons \text{Red}$. Providing the $E^\circ_e$ of the two reactions are adequately separated from each other, both reactions will be irreversible and only the anodic current for $M \rightarrow M^{n+} + n \, e^-$, and the cathodic current for
Ox + n e\textsuperscript{-} → Red need to be considered at the corrosion potential ($E_{\text{CORR}}$), and the corrosion current density ($i_{\text{CORR}}$) is then given by

$$i_{\text{CORR}} = i_a = |i_c|$$ (1-29)

The $i_{\text{CORR}}$ will have a BV-like relationship with applied potential ($E$) given by the Wagner-Traud equation [19].

$$i = i_{\text{CORR}} \left[ \exp \left( \frac{2.3(E - E_{\text{CORR}})}{\beta_a} \right) - \exp \left( \frac{2.3(E - E_{\text{CORR}})}{\beta_c} \right) \right]$$ (1-30)

where $\beta_a$ and $\beta_c$ are the anodic and cathodic Tafel coefficients, as illustrated in Figure 1.6.

Equation 1-30 can be plotted in the log form (known as an Evans diagrams) to illustrate the influence of the cathodic and anodic branches on the overall corrosion reaction $E_{\text{CORR}}$ and $i_{\text{CORR}}$. 
Figure 1.6: Current-potential relationship for a metal dissolution reaction, \( M \rightleftharpoons M^{n+} + ne^- \), coupled with the cathodic half of a redox reaction, \( \text{Ox} + ne^- \rightleftharpoons \text{Red} \), the solid lines show the BV relationship for the two reactions with the redox reaction assumed to have a small exchange current density and the metal reaction a large exchange current density. The red line shows the measurable sum of the anodic and cathodic currents with the value of \( i_{\text{CORR}} \) illustrated at \( E_{\text{CORR}} \) [18].

Figure 1.7: Evans diagram constructed from the Wagner-Traud equation [18].
1.4 Passive Film Formation

Passivity is a state of low corrosion rate achieved at a high anodic overpotential when a coherent, chemically inert solid film, usually an oxide or hydroxide is present on the metal (alloy) surface [20]. The influence of a passive film is best described by a polarization curve, at Figure 1.8, which shows the influence of an applied potential on the measured electrochemical current. At low overpotentials ($\eta$), the alloy anodically dissolves exhibiting a Tafel region known as the active region (“A” in Figure 1.8).

Eventually, as the potential is increased the current deviates from the Tafel relationship and begins to decrease as the formation of a passive film begins to suppress metal dissolution. The maximum current reached (point B) is known as the critical current density ($i_{Crit}$). This switch from increasing to decreasing current is known as an active to
passive transition. The passive region is established for $E$ greater than the passivation potential ($E_{\text{pass}}$). Subsequently, a low passive current density ($i_{\text{pass}}$) is maintained despite further increases in potential. At sufficiently high anodic potentials the current increases again. This increase could be the result of either to $\text{H}_2\text{O}$ oxidation to $\text{O}_2$ or to the transpassive dissolution of the passive oxide film due to oxidation of cations to higher, more soluble oxidation states. This is commonly observed for alloys containing Cr, Cr(III) in the $\text{Cr}_2\text{O}_3$ passive film being oxidized to Cr(IV) and dissolving as $\text{CrO}_4^{2-}$ [18]. For many alloys in not-too-aggressive environments, an active to passive transition may not be observed, since the alloy will be oxide-covered even at potentials able to support cathodic currents.

### 1.4.1 Models for Passive Film Growth

Several different models have been proposed to describe the formation of passive films [21–26]. Cabrera and Mott [21,25] modeled the formation of a passive oxide in a low temperature gas. In this model, known as the high field model, electrons are released by metal oxidation at metal-oxide interface and absorbed by oxygen atoms on the oxide surface. This leads to the establishment of an electrostatic potential field across the oxide layer due to charge separation. This high electric field forces the migration of metal cations through the growing film via cation vacancies to form oxide by incorporation of oxide anions formed by $\text{O}_2$ reduction. This model assumes that only cation transport leads to film growth, and neglects any contribution from anion transport.

Macdonald’s point defect model (PDM) [27] is a modified version of the high field model that takes into account the transport of both anions and cations. This model takes into account a number of important experimental observations, including the linear dependence of the film thickness on applied potential and the kinetics of film growth. The film is assumed to be composed of an inner barrier layer, which is responsible for the essential corrosion resistance, and an outer layer composed of hydrated metal species which makes only a minor contribution to corrosion protection. A number of important assumptions were made in the development of this model, including: (1) the oxide is a
point defect phase containing both cation and oxygen vacancies; (2) the concentration of point defects is much greater than in isolated, bulk oxides, indicating the presence of continuous defect generation/annihilation processes; (3) defects are generated and annihilated at the metal/film and film/solution interfaces; (4) the electric field strength is independent of the applied potential and uniform within the film; (5) the potential is distributed across the interphase regions with drops at the metal/film interface, the film/solution interface and across the film; and (6) the potential drop across the film/solution interface is linearly dependent upon the applied potential and the solution pH. This model successfully predicts the behaviour of oxide film growth on Ni-Cr-Mo alloys (particularly C22 alloy) by assuming the barrier layer is composed of a defective \( \text{Cr}_{2+x}\text{O}_{3-y} \) that can be either cation rich \((x > y)\) or anion rich \((y > x)\) due to the predominance of cation interstitials or oxygen vacancies, respectively [28–30].

Recently, Momeni and Wren [31] have developed a corrosion model based on mass and charge balance (MCB) that can predict metal oxide growth and dissolution rates as a function of time for a range of solution conditions. This model considers the electrochemical reactions at the metal/oxide and oxide/solution interfaces, and the metal cation flux from the metal to the solution phase through a growing oxide layer, and formulates the key processes involved using classical chemical reaction rate or flux equations. In the MCB model, the oxidation (or metal cation) flux must be equal to the sum of the oxide growth flux and the dissolution flux at all times. Although the detailed form of the charged species (cations, anions and vacancies) involved was not considered, the oxide film growth kinetics are very similar to those of the PDM. This model was able to predict the time-dependent potentiostatic oxide film growth behaviour on pure iron, Co–Cr and Fe–Ni–Cr alloys.
1.4.2 Passive Film on Ni-Cr-Mo Alloys

1.4.2.1 Effect of Alloying Element

Ni-Cr-Mo alloys have been shown to exhibit excellent passive behaviour over a wide range of potentials, pH values and temperatures [32–35], and many studies have focused on the role of alloying elements on their passive behaviour. Cr is the main alloying element maintaining passivity [36]. Early studies by Bouyssoux et al. [37] on Cr electrodes using X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) showed a bilayer structure with an inner Cr$_2$O$_3$ and outer Cr(OH)$_3$ composition. A polarization study of Alloy 625 and its main alloying elements, Ni, Cr, and Mo in (NH$_4$)$_2$SO$_4$ solutions with various pH values [38] showed that the polarization curves recorded on alloy C625 were similar to those obtained on Cr, indicating that the passive behavior of the alloy was strongly influenced by its Cr content. Electrochemical studies have shown that Cr additions to Ni suppress active dissolution, reduce the passive current density [11], and broaden the passive region [39]. This beneficial effect of Cr on passive behaviour is due to the higher concentration of Cr$^{3+}$ in the barrier layer on alloys with a high Cr content [40]. To obtain a protective passive layer, a minimum alloy Cr content is required. Hayes et al. [11] claim 11 wt.% is the critical threshold content to maintain passivity while the model developed by Newman et al. [41] predicts a minimum of 16 wt.% Cr leads to an ‘infinite’ cluster of oxidized Cr atoms. Based on potentiostatic polarization experiments on Ni-Cr-Mo alloys with various Cr and Mo contents, Lloyd et al. [1] observed lower passive currents, and a much slower achievement of steady-state on alloys with a Cr content > 20 wt.%. Mo has been shown to have a beneficial effect on the corrosion resistance of Ni alloys and stainless steels enhancing their resistance to both oxidizing and reducing acids [7], although the role of Mo in maintaining passivity is still unclear. Mo can exist in the passive film in two chemical states, Mo$^{4+}$ located in the inner barrier layer and as hydrated Mo$^{6+}$ in the outer layer [42]. It has been proposed that Mo(IV) replaces Cr(III)
in the passive film enabling the dehydration of the Cr oxide barrier layer and leading to an enhancement of passivity [43]. Furthermore, the segregation of $\text{MoO}_4^{2-}$ and $\text{CrO}_4^{2-}$ to the outer passive layer generates a cation selective region which increases the stability of the film in environments containing $\text{Cl}^-$ [44].

Lloyd et al. [1] investigated the passive film properties of a number of Ni-Cr-Mo (W) alloys with various Cr, Mo, (W) contents at passive and transpassive potentials in 1 M NaCl + 0.1 M $\text{H}_2\text{SO}_4$ solution. The anodically-formed passive film was analyzed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and XPS. The passive current density was shown to be controlled by the Cr content of the alloy with little to no influence from other elements such as Mo and W. The lower passive current recorded on the high Cr alloys was attributed to the growth of the Cr(III) oxide barrier layer at the alloy/oxide interface. At transpassive potentials, where dissolution of Cr as Cr(VI) becomes thermodynamically possible, it was claimed that Mo and W segregation to the outer regions of the film retarded the defect transport process that leads to the onset of transpassivity [45]. A more detailed study [46] of the oxide formed on the C22 alloy in 5 M NaCl solution in the potential range – 400 mV to 600 mV shows that destabilization of the Cr(III) layer formed in the passive region begins at potentials $>200$ mV with the oxidation of Cr(III) to Cr(VI) leading to a defective film and an overall thickening of the film due to enrichment of Mo(VI)/W(VI) species in the outer regions.

Tungsten (W) also appears to act like Mo and in enhancing passivity but has not been studied in any detail. This element is added to some of Ni-Cr-Mo alloys to enhance the solid solution strength [7]. A comparison of the C22 (Ni-22Cr-13Mo-3W) and C2000 (Ni-23Cr-16Mo-1.6Cu) in acidic solution indicate that the 3 wt.% W in C22 leads to a lower passive current density at high potentials [45].

Other alloying elements such as Fe, Co, Cu, Ti, are also added to Ni-Cr-Mo alloys in small quantities to improve alloy hardness, strength, resistance to damage from heat-treating operations, or corrosion resistance in a particular environment. Agarwal
[39] has summarized the effect of alloying elements on the aqueous corrosion of Ni-Cr-Mo alloys (Table 1-2).

Table 1-2: Alloying elements and their major effects on the aqueous corrosion of Ni-Cr-Mo alloys [39].

<table>
<thead>
<tr>
<th>Alloying Elements</th>
<th>Main Features</th>
<th>Other Features</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>Provides matrix for metallurgical compatibility to various alloying elements. Improves thermal stability and fabricability</td>
<td>Enhances corrosion resistance in mild reducing media. Alkali media, improves chloride SCC</td>
</tr>
<tr>
<td>Cr</td>
<td>Provides resistance to oxidizing corrosive media</td>
<td>Enhances localized corrosion resistance</td>
</tr>
<tr>
<td>Mo</td>
<td>Provides resistance to reducing (nonoxidizing) corrosive media.</td>
<td>Enhances localized corrosion resistance and chloride SCC. Provides solid solution strengthening</td>
</tr>
<tr>
<td>W</td>
<td>Behaves similar to Mo, but less effective. Detrimental to thermal stability in high Ni–Cr–Mo alloys</td>
<td>Provides solid solution strengthening</td>
</tr>
<tr>
<td>N</td>
<td>Austenitic stabilizer—economical substitute for nickel</td>
<td>Enhances localized corrosion resistance, thermal stability and mechanical properties</td>
</tr>
<tr>
<td>Cu</td>
<td>Improves resistance to seawater and sulfuric acid, detrimental to thermal stability in higher Ni–Cr–Mo alloys</td>
<td>Enhances resistance to H₂SO₄ and HF containing acid environments.</td>
</tr>
<tr>
<td>Ti, Cb, Ta</td>
<td>Carbon stabilizer</td>
<td>Improves HAZ and intergranular corrosion resistance</td>
</tr>
<tr>
<td>Si</td>
<td>High silicon (&gt; 4%) improves resistance to oxidizing mineral acids, sulfuric acid and nitric acid</td>
<td>Detrimental in certain corrosive environments</td>
</tr>
<tr>
<td>Fe</td>
<td>Provides matrix for metallurgical compatibility to various alloying elements</td>
<td>Reduces cost by replacing nickel and enhances scrap utilization</td>
</tr>
</tbody>
</table>

1.4.2.2 Effect of Temperature

Zhang et al. [47] studied the influence of temperature on the anodically-formed passive film on the C2000 (Ni-23Cr-16Mo-1.6Cu) from 25°C to 90°C by XPS and ToF-SIMS. The passive current density measured in potentiostatic polarization experiments at 0 V showed no dependence on temperature, with the SIMS analyses illustrating the reason behind this independence (Figure 1.9).
The passive films exhibit the expected layered structure with a Cr$_2$O$_3$/NiO inner layer with an intermediate Cr/Ni hydroxide layer, and an outermost layer of Mo oxide/hydroxide. The state of the Cu in the outer layer remained undetermined. By increasing the temperature from 25°C to 90°C (Figure 1.9 (a) to (c)) the overall thickness of each layer increased from d to 6 d, respectively. The increase in thickness should enhance passivity but this increase is accompanied by a rise in Ni content and a drop in
Cr and Mo content of the film. These two effects are counter-balancing and the overall passive current remains constant. The loss of Cr\textsubscript{2}O\textsubscript{3} in the barrier layer at 90°C is noteworthy, since a combination of a loss of Cr\textsubscript{2}O\textsubscript{3} in inner layer and a loose of Mo enrichment in the outer layer at high temperatures could eventually lead to passive film breakdown. A similar study on the C22 (Ni-22Cr-13Mo-3W) and C276 (Ni-15.5Cr-16Mo-3.7W) alloys [48] showed that, while the passive film composition on both alloys was similar to that observed on C2000, the layered structure was not as distinct on alloy C267 and its relative Cr content was lower than on C22. This lower Cr content appeared to influence the temperature dependence of the passive current which showed little change on C22 but a significant change on C276.

1.4.2.3 Effect of pH

Recently, Zhang et al. [49] investigated the role of pH on the passive film structure on C2000. XPS and ToF-SIMS analyses showed that decreasing the pH from neutral (7) to mildly acidic (4) and acidic (1) caused the film thickness to decrease, the outer layer in particular becoming thinner. This thinning was compensated by an increase in the overall Cr and Mo contents of the film. Figure 1.10 shows that the segregation of Cr and Mo between the inner and outer layer was still marked and the inner Cr\textsubscript{2}O\textsubscript{3} barrier layer still persisted at pH = 1. These findings are in agreement with those of Lloyd et al. [48] who reported a passive film thickness of ~ 2-3 nm on C22 at pH = 1 solution. A combination of electrochemical impedance spectroscopy (EIS) and atomic force microscopy (AFM) [34,50] on the passive oxide formed on C22 in solutions with a pH varying from 5 to -1 showed the thickness of the film decreased with a decrease in pH and reached 0 in a solution containing hydrochloric acid with pH = 0.5 at 60°C. This study suggests passive film breakdown occurs at a critical pH which changed with temperature and concentration of chloride in the solution. For example at 90°C, pH\textsubscript{Critical} = 0.5 for solution containing only HCl and no NaCl, for acidic solution containing 1 M NaCl it is 0.75 and for acidic 4 M NaCl solution, 2.5.
A more recent study on mill-annealed and thermally aged C22 yielded a critical pH value of 0.3 at 90°C for an acidic 1 M NaCl solution [33].

Mishra et al. [51,52] studied the passive film on a series of commercial Ni-Cr-Mo (W) alloys in a buffered chloride solution with an alkaline pH. They observed a secondary breakdown/passivation region at potentials beyond the breakdown potential at pH > 8.6. XPS analyses showed this breakdown can be attributed to the depletion of Cr/Mo, especially protective Mo(VI), in the film and partial repassivation due to the formation of Ni(OH)$_2$. 

Figure 1.10: ToF-SIMS cross-sectional images, recorded on C2000 after polarization at 0 V (22°C):
(a) pH = 4 and (b) pH = 1.
1.5 Passive Film Breakdown

Although passive films provide corrosion protection to a wide variety of metals and alloys, their disadvantage is their susceptibility to localized breakdown. While the remainder of the passive film may remain intact and continue to protect against general corrosion, localized corrosion at a breakdown site can lead to failure. Passivity breakdown becomes possible if the potential is forced into the active region, by the depletion of an oxidizing species, such as dissolved O\textsubscript{2}, which when present maintains passivity. A second possibility is that breakdown of a passive film occurs at high potentials in the presence of aggressive ions, usually anions [53].

1.5.1 Crevice Corrosion

Crevice corrosion is a form of localized corrosion that can occur on a wetted metallic surface confined within an occluded region. The tight geometry in a crevice limits the mass transport between the crevice area and the bulk electrolyte and can cause large differences in concentration and electrochemical potential between the creviced region and the exposed alloy (metal) surface. Within the creviced region the solution can become extremely aggressive leading to corrosion only at this location. Three different theories have been suggested to describe the condition required within an occluded region if crevice corrosion is to initiate.

1.5.1.1 Critical Crevice Solution (CCS) Model

The very first attempts to model the initiation of crevice corrosion were in 1973, when Crolet and Defranou [54] modeled the time required to develop a critical solution composition (low pH and high halide concentration). This model considered the effects of crevice geometry, alloy composition and solution chemistry. Later in 1978, Oldfield and Sutton [55,56] improved this model to predict the susceptibility of an alloy to crevice corrosion. The first step is the consumption of dissolved oxygen in the solution within the crevice leading to the establishment of an oxygen concentration cell between the
inside and outside of the crevice, with the metal inside the crevice being anodically polarized. In the second step, passive film dissolution leads to the accumulation of dissolved metal cation inside the crevice and their hydrolysis leads to proton ($\text{H}^+$) production and the acidification of the crevice solution. In order to maintain charge neutrality, aggressive anions (such as Cl$^-$) then migrate into the crevice increasing its salinity. As the pH decreases, the concentration of aggressive anions increases and the crevice solution eventually achieves a critical composition in which the passive oxide layer is not stable. When this occurs, active crevice corrosion leads to an increase in the anodic current density within the crevice.

This model predicts the most severe corrosion damage should occur in the deepest regions of the crevice where the initial solution composition should be most readily achieved. However, this is not generally the case with many crevice-corroding systems. Furthermore, for highly corrosion resistant alloys such as stainless steels and Ni-Cr-Mo alloys the hydrolysis of metal cations cannot acidify the solution enough for breakdown of the passive film [13,57].

### 1.5.1.2 IR Drop Model

Pickering developed another model [58] for initiation of crevice corrosion based on the ohmic potential drop (IR) between the regions outside and inside the crevice. The high current ($I$) inside the crevice region as a consequence of metal dissolution and the high solution resistance ($R$) due to the geometry of the crevice leads to a large potential (IR) drop that locates the electrode potential at a deep enough location in the crevice in the active region leading to the initiation of corrosion (Figure 1.11).
Figure 1.11 Schematic illustration of crevice corrosion on an alloy exhibiting active-passive behaviour, due to an IR drop within an occluded region [59]. The IR drop and the potentials at various locations are indicated on the propagating crevice.

The IR is affected by many factors such as crevice tightness, the length to depth ratio, solution chemistry and the presence of other physical objects, such as hydrogen bubbles, solid corrosion products, and salt films that may further block the crevice [57]. As indicated on the polarization curve a critical IR drop (IR*) is required to put a location within the crevice in the active region satisfying the conditions for crevice initiation. The distance into the crevice where the interfacial potential reaches $E_{\text{pass}}$ is denoted as $x_{\text{Crit}}$. While this model can justify the occurrence of crevice damage at a specific distance from the crevice mouth, it has some limitation. In this model the crevice solution chemistry is considered similar to that of the bulk solution with a pH close to the equilibrium pH for hydrolysis of cations accumulated in the crevice solution and no mass transport of species into, and out of, the crevice is considered. Moreover, this model relies on the active-passive transition for the initiation of crevice corrosion and cannot account for the crevice corrosion of a system which does exhibit such a transition.
A combination of the CCS and IR drop models has been used by Kelly and Stewart to investigate the initiation and propagation of active corrosion on the 300 series stainless steels [60,61], and a similar approach was used to investigate the crevice corrosion of alloy C625 [13,62].

1.5.1.3 Stabilization of Metastable Pits

Crevice corrosion is generally observed to occur in the potential region within which metastable pitting is observed. This is lower than the potential at which stable pitting occurs. A model was proposed by Stockert and Boehni [63] that suggests crevice corrosion initiates as a result of metastable pitting within the occluded crevice region. On an open surface the inability of a metastable pit to maintain the critical solution chemistry required for pit growth leads to its repassivation. However, the crevice geometry prevents dilution of the aggressive solution generated within a metastable pit allowing the critical chemical solution (CCS) to be achieved and maintained. With time, the increasing density of these events inside the crevice and their coalescence lead to stable crevice propagation. Results on the crevice corrosion of alloy C625 and alloy C22 [64,65] support this model, a combination of metastable pitting at a critical depth into the crevice being shown to lead to initiation.

1.5.1.4 Assessment of Crevice Susceptibility

Figure 1.12 shows a schematic polarization curve for an alloy which exhibits active-passive behaviour. If the alloy is susceptible to localized corrosion then a sudden increase in current density will be observed at the breakdown potential ($E_B$) within the passive region as indicated in the Figure 1.12 by the dashed line for $E > E_B$. If the electrode is creviced $E_B$ is described as $E_{Crev}$. Above this potential, crevice corrosion becomes possible. When the potential scan is reversed the current is higher on the reverse scan but eventually decreases to a value less than the passive current indicating repassivation. The potential at which this crossover occurs is termed the repassivation potential ($(E_R)$, $(E_{R,Crev}$ for a crevice). $E_{R,Crev}$ is a conservative parameter for assessing a
metal (alloy) susceptibility to crevice corrosion, since it represents the lower potential limit below which a crevice, originally forced to propagate by scanning the potential to \( E > E_{\text{Cre}} \), can no longer propagate [66]. \( E_{\text{Cre}} \) is a characteristic property of a given metal (alloy) and the more positive it is, the higher the resistance to crevice corrosion. However, \( E_{\text{Cre}} \) value changes with temperature, halide concentration, potential scan rate and the roughness of the surface within the crevice [66].

![Schematic polarization curve](image)

**Figure 1.12:** Schematic polarization curve for an alloy exhibiting active-passive behaviour showing the breakdown \((E_B)\) and repassivation \((E_R)\) potentials [66].

Although a number of electrochemical techniques can be used to evaluate the susceptibility of a material to crevice corrosion, one of three techniques is most commonly used to determine \( E_{\text{Cre}} \) and \( E_{R,\text{Cre}} \).

1. **The Cyclic Potentiodynamic Polarization (CPP) technique:** This method was originally developed to study the susceptibility to localized corrosion of Fe and Ni
alloys in chloride solution [67]. A cyclic anodic polarization scan is performed at a fixed scan rate from $E_{\text{CORR}} - 200$ mV up to a fixed potential and back to $E_{\text{CORR}}$. The presence of a hysteresis loop as illustrated in Figure 1.12 indicates the occurrence of localized corrosion and allows the evaluation of both $E_{\text{Crev}}$ and $E_{R,\text{Crev}}$, as indicated in the figure. Although this method is fast and easy, it has the shortcoming that both $E_{\text{Crev}}$ and $E_{R,\text{Crev}}$ are inevitably dependant on the potential scan rate, and hence cannot be considered characteristic values for the metal (alloy).

(2) Potentiodynamic-Potentiostatic-Potentiodynamic (PD-PS-PD) technique: This technique is similar to CPP but includes an additional step. After scanning the potential anodically to a pre-determined hold potential greater than $E_B$, localized corrosion is allowed to propagate by holding the potential constant for a period of time [68]. While in this method, creviced corrosion is allowed to propagate without applying a high potential, the hold potential required can change depending on the solution composition and temperature. Furthermore, the total charge during the potentiostatic step (i.e. the extent of crevice propagation) can change from experiment to experiment since the current can change with time during that step [69].

(3) Potentiostatic-Galvanostatic-Potentiodynamic (PD-GS-PD) technique: To avoid the issue of changing total charge from experiment to experiment, Mishra and Frankel [70] replaced the potentiostatic hold stage with a galvanostatic stage, which allows the total charge due to propagation to be controlled. As with the PD-PS-PD technique the potential is first scanned to a value greater than $E_{\text{Crev}}$. Then the electrode is subjected to a galvanostatic current until a known charge has been passed. The electrode is then switched back to potentiostatic control and the reverse scan is performed.
1.5.2 Breakdown and Repassivation Behaviour of Ni-Cr-Mo alloys

As noted in the previous section, crevice corrosion is possible only when the $E_{CORR}$ is $> E_{R,Crev}$ in the exposed environment of interest. Thus a knowledge of $E_{R,Crev}$ can be used as a criterion for materials selection. The values of $E_{R,Crev}$ for a specific material are well known to be influenced by solution chemistry, in particular the pH and the concentration of aggressive ions and oxyanions.

For the C22 alloy it has been shown that chloride is the only known ion that promotes crevice corrosion, other species such as nitrate, phosphate, sulfate, carbonate, fluoride and organic acids generally mitigating or inhibiting crevice corrosion when present at sufficiently high concentrations [71–75]. Among these species nitrate shows the best inhibitor properties, the main mechanism of inhibition being a reduction in local pH due to the reduction of nitrate to nitrogen [73].

In a study of the crevice corrosion susceptibility of the C625 (Ni-21Cr-9Mo), G30 (Ni-29Cr-5Mo-2.7W), G35 (Ni-33Cr-8Mo), C22 (Ni-22Cr-13Mo-3W), C22HS (Ni-21Cr-17Mo-1W) and BC1 (Ni-15Cr-22Mo) alloys at 60°C in chloride concentrations ranging from 0.1 M to 10 M [76], a linear relationship between $E_{R,Crev}$ and the logarithm of chloride concentration was observed, although a minimum chloride concentration was required for crevice initiation [72]. Dunn et al. [72] investigated crevice initiation on alloy C22 in solutions with pH values varying from acidic to basic at 95°C. In neutral and alkaline solutions $E_{CORR}$ was found to be $< E_{R,Crev}$ making crevice corrosion avoidable in the absence of an oxidizing species. However, in acidic solutions, which occur in occluded crevices, $E_{CORR}$ was $> E_{R,Crev}$, and crevice corrosion would be expected.

Temperature is another parameter expected to influence $E_{Crev}$ and $E_{R,Crev}$ by changing the rates of metal and oxide dissolution, the extent of cation hydrolysis and the migration of ions inside a creviced region [65]. A number of studies have shown that, in general, an increase in temperature causes a decrease in both $E_{Crev}$ and $E_{R,Crev}$ [72,77–80]. In the
presence of chloride ions, $E_{R,\text{Crev}}$ is a function of temperature ($T$) and chloride concentration ([Cl$^-$]),

$$E_{R,\text{Crev}} = (A + BT) \log([\text{Cl}^-]) + CT + D$$ (1-31)

where $A$ and $B$ and $C$ and $D$ are constants [79,80].

Since temperature is a critical factor in crevice initiation, crevice corrosion can be prevented at any applied potential if the temperature is low enough. This temperature limit is named the protection temperature ($T_{\text{Prot}}$), and the higher $T_{\text{Prot}}$, the better the crevice resistance of the alloy.

Recently, Mishra et al. [77] investigate the role of temperature on the crevice corrosion behaviour of a series of Ni-Cr-Mo alloys in 1 M NaCl solution using the PD-GS-PD technique. While all the alloys showed a general decrease in $E_{\text{Crev}}$ with increasing temperature (Figure 1.13), the response of the alloys to temperature could be divided into two main groups based on their alloy composition.

![Figure 1.13: The dependence of $E_{\text{Crev}}$ on temperature for a series of commercial Ni-Cr-Mo alloys [77].](image-url)
Alloys with both a high Cr and high Mo (Mo + W) content had higher $E_{Crev}$ values, while alloys with either a high Cr or a high (Mo + W) content had relatively lower $E_{Crev}$ values at all temperatures. These results indicate that, while Cr may be the main alloying element required for passivity, a minimum Mo content (> 9 wt.%) is necessary to achieve the maximum film stability against breakdown under creviced conditions. If the $T_{Prot}$ is considered as the key indicator of crevice corrosion resistance, then the values shown in Figure 1.14 can be used to rank the influence of alloy composition, with resistance to crevice corrosion increasing in the order,

High Cr-Low Mo < Low Cr-High Mo < High Cr-High Mo < High Cr-High Mo + W [77].

![Figure 1.14: $T_{Prot}$ as a function of (Mo + W) content (wt.%) for a series of commercial Ni-Cr-Mo alloys [77].](image)
A number of studies have linked the crevice corrosion resistance to alloying elements using the pitting resistance equivalent number (PREN) which is mainly affected by the Mo concentration [81].

\[
\text{PREN} = \% \text{Cr} + 3.3 \times (\% \text{Mo} + 0.5\% \text{W})
\]  

The value of \(E_{R,Crev}\) has been reported to increase with the PREN value [76,77,80]. Zadorozne et al. [81] employed the Stern-Geary method to calculate corrosion rates for BC1, C22 and C22-HS alloy in an HCl solution at 90°C and reported that anodic dissolution in the active region was controlled by the Mo content of the alloy resulting in a higher crevice corrosion resistance for the BC1 alloy and its significantly higher \(E_{R,Crev}\) value compared to the other two alloys.

### 1.6 Crevice Propagation

While crevice initiation can be a prolonged relatively slow process, propagation can be rapid due to the highly corrosive crevice environment and is, hence, the key process which must be controlled if damage is to be avoided.

#### 1.6.1 Role of Alloying Elements

The role of alloying elements in crevice propagation is of critical importance. Published studies have indicated a major role for Mo in determining the crevice propagation behaviour [3,13,82,83]. Kehler and Scully [64] compared the crevice corrosion of alloy 625 and C22 in an acidic solution. Both alloys contain 20 wt.% Cr, but differ in their Mo or (Mo + W) contents. Their results indicated a lower rate of metastable corrosion events and a lower depth of crevice penetration for the higher Mo containing C22 alloy. Alloying with Mo was shown to suppress \(i_{\text{Pass}}\) and to lower the anodic dissolution rate in the active region, consequently decreasing the crevice propagation rate [13]. Lillard et al. [13] compared the crevice corrosion of the alloys C276 (Ni-15.5Cr-16Mo), C625 (Ni-22Cr-9Mo) and G3 (Ni-22Cr-6Mo) in several simulated CCS solutions and observed
a better crevice corrosion resistance for C276 compared to 625 and G3, due to the alloys higher Mo content. They suggested that Mo oxidized to MoO₂, and possibly MoO₄²⁻, at high potentials when the solution pH is close to neutral in the initial stages of crevice corrosion,

\[
\text{Mo} + 2 \text{H}_2\text{O} \rightarrow \text{MoO}_2 + 4 \text{H}^+ + 4 \text{e}^- \quad (1-33)
\]

\[
\text{MoO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 4 \text{H}^+ + 2 \text{e}^- \quad (1-34)
\]

It was proposed that MoO₄²⁻ inhibits crevice propagation temporarily by suppressing Cl⁻ migration into the crevice and by competing for adsorption sites inside the crevice. As the crevice solution acidifies through reaction (1-33) and (1-34) and hydrolysis of other metal cations such as Cr⁶⁺ occurs, MoO₄²⁻ becomes thermodynamically unstable.

Formation of molybdates at active sites has been proposed as the key role of Mo in controlling the crevice corrosion resistance of Ni alloys [3,13,83]. Jakupi et al. [84] studied the crevice corrosion of C22 under galvanostatic polarization and analyzed the corrosion product accumulated within the corroded region using XPS, energy-dispersive X-ray spectroscopy (EDS) and Raman spectroscopy. The damaged regions were shown to be enriched in Mo, O and W while depleted in Ni and Cr. Raman spectroscopy identified the Mo enriched corrosion products as a mixture of the oxide MoO₃ and polymeric species such as Mo₇O₂₄⁶⁻ and Mo₈O₂₆⁴⁻. XRD (X-ray diffraction) analyses on these corrosion products, performed by Shan et al. [83], confirmed their amorphous nature, no diffraction pattern being observed. The formation of polymeric species is due to the thermodynamic instability of MoO₄²⁻ at low pH as suggested by the reactions,

\[
4.5 < \text{pH} < 6.5 \quad 7 \text{MoO}_4^{2-} + 8 \text{H}^+ \rightleftharpoons \text{Mo}_7\text{O}_2\text{O}_{24}^{6-} + 4\text{H}_2\text{O} \quad (1-35)
\]

\[
1.5 < \text{pH} < 2.9 \quad 8 \text{MoO}_4^{2-} + 12 \text{H}^+ \rightleftharpoons \text{Mo}_8\text{O}_{26}^{4-} + 6\text{H}_2\text{O} \quad (1-36)
\]

It has been suggested that these proton consuming reactions inhibit corrosion by neutralizing the critical crevice solution.
Shan et al. conducted a series of EDS and AES analyses of corrosion products after various extents of crevice propagation and showed that propagation is controlled by the deposition of Mo and W [83]. Their results are summarized in Figure 1.15. The solid corrosion products within the crevice corroded area were depleted in Ni, Cr, and enriched in amorphous Mo and W oxides which are insoluble in HCl solutions. The corrosion products on the alloy surface outside the crevice possessed high Cr/Ni and Mo/Ni ratios due to the lower solubility of chromium ions once neutral pH conditions were encountered [83].

![Figure 1.15](image)

Figure 1.15: (a) Sketch showing the distribution of corrosion products inside and outside a crevice on C22: (b) qualitative distribution of metal elements in the corrosion products [83].

Confocal laser scanning microscopy (CSLM) was employed by Jakupi et al. [84] to study the distribution and penetration depth of crevice corrosion damage on C22 after galvanostatic treatments at various applied currents. By using a constant applied current the rate of propagation was effectively controlled. The propagation, or corrosion damage profile, was found to depend on the applied current. The current was found to control the rate of formation of molybdate which caused the current to relocate to new areas within the crevice corroding region. At high propagation rates, the accumulation of molybdate inhibited penetration into the crevice resulting in the spread of damage across the surface. By contrast, at low applied currents the propagation rate can be sustained locally leading to deeper crevice penetration, since the accumulation rate of molybdate was significantly reduced.
1.6.2 Role of the Cathodic Reaction

Crevice corrosion involves the separation of the anode (within the crevice) and cathode sites (on the surface external to the cathode), and corrosion can only propagate if supported by the external cathodic reaction. A simple way to determine the crevice propagation rate is to galvanically couple a creviced specimen to a considerably larger external cathode of the same material through a zero resistance ammeter.

Jakupi et al. [85] measured the current flowing between a galvanically coupled, creviced C22 electrode and an external cathode in 5 M NaCl and 120°C for four days. Crevice initiation was detected by a peak in the current of 15 μA and a drop in potential of the crevice electrode to -170 mV. Eventually the current decreased to a plateau of 4 μA. However, examination of the crevice surface showed that while corrosion initiated, propagation was limited by rapid repassivation. This was attributed to a lack of a supporting cathodic reaction to sustain active dissolution, O2 reduction on the external cathode surface being extremely slow. Subsequent experiments showed that a galvanostatic current of > 5 μA is needed to ensure stable crevice propagation [85,86].

Bocher and Scully [87] investigated the influence of a limited cathode area on the propagation of crevice corrosion on stainless steel (Fe-18Cr-8Ni-2Mo) in 0.6 M NaCl at 50°C. The rate of propagation of a potentiostatically activated crevice was limited by decreasing the area of the galvanically coupled Pt cathode. By decreasing the cathodic surface area and consequently the cathodic current, the active anode sites got smaller in area and relocated to active areas deeper inside the crevice until repassivation occurred when the potential at the crevice mouth drops to $E_{R,Crev}$.

1.6.3 Role of Microstructure

The susceptibility to corrosion of alloys is expected to be influenced by the microstructure and grain boundary properties of the alloy. The effect of grain orientation has also been studied [88,89]. The corrosion rate of C22 in 3 M HCl, when the passive
film is fully dissolved, was linked to the grain orientation of the alloy using EBSD and atomic force microscopy (AFM) and varied with crystallographic plane in the order \{111\} < \{100\} < \{110\}; i.e., the rate was inversely proportional to the average coordination number for that crystallographic orientation. In a mildly acidic solution (1 M HCl), when a thin oxide layer exists on the alloy surface, the dissolution anisotropy is determined by competition between growth and dissolution of the passive film in the following order \{111\} < \{110\} < \{100\} [88]. A more recent study of the effect of grain orientation and the corrosion of a FCC FePd alloy [89] shows that the corrosion rate is lowest on the three low index orientations (\{111\},\{100\} and \{110\}) and increases when the grain orientation deviates from the \{100\} and \{111\} orientations.

Jakupi et al. [4] observed that crevice initiation on C22 occurred mostly on grain boundaries, and used electron backscatter diffraction (EBSD) to reveal a preferential intergranular attack on “random” boundaries compared to low energy \(\Sigma\) boundaries. It was suggested that the excellent resistance of this alloy to crevice corrosion is due to the high (> 50\%) percentage of \(\Sigma\) boundaries in microstructure of alloy. Kobayashi et al. [90] found that the preferential crack path during intergranular stress corrosion of Ni choose predominantly the high energy random boundaries and an increase in density of \(\Sigma\) boundaries decreased the length of cracks. While the enhanced properties of \(\Sigma\) boundaries is a well-known phenomenon, no study has focused on the compositional differences between random and \(\Sigma\) boundaries.
1.7 References:


URL: http://www.haynesintl.com/HybridBC1AlloyPrelimPresentation120409.pdf


Chapter 2

2 Methods and Materials

2.1 Introduction

This chapter briefly reviews the principles of the electrochemical and surface analytical techniques used in this project. However, more specific information on sample preparation and experimental parameters will be provided in the experimental and results sections of subsequent chapters.

2.2 Electrochemical Experiments

2.2.1 Sample Preparation

Flat discs of different Ni-Cr-Mo alloys (see Table 1-1 alloy compositions) with a diameter of 1 cm and a height of 0.5 cm were cut from plate materials provided by Haynes International (Kokomo, IN, USA). A small hole was drilled in the back of the disc and a threaded connecting rod of the same material provided a connection to external circuits. The connecting rod was insulated by Teflon PTFE heat shrink tubing to avoid exposure to the electrolyte. The disks were then mounted in a heat resistant epoxy resin (Dexter Hysol resin EE4183; hardner HD3561) to ensure only a single disc face, 0.78 cm² in surface area, was exposed to the electrolyte. Prior to each experiment, the cylindrical discs were ground with a series of silicon carbide papers (from 180 to 1200 grit) using water as a lubricant, and then ultrasonically cleaned for ten minutes in a 50/50% mixture of ethanol and water solution, rinsed with deionized water, and dried using Ar gas.
2.2.2 Electrochemical Cell

Figure 2.1 shows a schematic of the three electrode glass cell used in experiments. A 99.95% pure platinum plate with a surface area of 2.4 cm$^2$ was used as a counter electrode (CE). A home-made silver/silver chloride electrode (RE) immersed in a saturated KCl solution (0.197 V vs. NHE), was used as the reference electrode [1].

The cell was designed with a Luggin capillary in the reference electrode arm to reduce the potential drop due to solution resistance. Solution in both the counter and reference electrode arms of the cell were separated from the electrolyte in the main cell body by porous frits to avoid contamination. The cell was surrounded by an outer glass jacket through which water was circulated from a thermostatic bath ((Isotemp 3016H, Fisher Scientific) to maintain the solution temperature to within ± 1°C. All electrochemical experiments were conducted using a Solartron 1287 potentiostat and a Solartron 1255 frequency response analyzer (FRA) was used for electrochemical impedance spectroscopy (EIS) experiments. To avoid interference from external sources of electrical noise, the cell was placed in a grounded Faraday cage.

Figure 2.1: Schematic of the standard three electrode glass cell used.
2.2.3 Electrolyte Solutions

All experiments were conducted in 5 M NaCl solutions prepared using NaCl crystals (Caledon Ltd, GR ACS grade) and type I deionized water with a resistivity of 18 MΩ.cm. The pH of solutions was adjusted to the required value using 0.5 M HCl and NaOH solutions. To obtain a buffered solution with a pH = 9, 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ was added to the chloride solution. An Orion Model 250A pH meter was used to measure the pH before and after each experiment.

Before all deaerated experiments, the solution was purged with ultra-high purity Ar for 1 hour to minimize the oxygen concentration, and a flow of Ar was subsequently maintained throughout the experiment.

2.2.4 Electrochemical Techniques

2.2.4.1 Corrosion Potential ($E_{CORR}$) Measurements

A straightforward and easily measurable electrochemical parameter is the corrosion potential ($E_{CORR}$). The $E_{CORR}$ is obtained by measuring the potential of a freely corroding working electrode with respect to the reference electrode. $E_{CORR}$ lies between the equilibrium potentials for the anodic and cathodic half reactions involved in the overall corrosion process. At $E_{CORR}$ the rates of anodic and cathodic half reactions are equal, all the electrons generated by oxidation reactions being consumed by reduction reactions on the same metal surface [2]. Consequently, $E_{CORR}$ is determined by the kinetics of the corrosion reaction and should not be mistaken for an equilibrium potential. The $E_{CORR}$ of a metal in a solution is indicative of the activity of the metal surface and the oxidizing power of the solution. Although no quantitative rate information is obtained by this measurement, a lot of mechanistic information can be obtained by determining the dependence of $E_{CORR}$ on experimental parameters such as time, solution concentrations, temperature and pH.
2.2.4.2 Potentiostatic Polarization

In potentiostatic polarization experiments, the current response of the working electrode at a constant applied potential \((E)\) is determined as a function of time. Choosing an applied \(E\) more positive than \(E_{CORR}\) allows us to study the anodic reaction while applying a negative \(E\) with respect to \(E_{CORR}\) allows investigation of the cathodic reaction.

Prior to potentiostatic experiments, the working electrode was cathodically cleaned by applying a negative \(E\) (-1 V) for 1 hour, to remove any oxide film or contamination from the electrode surface. To study the formation of passive films and their transpassive breakdown the electrode was anodically polarized to positive potentials.

In this project, potentiostatic polarization experiments were performed on a series of Ni-Cr-Mo alloys at room temperature and in solutions with pH values of 7 and 9. The applied potential profile is illustrated in Figure 2.2. A series of potentials was applied to the working electrode for 2 hours and the current response recorded. At the end of each 2 hour period an EIS measurement was performed, as indicated in the figure inset, to determine the properties of the oxide film formed on the electrode surface at that potential. The potential was then increased and the procedure repeated at 100 mV intervals up to a potential of 600 mV.

Figure 2.2: Potential \((E)\) vs. time profile applied in potentiostatic polarization experiments. The inset shows an EIS spectrum was recorded at the end of each polarization step.
In some experiments the potential was then reversed from 600 mV and similar measurements performed at 100 mV intervals down to -1 V to investigate the reformation of the passive film after transpassive dissolution. The final current recorded at the end of each polarization step could then be plotted as function of applied potential, and the EIS spectra analyzed using equivalent circuits containing appropriate electrical elements.

2.2.4.3 Potentiodynamic Polarization

In a potentiodynamic polarization experiment $E$ is scanned linearly at a known scan rate and the current ($I$) response recorded as a function of potential, known as a polarization curve. Polarization curves provide a lot of information on the behavior of a metal in a specific solution and are used to identify the potential regions of activity, passivity, localized corrosion and transpassivity.

In this study, potentiodynamic polarization curves were measured on a series of Ni-Cr-Mo alloys in 5 M NaCl + 3 M HCl solution at 75°C. Before recording the curves, the $E_{CORR}$ was measured until a steady state condition was achieved (i.e., $E_{CORR}$ changed by $< 5$ mV over a 10 minute period). Subsequently, E was scanned at 0.16 mV/s from 50 mV below $E_{CORR}$ up to the anodic potential value at which an abrupt increase in current density occurred [3,4].

2.2.4.4 Electrochemical impedance spectroscopy

EIS can separate the ohmic solution resistance from the polarization resistance; it can also measure many other properties of the solution/electrode interface by separating the component processes on the frequency scale [2].

EIS is a useful tool in characterizing oxide layer properties and surface reaction mechanisms [5,6]. As in other spectroscopies, an excitation is applied to the system and its response observed. In EIS, a small alternating $E$ perturbation in the form of a sine wave is applied to the working electrode at a number of discrete frequencies ($\omega$) and the sinusoidal current response recorded, as shown schematically in Figure 2.3.
Figure 2.3: Illustration showing the sinusoidal current response to a sinusoidal $E$ input: $\theta$ indicates the phase angle between the two signals.

The potential and current are changing with time as below:

$$E(t) = E_0 e^{-j\omega t} \quad (2-1)$$

$$i(t) = i_0 e^{-j(\omega t + \theta)} \quad (2-2)$$

$E_0$ and $i_0$ are the amplitude of the potential and current signals respectively, $\omega$ is the angular frequency, and $\theta$ indicates the phase angle between the two signals.

The impedance ($Z$) can be defined as:

$$Z(\omega) = \frac{E(t)}{i(t)} \quad (2-3)$$

This is a more general expression of Ohm’s law which takes into account the frequency dependence of the impedance. It is important to note that $Z$ is a complex number with real (in phase) and imaginary (out of phase) components $Z'$ and $Z''$, where:

$$Z = Z' + jZ'' \quad (2-4)$$
The magnitude of the impedance is given by:

\[ |Z| = \sqrt{Z'^2 + Z''^2} \]  \hspace{1cm} (2-5)

and the phase angle \((\theta)\) by:

\[ \theta = \tan^{-1}\left(\frac{Z''}{Z'}\right) \]  \hspace{1cm} (2-6)

Figure 2.4 shows an example of an impedance vector and its real and imaginary components in the complex plane.

A simple electrode-solution interface can be described by two components: (1) the double layer capacitance \((C_{dl})\) due to charging/discharging the electrical double layer, and (2) a faradaic reaction (charge leakage across the interface) which has the form of a resistance known as the charge transfer resistance \((R_{CT})\). These two components are in parallel with each other and in series with a solution resistance \((R_s)\) whose value is determined by the electrolyte concentration.
If an $E$ sine wave is applied to a circuit containing only a resistor, $R$, the resulting current will be:

$$i = \left[ \frac{E_0}{R} \right] \sin(\omega t) \quad (2-7)$$

And since $E$ and $i$ are at the same frequency and same phase, the impedance can be calculated from the relationship:

$$Z(\omega) = \frac{E(t)}{i(t)} = \frac{E_0 \sin(\omega t)}{\frac{E_0}{R} \sin(\omega t)} = R \quad (2-8)$$

If an $E$ sine wave is applied to a circuit containing only a capacitance, current flow happens only when there is a change in $E$.

$$i = C \frac{dE}{dt} \quad (2-9)$$

By taking the derivative of $E$ versus time, one can calculate $i$ as a function of $E$:

$$i = \omega CE_0 \sin(\omega t + \frac{\pi}{2}) \quad (2-10)$$

In this case, $E$ and $i$ are still at the same frequency, but they are $\pi/2$ out of phase. In impedance this phase change is represented by $j$ ($j^2 = -1$)

Therefore the impedance of this circuit is
\[ Z(\omega) = \frac{1}{j\omega C} \] (2-11)

The inverse total impedance of two parallel impedances is the sum of the reciprocals of the two elements,

\[ \frac{1}{Z_t} = \frac{1}{Z_1} + \frac{1}{Z_2} \] (2-12)

And two impedances in series add in the usual arithmetic way,

\[ Z_t = Z_1 + Z_2 \] (2-13)

Thus for a resistor and capacitor in parallel:

\[ \frac{1}{Z(\omega)} = \frac{1}{R} + j\omega C \] (2-14)

and by adding the \( R_s \) to the circuit above in series, the total impedance of the interface can be calculated and rearranged to yield the complex equation:

\[ Z(\omega) = \left[ R_s + \frac{R_{CT}}{1 + \omega^2 C_{dl}^2 R_{CT}^2} \right] - j \left[ \frac{\omega C_{dl}^2 R_{CT}^2}{1 + \omega^2 C_{dl}^2 R_{CT}^2} \right] \] (2-15)

Plotting the equation above in the complex plane results in a semicircle with diameter of \( R_{CT} \) and centre of \( R_s + R_{CT}/2 \) (Figure 2.5). This representation of impedance data is called a Nyquist plot.
Figure 2.5: Schematic representation of a Nyquist plot corresponding to a one time constant electrical circuit.

Another method often used to evaluate EIS data involves plots of log|Z| and θ versus log ω. These data presentations are known as Bode plots and are illustrated for an one time constant circuit in Figure 2.6 [7]. Both Nyquist and Bode plots were used in this project.

Figure 2.6: Bode data presentation mode in EIS.
When an oxide is present on a surface in contact with solution, the resistance of the interface is the polarization resistance \((R_p)\) which is the sum of the charge transfer resistance and the film resistance \((R_{film})\) which are in series. When the \(R_{film}\) is large (a passive film) it dominates and the \(R_p\) becomes \(~\) equal to the \(R_{film}\). There are also two capacitances, the double layer capacitance and the film capacitance \((C_{film})\). These are also in series but add as the reciprocals. Since \(C_{film}\) is the smallest it dominates the sum. Consequently the behaviour of an equivalent circuit representing a passive interface can be represented by the one time constant circuit, shown in Figure 2.7.

\[
Z = \frac{Z_0}{(j\omega)^n}
\]  

(2-16)

Where the exponent \(n\) can vary from 0 to 1; and when \(n \to 1\) the CPE represents an ideal capacitor and when \(n \to 0\), it represents a resistor. Typical \(n\) values observed for the non-ideal capacitances of solid electrodes are in the range of 0.85-0.95.
In the equivalent electrical circuit used for fitting data in this study, all capacitances were modeled as CPEs. As an indication of the deviations from ideal behaviour values of $n$ are reported with the other fitted parameter values.

Prior to EIS measurements on oxide covered surface, cathodic cleaning of the electrode at $E = -1$ V was followed by growth of an oxide film at a constant $E$ for 1 h. An EIS measurement was then performed at the same applied potential, before changing to the next potential as shown in Figure 2.2.

All electrochemical measurements were made with a Solatron 1287 potentiostat coupled to a 1255B Solatron Frequency Response Analyzer (FRA). Corrware and Zplot software were used for running the measurements. EIS measurements were performed using a sinusoidal input $E$ with an amplitude of 10 mV over a frequency range of $10^6$ to $10^{-3}$ Hz.

Kramers-Kronig transformations were then performed on the collected data to check their validity and to ensure that steady-state was maintained over the duration of the measurement [8].

### 2.3 Crevice Corrosion Experiment

#### 2.3.1 Crevice Corrosion Specimen

The design of the working electrode used in crevice corrosion experiments is shown in Figure 2.8. The V-shape of the working electrode ensures that only a well-defined area of the electrode surface will be subject to crevice corrosion. The thickness of the electrode is 3.17 mm and the dimensions of the crevice surface are 15 mm (width) by 26 mm (length). A 3-48 threaded hole was tapped in one end of the creviced sample. This tapped hole was used to connect the crevice assembly to a sheathed C22 rod used to suspend the creviced electrode in the electrolyte and to allow electrical contact to external circuitry. The crevice was formed by sandwiching a small wafer of PTFE with an area of $\sim 4$ cm$^2$ between the metal surface and an Udel (Polysulfone) coupon. The assembly was held together using isolated bolts and nuts fabricated from the same material. To adjust
crevice tightness, a PTFE “feeler” strip made from the same crevice former material was used.

![Diagram of crevice working electrode](image)

**Figure 2.8: Schematic showing the design of the creviced working electrode [9].**

Prior to assembly, the crevice-forming face of the working electrode, the PTFE crevice former, and all bolts and nuts were wet polished with silicon carbide papers of 320, 600, 800, 1000, 1200 grits. All parts of the crevice assembly were then sonicated in ethanol, rinsed with deionized water, and dried with Ar gas.

Before tightening the crevice assembly, the metal electrode and the PTFE crevice former were immersed in the electrolyte solution to be used in to ensure the presence of electrolyte in the crevice interior. When performing a crevice corrosion experiment, the crevice assembly was submerged in the electrolyte, so that the electrolyte solution level was above the crevice forming face of the electrode but below the bolts and nuts used for tightening the crevice. This ensures only a single creviced area is exposed to the electrolyte.

### 2.3.2 Crevice Corrosion Cell and Solution

The electrochemical cell used in crevice experiments is shown in Figure 2.9. The cell was a constructed inside a Hastelloy pressure vessel (Parr Instrument Co., model 4621). A
Teflon liner was used to isolate the pressure vessel body from the electrolyte. The lid was modified to accept four sealing glands for electrode feedthroughs. All connecting rods were made from the same material and isolated using heat shrink Teflon (PTFE) tubing. The working electrode assembly was suspended in the middle of the cell from the threaded end of the V shaped sample (as illustrated in Figure 2.9).

All potentials were measured using a home-made Ag/AgCl reference electrode separated within a PTFE container and filled with saturated KCl solution [10]. The counter electrode, made from the same material as the working electrode, was cylindrical with a diameter of 68 mm, a length of 50 mm, and a thickness of 0.3 mm. The surface area of the counter electrode was ~50 times that of the working electrode to simulate the small anode/ large external cathode geometry. In some experiments, the $E_{\text{CORR}}$ of a planar electrode, 20 mm in length and 5 mm in width and thickness, was also measured for comparison to that of the crevice corroded electrode.

![Figure 2.9: Schematic showing the electrochemical cell used in crevice corrosion experiments [11].](image)
In all experiments, a 5 M NaCl solution was used. To increase the concentration of dissolved oxygen in the solution the electrolyte was aerated by robust agitation. To prevent boiling of the solution during the experiment, and to ensure a proper sealing of the cell, the pressure vessel was pressurized with UHP Nitrogen gas to a pressure of 80 Psi (0.5 MPa). An autoclave heater (Parr Instrument Co. model 4913) was used to heat and maintain the cell at the desired temperature.

On completion of the experiment, the creviced specimen was examined visually, rinsed in deionized water and ethanol, and dried using UHP Ar gas. The corroded specimen was then photographed using a digital camera. The images obtained were used to measure the area of the surface corroded using Image Pro analysis software.

2.3.3 Electrochemical Techniques

2.3.3.1 Galvanostatic and Galvanodynamic Polarization

Galvanostatic and galvanodynamic polarization can be used to measure the polarization behaviour by applying either a constant current, or a constant current scan rate, respectively. The current is applied between the working and counter electrodes using a current source while recording the $E$ between the working and reference electrodes [12]. In this technique, the $E$ between the working and reference electrodes is automatically adjusted to the value required to maintain the applied current. These techniques are generally called chronopotentiometric techniques, because the potential is determined as a function of time.

While useful in controlling the overall corrosion rate, chronopotentiometry doesn’t allow access to the passive region in a galvanostatic $E$-$i$ curve. As shown in Figure 2.10, when the current is increased to slightly $> i_{\text{crit}}$, a current of this magnitude can only exist in the transpassive region, and the electrode potential would very rapidly shift to the transpassive region [13].
In this study both galvanostatic and galvanodynamic polarization techniques were used. In galvanostatic experiments, a constant coulombic charge was applied to the working electrode by applying specific anodic currents of (200 $\mu$A, 100 $\mu$A, 80 $\mu$A, 40 $\mu$A, 20 $\mu$A and 10 $\mu$A) for the appropriate times. Prior to each experiment, $E_{CORR}$ was monitored for 5 hours as the temperature increased and stabilized. A WaveDrive 20 bipotentiostat was employed for all chronopotentiometry measurements. In galvanodynamic polarization experiments, the current was decreased from a higher current (80 $\mu$A or 40 $\mu$A) at a constant rate of 0.464 nA/s for 48 hour or 0.116 nA/s for 96 hour, respectively. After galvanodynamically decreasing the current to zero, $E_{CORR}$ was measured for at least 24 h as the cell cooled down.

In some galvanodynamic polarization experiments, once the applied current reached zero, whether the crevice continued to propagate was determined using a zero resistance ammeter to measure the current flowing between the counter and creviced electrodes under open circuit conditions.

Figure 2.10: Schematic showing anodic polarization curves obtained galvanostatically and potentiostatically [14].
2.4 Surface Analytical Techniques

2.4.1 Scanning Electron Microscopy and Energy-dispersive X-ray Spectroscopy

A scanning electron microscope (SEM) produces an image of a surface by scanning with a focused beam of electrons. Using electrons as an illumination source provides a resolution of about 25 Angstrom. In electron microscopes the electrons are emitted from an electron gun with an energy of 2-40 keV. A schematic of a standard SEM is shown in Figure 2.11. The electron beam is passed through a series of electromagnetic condenser lenses where it is focused down to $10^{-3}$ times its original size to a focal point. The fine electron probe produced is then scanned across a selected area of the specimen surface using deflection coils, a procedure known as rastering [15].

![Figure 2.11: Schematic of a scanning electron microscope.](image-url)
The electron beam interacts with the specimen surface to produce different emissions from specific emission volumes within the sample. These emissions include secondary, backscattered and Auger electrons, and characteristic X-rays (Figure 2.12). By using different detectors to collect these signals one can determine many characteristics of the surface such as its topography, crystallography, composition, etc.

Figure 2.12: The different emissions produced when an incident electron beam interacts with a material surface.

Secondary Electrons (SE)

Secondary electrons are a result of the inelastic collision and scattering of incident electrons with specimen electrons. These electrons come from a very shallow depth near the surface and provide high spatial resolution images. These electrons are mainly used to provide surface topographical information [15].

Backscattered Electrons (BSE)

Backscattered electrons (BSE) are a result of an elastic collision and scattering of the incident electrons by specimen nuclei or electrons. Since elastic scattering involves only a small change in energy, BSE have energies as high as those in the incident beam. Since these electrons are produced from deeper locations than SEs they do not provide a similar well resolved image. However, the intensity of these electrons is a function of the atomic
number of the elements in the surface and a brighter BSE image indicates a greater atomic number [16]. These electrons therefore, provide information on the surface composition and crystallographic information. This will be discussed when describing the electron backscatter diffraction technique.

**Characteristic X-rays**

When a high energy incident electron beam ejects an electron from the inner shell of an atom, electron holes are produced. Subsequently electrons from a higher energy level will relax to fill the hole and the difference in energy between the two states will be emitted in the form of an X-ray which is characteristic of the elements atomic structure. By measuring the energy of these X-rays using an energy dispersive X-ray spectrometer, information about the elemental composition of specimen can be obtained [15].

In this project, a Leo 1540 FIB/SEM with a 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 alloys.

The depth of crevice corrosion damage was estimated using SE and BSE imaging of a crossed section sample and EDS maps were also produced from the corrosion damaged interface.

### 2.4.2 Transition Electron Microscopy

Transmission electron microscope (TEM) yields information on a material by passing electrons through it. TEM enables the structure of materials to be examined with a resolution approaching atomic scale, and can provide information about crystal defects such as dislocations, stacking faults, precipitates and interfaces [17].
When an accelerated electron beam with an energy of 100-1000 keV hits a very thin (typically 100 nm or less) TEM specimen, different signals are emitted from the surface (Figure 2.13). The transmitted electrons (unscattered, elastically scattered and inelastically scattered) can be used to form an image.

Three contrast mechanisms can contribute to an image:

1- Absorption Contrast

This is the most common mode of operation in TEM and is known as bright field imaging. It is formed by inelastically scattered electrons that lose their energy when they interact with atoms in a material. Since heavier elements or thicker samples lead to a higher energy loss by these electrons, the variation in energy loss can be used to form an image in which regions with a higher atomic number appear darker.
2- Diffraction Contrast

When an electron beam encounters a crystalline structure, diffraction will occur. This diffraction is a function of crystal structure based on Bragg’s law. Using the diffraction patterns acquired, information about the crystal structure and preferred orientation of a specimen is obtained [17]. An objective aperture is used to select the beam used to form the image. If an undiffracted beam is chosen a bright-field image (BF) is formed. When diffracted electrons are used, a dark-field image (DF) is obtained [19]. This is shown schematically in Figure 2.14.

![Figure 2.14](image)

Figure 2.14: The use of an objective aperture in TEM to form (A) bright field and (B) dark field images by collecting direct or scattered electrons, respectively [18].

Scanning Transmission Electron Microscopy

Scanning transmission electron microscopy (STEM) is a combination of a TEM and a SEM. STEM works on the same principal as the SEM by using a focused probe to scan over the specimen using scanning coils.
The advantage over SEM is that, because of the thinness of the specimen, transmission modes of imaging are also available allowing the formation of high resolution images. Scanning the beam over the surface of the specimen makes these microscopes suitable for quantitative analyses such as EDS mapping; electron energy loss spectroscopy (EELS) and annular dark-field imaging (ADF). Like TEM, STEM allows the formation of bright field and dark field images depending on the electrons that are collected in the imaging mode.

In the ADF imaging mode an annular detector is used to collect the scattered electrons through an aperture that only allows scattered electrons to pass through. These electrons are then used to form an image. The main unscattered beam is collected with an EELS detector which is used for chemical analysis of the specimen [19].

**Electron Energy Loss Spectroscopy**

Electron energy-loss spectroscopy (EELS) is an analytical technique that measures the change in kinetic energy of electrons after they have interacted with a material with the energy loss being unique to each element and its oxidation state [20]. By recording the electron energy loss spectra at a specific location on a specimen, mechanical and electronic properties (such as bandgap energy) and the chemical composition of very small features like defects, precipitates and grain boundaries are measurable. Elemental maps showing the location of a selected element can also be produced [19]. EELS can detect and quantify all the elements in the periodic table and is especially good for analyzing light elements. Furthermore, EELS offers better spatial resolution and analytical sensitivity than EDS.

In this project TEM samples were prepared from a sigma and a random grain boundary in a C22 alloy, using a focused ion beam technique (FIB). The TEM specimen was analyzed using a FEI Titan 80-300 microscope. EELS maps were recorded in STEM mode with a step size of 1.5 nm. Diffraction patterns and ADF images were also acquired in STEM mode.
2.4.3 Electron Backscatter Diffraction

Electron backscatter diffraction (EBSD) is a SEM-based technique that provides information about the crystallographic nature of a material such as crystal orientation, grain size, grain boundary characteristics and the misorientation between adjacent crystalline grains. In EBSD a stationary electron beam with an energy of 10-30 keV strikes a tilted crystalline sample (at 20° to the incident beam) and low energy backscattered electrons are diffracted from the sample. These electrons are subject to path differences and, therefore, their constructive and destructive interferences form a pattern on a fluorescent screen. This pattern is called a Kikuchi pattern and is characteristic of the crystal structure and orientation of the sample region from where it was acquired [21,22]. Figure 2.15 shows the formation of Kikuchi patterns in an EBSD phosphor detector.

![EBSD Diagram](image)

**Figure 2.15:** Kikuchi patterns formed on a phosphor detector in an EBSD setting [22].

The formation of Kikuchi patterns can be explained by Bragg’s law,

\[ n\lambda = 2d \sin \theta \]  

(2-17)
where \( n \) is an integer, \( \lambda \) is the wavelength of the incident electron beam, \( d \) the distance between atomic layers in a crystal, and \( \theta \) is the angle of incidence of the electrons on the diffracting plane. Therefore, the width of Kikuchi bands is related to the space in between the diffracting plane [18].

In this study EBSD analyses were used to investigate the effect of crystallographic parameters on the corrosion behavior of Ni-Cr-Mo alloys. EBSD analyses were performed in the Zaplab laboratory in the department of Earth Sciences, Western University. An HKL channel 5 EBSD system with a field emission gun scanning electron microscope (SEM) operated at 20 kV was used to obtain grain orientation data. A step size of 1 \( \mu \)m was used to map the surface. The software program “Tango” (Oxford instruments) was used to analyze and map the EBSD data.

### 2.4.4 Confocal Laser Scanning Microscopy

Confocal laser scanning microscopy (CLSM) was first introduced in the late 1980s by Marvin Minsky and since then has been commonly used to image a wide range of biological samples [23]. Because CLSM, unlike conventional microscopy, has the ability to discard the light that does not come from the focal plane, performing optical slicing and constructing three-dimensional (3D) images is possible. CLSM provides high image resolution, great image quality and quantitative image analysis. Because of these unique features, CLSM is now widely used in the study of a variety of materials and processes like corrosion [24]. Figure 2.16 shows the basic principal of a confocal laser microscope in the reflection mode used in this study.
As illustrated in Figure 2.16, the pinhole is illuminated by a laser: light emerging from the pinhole passes through a beam splitter and is focused on a focal plane on the sample by an objective lens. Light coming from this spot (either by reflection, scattering, or fluorescence) is then reflected by the beam splitter towards the pinhole in front of the detector.

Light reflected from points other than the focal plane cannot go through the pinhole and are not detected by the detector [24]. Eliminating unwanted light in CLSM enhances the depth resolution and sharpens the image quality. The laser is scanned across the surface to provide a high resolution image. 3D profiles are produced by changing the focal plane in the z-direction at set micrometer intervals. The images collected at each focal length are stitched together to produce a 3D profile of the surface.

Figure 2.16: Schematic of a CLSM arrangement in the reflection mode [24].
In this study, CLSM was used to collect 2D and 3D profiles of individual corroded grains in the C22 alloy to determine differences in corrosion damage profiles on grains of different orientations. CLSM was conducted using the LSM 510 confocal microscope in the Biotron facility at Western university.

### 2.4.5 X-Ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive analytical technique widely used to study the chemical composition of the top 5–30 Å of a specimen sample [14]. An important advantage of XPS is the ability to identify not only the elemental composition but also the oxidation state of elements. The kinetic energies of photoelectrons ejected from a sample surface are measured when the surface is irradiated by soft X-rays, generally from Al Kα or Mg Kα sources, which have an energy in the range of 1–2 keV [25].

The process of photoemission is shown schematically in Figure 2.17. An X-ray photon, with an energy $h\nu$, penetrates the surface. If this energy is absorbed by an electron from the core level of an element with a binding energy of $E_B$, electron excitation occurs. The kinetic energy ($E_K$) of the ejected electron is analysed by an electron spectrometer. While the $E_K$ of the emitted electron is a function of the energy of the X-ray photon and is independent of the sample analysed, $E_B$ is characteristic for a specific element, its oxidation state, and its local chemical and physical environment [26]. The binding energy can be calculated using the equation,

$$E_B = h\nu - E_K - W$$  \hspace{1cm} (2-18)

where $W$ is the work function of the spectrometer.

The photoelectron spectrum will reproduce the electronic structure of an element accurately since all electrons with a binding energy less than the photon energy will be excited and subsequently identified in the XPS spectrum [26]. A typical spectrum is
presented as a graph of intensity (usually the number of electrons detected) vs. $E_B$. Each peak in the binding energy corresponds to a specific element and the peak intensity is related to the concentration of that element in the sample surface.

XPS analyses were performed with a Kratos Axis Ultra XPS at surface science Western (SSW) using an Al Kα (1486.8 eV) radiation source. The Au 4f 7/2 metallic gold binding energy (83.95 eV) was used as a reference point for calibration of the instrument work function.

![Figure 2.17: Schematic showing the ejection of a core level electron in XPS.](image)

Survey spectra and high resolution spectra were recorded on all samples for the Ni 2p, Cr 2p, Mo 3d, C 1s and O 1s spectral regions. To fit the XPS spectra, commercial CasaXPS™ software was used. If required, charging in XPS spectra was corrected for by fixing the C binding energy in the C 1s spectrum at 284.8 eV.
2.4.6 Auger Electron Spectroscopy

Auger electron spectroscopy (AES) is a highly surface sensitive technique in which the energy of an emitted electron from the surface of a material is used to determine the surface composition.

The use of a finely focused input electron beam enables surface analysis with a high spatial resolution. The area of the sample surface analysed is usually $10^6$-$10^8$ times smaller than that analyzed by SEM/EDS.

AES is a three electron process that leads to emission of secondary, backscattered and Auger electrons. However, only Auger electrons are used for surface analyses. The surface is bombarded by an electron beam with an energy of 3-10 eV. As shown in Figure 2.18, as with XPS, core level electrons are ejected. These secondary electrons, unlike XPS, have no analytical information but can be used to image the surface. The ejection of an electron from a core level (e.g., the K level) ionizes the atom, the ground state is restabilized when an electron from a higher level (L$_1$ in Figure 2.18) relaxes to fill the electron vacancy [26]. Energy conservation dictates that another electron then be ejected from the atom (from the L$_{2,3}$ Figure 2.18). This electron is the Auger electron.

![Figure 2.18: Schematic of the three electron process involved in Auger electron spectroscopy.](image)
The kinetic energy of an Auger electron is equal to the difference between the energy of the core hole and the energy levels of the two outer electrons:

\[ E_{Auger} = E_K - E_{L1} - E_{L2} \]  \hspace{1cm} (2-19)

where \( E_K \) is the energy of the K level, \( E_{L1} \) and \( E_{L2} \) are the energies of the \( L_1 \) and \( L_2 \) levels, respectively. Since the kinetic energy of an Auger electron is a function of the atomic energy levels, which are characteristic for atoms, Auger electrons can be used to determine the chemical composition of a material.

Auger spectroscopy can also be used to determine the distribution of elements in a film as a function of depth; i.e., to generate a depth profile. For this purpose, the surface is bombarded with an \( Ar^+ \) ion beam with an energy of 5 to 10 keV and successive layers of the surface removed in a controlled manner. After removal of each layer the composition is re-determined and a depth profile produced in the form of the relative concentration of elements detected vs. sputtering time.

Auger analyses were performed at Surface Science Western with a PHI 660 Auger electron spectrometer instrument with excitation energy of 5 keV. An \( Ar^+ \) ion beam was used as the sputtering source in depth profilometry and the signal strengths for Ni, Cr, Mo and O were recorded as a function of sputtering time.
2.5 References


Chapter 3

3 The Role of Alloying Elements on the Crevice Corrosion Behaviour of Ni-Cr-Mo Alloys

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Abstract

The roles of alloying elements Mo, Cr and W in resisting crevice corrosion of commercial alloys C22 (UNS N06022), C625 (UNS N06625) and BC1 (UNS N10362) have been studied under galvanostatic conditions in 5 mol·L⁻¹ NaCl at 150°C. Corrosion damage patterns were investigated using surface analytical techniques such as scanning electron microscopy (SEM) and optical imaging, and the corrosion products characterized by energy dispersive X-ray spectroscopy (EDS) analysis.

While the Cr content of the alloy is critical in controlling initiation of crevice corrosion, the rate of activation (passive-to-active transition) is influenced by both the Cr and the Mo (and W) contents. The alloy’s Mo content also determines the distribution of corrosion damage within the crevice. In alloys with high Mo content, corrosion propagates laterally across the surface, while in alloys with low Mo content it penetrates into the alloy. This can be attributed to the accumulation of molybdates (and tungstates) which stifle alloy dissolution at active sites. Thus, as the Mo content of the alloy increases in the order C625 (9 wt.% Mo) < C22 (13 wt.% Mo (3 wt.% W)) < BC1 (22 wt.% Mo) the depth of corrosion penetration decreases.
In addition, once crevice corrosion initiates and the crevice acidifies, metal oxidation can also couple to proton reduction inside the crevice. The role of internal proton reduction in driving the crevice corrosion of these Ni alloys was found to be quite significant; greater than 50% of the corrosion damage is caused by proton reduction inside the crevice.

**Keywords:** Ni-Cr-Mo alloys, Crevice corrosion, Molybdenum, Galvanostatic polarization

### 3.1 Introduction

Extensive industrial effort has been invested in the design of nickel superalloys able to resist corrosion in aggressive media. This is generally achieved by alloying Ni with various amounts of Cr and Mo, along with small amounts of other alloying elements such as W, Cu, and Fe [1]. Mo is known to enhance the corrosion resistance in reducing conditions, while Cr is a beneficial element under oxidizing conditions [2,3]. While the properties of the oxides which protect these alloys generally enforce good passive corrosion behaviour, the function of individual alloying elements in resisting localized corrosion processes, in particular pitting and crevice corrosion, is not fully understood, and optimization of alloy composition for corrosion reliability and cost has not yet been achieved.

Ni-Cr-Mo alloys show a great resistance to general corrosion [3], but under aggressive conditions they can suffer localized corrosion, such as pitting and crevice corrosion. The effects of many factors, such as temperature, pH, and the presence of aggressive halides, on the crevice corrosion of these alloys have been studied, and in general the susceptibility to crevice corrosion was found to increase when the temperature and chloride concentration were increased [4–7]. Generally, the localized corrosion performance of passive metals and alloys is assured by aggressive electrochemical testing, and a wide range of Ni-Cr-Mo alloys have been investigated.
Many researchers have investigated the role of alloying elements on the localized corrosion of Ni alloys [8–10]. To date, studies have shown that Cr is the primary alloying element for maintaining passivity [11–17]. Lloyd et al. [11,18] studied the passive behavior in acidic solutions of five Ni-Cr-Mo alloys with varying amounts of Cr and Mo, and found much lower passive dissolution currents, and a much slower attainment of steady-state passive conditions, on those alloys with >20% Cr content.

Kehler and Scully [19,20] found that the rate of occurrence of metastable corrosion events in acidic solution increased with a decrease in alloy Mo content. Studies in simulated crevice solutions on a series of Ni-Cr-Mo alloys performed by Lillard et al. [21] showed that, as the Mo content of the alloy increased, the passive current density and the dissolution rate associated with the active region decreased. A decrease in crevice corrosion rate resulting from an increase in Mo content has also been reported [22].

Mishra et al. [23] studied the effects of Cr, Mo, and W on the crevice corrosion of a number of commercial Ni-Cr-Mo(-W) alloys in 1.0 mol·L⁻¹ sodium chloride and demonstrated the synergistic influence of Cr and Mo in controlling passive film breakdown. The “protection temperature” was used to rank the resistance of these alloys to crevice corrosion, and the following ranking was achieved: high Cr + low Mo < low Cr + high Mo < high Cr + high Mo < high Cr + high (Mo + W).

While these studies [23,24] yield little mechanistic information, an alloy’s resistance to localized corrosion is generally attributed to the quality and composition of the passive film and how this is influenced by alloy composition and microstructure. A combination of electrochemical impedance spectroscopy (EIS) and X-ray photoelectron spectroscopy (XPS) measurements on the C22 alloy (UNS N06022), in neutral pH solution and at different applied potentials, showed that the resistance of the oxide film ($R_{film}$) is controlled by its $\text{Cr}_2\text{O}_3$ content, and that once the transpassive potential region is reached, $R_{film}$ decreases, accompanied by a dramatic increase in the $\text{Cr(OH)}_3$ content of the film [25]. A later XPS and time-of-flight secondary ion mass spectrometry (ToF-SIMS) study
on the same system showed that transpassive dissolution is accompanied by the accumulation of Mo(VI) and W(VI) species in the outer region of the film [26]. More recently, Zhang et al. [26–28] studied the properties of the oxide film on Ni-Cr-Mo alloys as a function of applied potential, temperature and pH, employing various surface analytical techniques, such as angle-resolved XPS, synchrotron radiation XPS (SR-XPS), ToF-SIMS, and scanning electron microscopy SEM. The presence of a layered structure in the passive film (< 5 nm) was demonstrated, with an inner Cr₂O₃ layer, outer Cr/Ni hydroxides and Mo/Cu or Mo/W oxide in the outermost surface.

Once the passive film breaks down and stable propagation is established, the role of alloying elements in repassivation of the crevice becomes important. Published studies have indicated a role for Mo in determining the crevice propagation rate [9,21]. Jakupi et al. [29] studied the crevice corrosion of C22 (UNS N06022) under galvanostatic polarization, and suggested that propagation was controlled by the Mo content, and the damage distribution depended on a combination of applied current and the deposition of Mo-containing solids. Enrichment of corrosion products comprising O, Mo and W was also reported by Shan et al. suggesting that propagation is controlled by the deposition of Mo and W [10].

The goal of this research is to expand on previous studies by investigating three commercial alloys with various Cr and Mo contents in an attempt to confirm that Cr and Mo work synergistically to control crevice corrosion susceptibility and propagation [23]. Our main interests are in the passive-to-active transition and the propagation process, in particular the distribution of corrosion damage and how it is influenced by the composition of the alloy. To achieve this goal, crevice corrosion was driven galvanostatically, to guarantee initiation and also to prevent repassivation. In this manner one can isolate the propagation stage and control the total amount of corrosion damage.
3.2 Experimental Procedure

The compositions of the alloys used in this study are listed in Table 3-1. All alloys were supplied by Haynes International, Kokomo, Indiana (USA). The specimens were machined and bent into a V-shape to produce an artificial crevice assembly containing only one crevice. The crevice electrode design has been described elsewhere [29–31].

<table>
<thead>
<tr>
<th>Alloy/Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>C22 (UNS N06022)</td>
<td>56</td>
<td>22</td>
<td>13</td>
<td>3</td>
<td>3</td>
<td>2.5</td>
<td>0.01</td>
<td>0.5</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>BC1 (UNS N10362)</td>
<td>62</td>
<td>15</td>
<td>22</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>0.01</td>
<td>0.25</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>C625 (UNS N06625)</td>
<td>62</td>
<td>21</td>
<td>9</td>
<td>-</td>
<td>5</td>
<td>1</td>
<td>0.10</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
</tr>
</tbody>
</table>

A 0.8 mm thick PTFE slice was used as a crevice former to produce a crevice with an area of ~ 4 cm². Each sample was wet-ground with silicon carbide paper from a 180 to a 1200 grit finish, ultrasonically cleaned in methanol, and rinsed in ultra-pure deionized water. All tests were performed at 150°C in a 5 M NaCl solution. The solutions were prepared from reagent grade NaCl and Type-I water (resistivity of 18.2 MΩ·cm²) obtained from a Milli-Q Academic A-10 system. A new solution was used for each experiment.

3.2.1 Electrochemical Cell

All the crevice corrosion experiments were conducted inside a cylindrical pressure vessel with a 100 mm inner diameter and a volume of 1000 cm³. The working electrode was suspended near the center of the cell using a cylindrical rod of the same material from which the crevice was formed. The rod was connected to a tapped hole in one end of the
creviced electrode. To avoid galvanic corrosion, the counter electrode was made from the same material as the crevice. To mimic the usual crevice corrosion geometry, the surface area of the counter electrode was much larger than that of the creviced electrode. The reference electrode was a homemade Ag/AgCl electrode in a saturated KCl solution [32]. Before and after each experiment its potential was checked against a saturated calomel electrode (SCE) that was used only as a reference electrode, and the difference was always -45 ± 3 mV.

For each experiment, 500 cm³ of electrolyte solution was air saturated by agitation in air. The sealed assembly was then pressurized with 400 kPa of ultra-high purity Ar gas (Praxair) to ensure proper sealing of the pressure vessel. In this study two galvanostatic currents, 10 μA and 200 μA, were applied to the working electrode at 150°C and the crevice potential (E_c) response measured using an a WaveDrive 20 bipotentiostat (Pine Instruments).

### 3.2.2 Analyses of Corroded Electrodes

After the experiment the creviced electrodes were washed with de-ionized water and rinsed with ethanol and dried using Ar gas. The crevice corroded surface and depth of corrosion propagation were then examined by optical microscopy, SEM, and energy-dispersive X-ray spectroscopy (EDS).

A LEO (Zeiss) 1540XB FIB/SEM was used for imaging in secondary and backscatter modes and a beam energy of 10 KeV was used for all EDS analyses.

To measure the depth of corrosion penetration, the sample was polished from the edge of the sample toward the center of the corroded area until the center was reached. Image analysis software (Image Pro Plus) was used to measure the total damaged area within the crevice and also the maximum depth of crevice penetration. EDS was used to determine the composition of the corrosion products on the corroded surface and to map the corrosion front on a cross-sectioned crevice.
A series of BC1 alloy specimens were weighed before and after corrosion weight loss ($W$) measurements were performed after corrosion due to constant applied charge ($Q_A$—the applied current multiplied by the time for which it was applied). The dark-colored, gel-like corrosion products were removed by wiping immediately on completing the experiment. The specimen was then rinsed with water and ultrasonically cleaned in ethanol for 5 min and dried in UHP Ar. The working electrode was dried in the desiccator for 1 day before being weighed. An uncertainty in $W$ arises from the fact that some corrosion products that segregated to grain boundaries could not be removed by this method, which leads to an under-estimation of $W$.

A 10 ml volume of the solution, sampled after the corrosion experiment, was analysed by inductively-coupled plasma mass spectrometry (ICP-MS) to measure the amounts of dissolved Cr, Mo and Ni in the solution. The detection limit was 0.2 μg/L for dissolved Mo and Cr and, for Ni, 0.001 μg/L.

### 3.3 Results and Discussion

#### 3.3.1 Crevice Corrosion under Galvanostatic Conditions

![Diagram](image)

Figure 3.1: Schematic of the $E_C$-time response to an applied current showing the three distinct regions of anodic oxide film growth (1), crevice activation (2) and crevice propagation (3).
Figure 3.1 shows a schematic illustration of the $E_C$ response of an alloy on application of a constant current. Three distinct regions are observed:

1. At short times $E_C$ increases with time as the applied current forces the anodic growth of the passive oxide film.
2. $E_C$ reaches a maximum and then decreases as the alloy undergoes the passive-to-active transition associated with activation of corrosion sites within the creviced region.
3. $E_C$ achieves an approximately steady-state value indicating the establishment of active propagation conditions within the crevice.

The activation stage (2) represents the period required to establish a sufficiently large IR drop and critical crevice solution [33,34] to place the creviced locations in an active region [35].

Figure 3.2 (a) and Figure 3.2 (b) show the measured $E_C$ for currents of 10 μA, applied for 4 days, and 200 μA, applied for 6 days, for the three alloys. A previous study [29] showed that a minimum current of 10 μA was needed to initiate crevice corrosion in a crevice of the same geometry on the C22 alloy at 120°C. Therefore, the 10 μA current was chosen to study the stages involved in the transition from passive to active behaviour. At the higher current this transition was rapid and the electrode was in the active propagation stage for the majority of the experiment.

In stage 1, $E_C$ rose rapidly and at an effectively identical rate for the two high-Cr alloys (C22 and C625) and to a higher value than for the low-Cr alloy (BC1). Although only a qualitative feature, this increase illustrated the more rapid growth of the Cr(III) oxide barrier layer associated with passivity on the high-Cr alloys [36]. The slower rise in $E_C$, and lower potential threshold for the onset of activation, for the BC1 alloy could then be attributed to its lower Cr content. At the higher applied current, the difference in behaviour between the high and low-Cr alloys in stage 1 became distinctly more marked. A considerably higher potential threshold was observed for the C22 and C625 alloys and
that for the BC1 alloy was significantly reduced. While the absolute value of $E_C$ had no particular significance, the comparative effect was consistent with the influence of Cr content on breakdown potentials [23].

![Figure 3.2](image.png)

Figure 3.2: $E_C$ versus time for the three alloys: (a) and (b) under galvanostatic polarization at 10 μA; and (c) and (d) under galvanostatic polarization at 200 μA.

The activation pattern (stage 2) also varied with alloy composition and applied current, Figure 3.2. As expected, the time required to complete activation was shorter at the higher applied current (Figure 3.2 (c)) and predominantly determined by Cr content, being completed in ~ 45 min to 1 h for the high-Cr alloys but almost instantaneously for the low-Cr-containing BC1 alloy. Passivity was not established on the BC1 alloy prior to the activation of crevice corrosion.
At the lower applied current, however, activation occurred much more slowly, and the time required to complete the activation process was not directly related to the Cr content of the alloy. Despite the high Cr content, activation occurred in 1 h on the C625 alloy with a Mo content of only 9 wt.%. For the BC1 alloy, activation required 3 to 4 h despite the significantly lower Cr content, showing that once the Cr(III) oxide layer was breached the establishment of active crevice propagation conditions was predominantly controlled by the Mo content. Closer inspection of the $E_C$-time plot for the BC1 alloy during the activation stage detected minor negative-going transients (not shown in Figure 3.2 (a)), which are typical of metastable film-breakdown/repair events [37]. As noted previously [20,38], such transients have been attributed to the suppression by Mo of breakdown events that lead to establishment of active crevice sites. While the very high Mo content could suppress these minor metastable events, it could not prevent eventual activation at such a low Cr content.

For the C22 alloy, the passive-to-active transition was not so readily achieved, and major fluctuations occurred, the alloy apparently making a number of major attempts to activate before finally achieving the fully activated state. Since the Cr and Mo contents are inverted in this alloy compared to those in the BC1 alloy (Table 3-1), this behaviour was consistent with an improved ability to resist film breakdown, due to the high Cr content, but a lower ability to resist activation, due to the lower Mo (or Mo + W) content. The competition between these two processes results in a slightly longer period to complete activation on C22 than on the BC1 alloy.

Once active corrosion was fully established (stage 3), $E_C$ achieved an approximately steady-state value for all three alloys, Figure 3.2 (b) and (d). As shown in Figure 3.3, the average $E_C (\pm \sigma)$ over the propagation time in stage (3) was proportional to the Mo content of the alloy, but only slightly dependent on the applied current. This suggests that the chemistry in active locations within the crevice was controlled predominantly by Mo. Although, when determined using an external reference electrode, the value of $E_C$
measured is the potential outside the crevice mouth, it is influenced by the potential achieved at the active locations within the crevice.

Figure 3.3: $E_C$ as a function of alloy Mo content for crevice corrosion with applied currents of 10 and 200 μA: the range shows the average, maximum and minimum $E_C$ at each current.

Thus, the increasingly positive $E_C$ observed (for the same applied current) as the alloy Mo content increased indicated that active conditions were more difficult to sustain on alloys with high Mo content, consistent with the expectation that Mo will suppress the active dissolution rates. The lack of dependence of $E_C$ on applied current indicates that the active corrosion process is not solely driven by the externally applied current but is also dependent on other reactions occurring inside the crevice. The important role of internal crevice reactions has been noted before in the crevice corrosion of titanium [32,39], with a large fraction of corrosion being driven by internal proton reduction leading to hydrogen evolution.
Both the absolute value of, and the fluctuations in, $E_C$ were dependent, in amplitude and frequency, on the Mo content, Figure 3.2 (d). A possible explanation for this behaviour is that the fluctuations indicated the propagation of active corrosion within freshly exposed (activated) sites, which would exhibit a low $E_C$, with the eventual rise in $E_C$ indicating the build-up of Mo at those locations. Such a process would be rapid for the high-Mo BC1 alloy, on which $E_C$ was steady, but slower for low-Mo C625, on which $E_C$ fluctuated significantly.

### 3.3.2 EDS and SEM Analyses

Figure 3.4 shows an optical image of the corroded surface of the BC1 alloy after corrosion at an applied current of 200 $\mu$A, and the stained Teflon crevice former removed from it. As expected, the crevice initiated near the edge (crevice mouth) and propagated both along the edge and into the creviced region. Beyond the actively corroded area, the majority of the uncorroded creviced area was stained by acid, and probably also some redeposited corrosion products which diffused out of the active area.

![Figure 3.4: The surface of the BC1 alloy and the removed Teflon crevice former after crevice corrosion at 200 $\mu$A and 150°C for 6 days.](image)

Figure 3.5 (a) and (b) show the corrosion product deposit within the crevice and at the crevice mouth, respectively. The flaky product within the crevice indicated the formation of a hydrated layer which dried and cracked on removal from the cell. Minimal
deposition of corrosion product was observed outside the crevice mouth. Similar corrosion product morphology was observed on the C22 and C625 alloys for locations both inside and just outside the crevice. The EDS analysis, Figure 3.5 (c), shows that the dominant alloying element present in the deposit within the crevice was Mo.

Figure 3.6 shows SEM images and the corresponding EDS maps for Ni, Cr, Mo and O, for all three alloys after corrosion with an applied current of 200 µA. The elemental analyses show similar trends for all three alloys. The signal intensities show that both Ni and Cr are depleted in the actively corroded areas while Mo and O are enriched with respect to the base metal composition, as expected based on the EDS spectrum in Figure 3.5 (c). The intensity of the Mo signal recorded on the BC1 alloy, which has the highest Mo content, is 2.7 times more than that of the base metal, while this ratio is 2.6 and 2 for C22 and C625, respectively. For all three alloys, the enhanced signal for Mo in the actively corroded areas is consistent with previous observations on the C22 alloy [36,40]. The irregular corrosion front between the actively corroded area and the uncorroded alloy suggests that the propagation of this front is slightly enhanced along the grain boundaries in the alloy, particularly for the two high-Mo containing (Mo + W for C22) alloys.

![Image](image.png)

**Figure 3.5:** Corrosion morphology of the BC1 alloy (a) in the creviced region, (b) crevice mouth region, and (c) EDS analysis of the corrosion products at the location marked with an X.

Table 3-2 summarizes the EDS analyses of the crevice corroded areas on the three alloys after corrosion at 200 µA. The values are the average of three measurements within each
creviced area. For all three alloys, comparison of these results to the original elemental content of the alloys, Table 3-1, confirms the common feature of Cr and Ni depletion and Mo enrichment (Mo + W for C22). The high Cl and low Na signals reflect the ionic migration of Cl\(^-\) ions into the creviced region to balance the positive charges created in the crevice by the oxidation half-reaction, and to compensate for the excess of anions outside the crevice due to oxygen reduction to hydroxide ions or water reduction to hydrogen and hydroxide ions on the CE [36,41].

ICP-MS analyses of the bulk electrolyte after crevice corrosion of the C22 alloy detected 346 µg·L\(^{-1}\) of Ni, 74.4 µg·L\(^{-1}\) of Cr, and 16 µg·L\(^{-1}\) of Mo, (79.4%:17%:3.6% Ni:Cr:Mo by wt.) confirming the dissolution and transport out of the crevice of Cr, and especially Ni, and the relative retention of Mo within the crevice. Although no analyses were performed for the other two alloys, similar active dissolution behaviour would be expected. Since EDS analyzes to a depth of a few micrometers, the small Ni signal detected for the C625 alloy, Table 3-2, suggests that the Mo corrosion product layer may have been thinner on the creviced surface of this alloy.

Table 3-2: EDS analyses of corrosion products (wt.%).

<table>
<thead>
<tr>
<th>Alloy/Elements</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>O</th>
<th>Na</th>
<th>Cl</th>
<th>W</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>C22</td>
<td>-</td>
<td>13.60</td>
<td>35.94</td>
<td>28.37</td>
<td>1.25</td>
<td>9.28</td>
<td>11.55</td>
<td>-</td>
</tr>
<tr>
<td>BC1</td>
<td>-</td>
<td>5.07</td>
<td>60.23</td>
<td>23.33</td>
<td>1.11</td>
<td>8.79</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>C625</td>
<td>3.8</td>
<td>11.6</td>
<td>18.3</td>
<td>30.9</td>
<td>9.0</td>
<td>11.6</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>
Figure 3.6: SEM images of the crevice corrosion fronts and the Ni, Cr, Mo and O EDS maps on the surfaces of the BC1, C22 and C625 alloys. The EDS maps are on the same scale as the SEM images.

### 3.3.3 Distribution of Corrosion Damage

Figure 3.7 and Figure 3.8 show the damaged areas within the crevice and a set of polished cross sections for all three alloys after crevice corrosion at 10 µA and 200 µA, respectively. The damaged areas are marked in red and the edge (mouth) of the crevice is defined by the white dashed lines. In all cases, only a single location within the crevice is corroded, and, with the exception of the crevice on C625 propagated at 10 µA (Figure 3.7 (a)), the damaged areas are all close to the edge (mouth) of the crevice, as expected. Using these damage maps and cross sections, crevice penetration depths and corroded surface areas were measured, Figure 3.7 and Figure 3.8 ((g) and (h)). Since the penetration depths reported are measured as the deepest location on the single cross sections shown, they are not necessarily the maximum penetration depths within the entire damaged region.

The applied charge ($Q_A$) in experiments employing a current of 10 µA was 3.46 C on all three alloys and 103.68 C in the experiments with a current of 200 µA. The charge
calculated from volume of material loss by corrosion is defined as \( Q_V \) and is calculated by equation (3-1).

\[
Q_V = \frac{\rho \times n \times F}{M} \times V
\]  

(3-1)

where \( M \) is the effective molar mass (the weighted average molar mass based on alloy composition) and \( F \) is the Faraday constant, \( \rho \) is the density and \( n \) is the number of equivalent moles of electrons and \( V \) is the corroded volume. The three alloys have similar densities 8.83 g.cm\(^{-2}\) (BC1); 8.69 g.cm\(^{-2}\) (C22); 8.44 g.cm\(^{-2}\) (C625)) and the number of equivalents of electrons per mole of metal atoms involved in the corrosion reaction for all alloys is nearly identical, since they contain the same alloying elements. To estimate the volume of damage accumulated on the three alloys, the depth of the crevice was multiplied by the area corroded. As shown in Figure 3.7 and Figure 3.8, at both applied currents the corroded volumes \( V \) are effectively the same for all three alloys (~0.32 mm\(^3\) (10 µA) and ~6 mm\(^3\) (200 µA)) despite the 30-fold difference in total applied charge. This similarity indicates that \( Q_A \) is directly proportional to \( Q_V \), with the alloys having similar \( Q_A/Q_V \) ratios at each applied current (within the error range of the crevice depth and surface area measurements). An equivalent charge \( Q_W \) can also be calculated from the weight change \( W \) due to corrosion using equation 3-2, 

\[
Q_W = \frac{W \times n \times F}{M}
\]  

(3-2)

where \( W \) is the weight change due to corrosion. These \( Q_W \) values will be an underestimate since not all the corrosion products accumulated in the grain boundaries could be removed. The ratio \( Q_A/Q_W \) is a measure of the fraction of the corrosion driven by the external applied current. A value of \( Q_A/Q_W = 1 \) would indicate all the crevice corrosion was due to the external applied current and none was supported by the reduction of protons in the extremely acidic crevice environment inside the crevice.
Three weight loss measurements were made on corroded BC1 crevices and converted to $Q_w$ to estimate the $Q_A/Q_w$ ratio. Each weight loss measurement was for an accumulated $Q_A$ of 6.9 C and they yielded $Q_A/Q_w$ ratios of 48.4%, 29.4%, 22.6%. While variable, and bearing in mind that these $Q_w$ values are underestimates, the $Q_A/Q_w$ ratios indicate that $\geq 50\%$ of the overall crevice damage was caused by proton reduction inside the crevice. This offers an explanation for the observed independence of $E_C$ on applied current once the crevice is initiated (Figure 3.2).

Although the total volume of corrosion may be the same on each alloy, its distribution varies markedly from alloy to alloy. As the Mo content of the alloy increases in the order

\[
C625 (9\% \text{ Mo}) < C22 (13\% \text{ Mo (3\% W)}) < BC1 (22\% \text{ Mo})
\]

the depth of penetration decreases, while the area corroded increases.
Figure 3.7: Alloy surfaces after crevice corrosion at an applied current of 10 μA. The top row shows optical images of the crevice-corroded surface areas of (a) C625, (b) C22 and (c) BC1 alloys. The corroded region is coloured red. The dashed white lines in (a) – (c) show the edge of the creviced region as defined by the location of the crevice former. The middle row gives SEM images of crevice-corroded cross sections of (d) C625, (e) C22 and (f) BC1 and the bottom row plots (g) the maximum crevice depths, (h) crevice-corroded surface areas and (i) crevice region volumes for the three alloys.
Figure 3.8: Alloy surfaces after crevice corrosion at an applied current of 200 μA. The top row shows optical images of the crevice-corroded surface areas of (a) C625, (b) C22 and (c) BC1 alloys. The corroded region is coloured red. The dashed white lines in (a) – (c) show the edge of the creviced region as defined by the location of the crevice former. The middle row gives SEM images of crevice-corroded cross sections of (d) C625, (e) C22 and (f) BC1 and the bottom row plots (g) the maximum crevice depths, (h) crevice-corroded surface areas and (i) crevice region volumes for the three alloys.

Figure 3.9 shows that the depth of crevice penetration decreases markedly as the Mo + W content of the alloys increases (W is present only in C22 but enriched like Mo within the crevice (Table 3-2) and known to exert an identical influence on crevice propagation [31]). Figure 3.10 shows the depth of penetration as a function of the Mo + W content of the original alloys (Table 3-1) for both applied currents. For a sufficiently high Mo + W content the penetration depth is only marginally dependent on the applied current, confirming that the dominant factor controlling active propagation is the chemical influence of Mo + W. By contrast, the depth of penetration on the C625 alloy increases
markedly when the applied current is increased, a strong indication that active propagation is still mainly controlled by the cathodic reaction proceeding outside the crevice, which could reflect a higher $Q_v/Q_w$ ratio, although this remains to be demonstrated.

The damage maps in Figure 3.7 and Figure 3.8 show that, besides the total area actively corroded, the lateral dimensions of damage propagation also vary with the alloy composition. This is particularly noticeable for the C22 and BC1 alloys. For both alloys propagation follows the edge of the crevice, but there is a more marked tendency for propagation towards the centre of the crevice on BC1 than on C22. While observable in experiments with an applied current of 200 µA, Figure 3.8 ((b) and (c)), it is more obvious in experiments at the lower current (10 µA), Figure 3.7 ((b) and (c)). This ability to propagate more deeply into the crevice could reflect the lower Cr content of the BC1 compared to C22; i.e., it is kinetically easier to activate areas at deeper locations on BC1. As discussed above, the results in Figure 3.2 show that activation involves a competition between breaching the Cr(III) oxide barrier layer and the tendency to repassivate the breakdown site by the accumulation of molybdate and tungstate deposits, and that activation is more readily achieved on the low-Cr-containing BC1. An explanation for this effect in terms of the potential distribution within the crevice (i.e., according to the IR drop model [35,42]) is not so readily constructed, indicating that chemical effects are dominant in determining crevice corrosion behaviour on these alloys at these enforced propagation rates.
Figure 3.9: The crevice depth in experiments at 200 μA vs. the content of Mo + W in the corrosion products (Table 3-2).

Figure 3.10: The crevice depth for experiments at both applied currents as a function of the Mo + W content in the uncorroded alloys (Table 3-1).
3.3.4 Chemistry in Crevice-Corroded Regions

The local chemistry within the active crevice is clearly a key feature in controlling the activation of corrosion and the propagation of the accumulated damage. The pH in active locations could approach zero [20,43]. Potential-pH diagrams for the three key elements (Ni, Cr, Mo), calculated for 4 M NaCl (at 120°C) show that both Cr₂O₃ and NiO are unstable at pH < 3. Cation solubility is increased by the formation of chloride complexes (e.g., CrCl²⁺, NiCl⁺). Thus, the loss of Cr and Ni as soluble species from the creviced area, detected by solution analyses and indicated by their absence from the corrosion products deposited within the crevice, is not surprising. The redeposition of Cr, as Cr(OH)₃ or Cr₂O₃, at the higher pH values prevailing outside the crevice would be expected [40].

The role of Mo in controlling the active corrosion within a propagating crevice has been previously investigated [29–31], and the accumulation of Mo(VI) as polymeric species such as Mo₈O₂₆⁴⁻ (and possibly also as Mo₇O₂₄⁶⁻ and Mo₃O₁₀²⁻) demonstrated using Raman spectroscopy [31]. Although undetected in this Raman analysis [31], W is expected to accumulate as polymeric tungstates also.

The initial dissolution of Mo within an activating crevice will be as MoO₄²⁻,

\[
\text{MoO}_2 + 2 \text{H}_2 \text{O} \rightarrow \text{MoO}_4^{2-} + 4 \text{H}^+ + 2\text{e}^- \quad (3-3)
\]

but even for pH values slightly < 6.5, paramolybdate species are known to form via proton-consuming reactions[44,45] such as:

\[
7\text{MoO}_4^{2-} + 8 \text{H}^+ \rightarrow \text{Mo}_7\text{O}_{24}^{6-} + 4\text{H}_2\text{O} \quad (3-4)
\]

Similar reactions are anticipated for W [41,44].
supporting our argument that W will exert an influence similar to that of Mo within an active crevice. It was previously suggested [31] that the ability of Mo (and W) to suppress crevice propagation can be attributed to this tendency to polymerize, with the extent of polymerization, and hence, proton consumption, increasing markedly as the pH decreases,

$$6 \text{WO}_4^{2-} + 7 \text{H}^+ \rightarrow \text{HW}_6\text{O}_2^5^- + 4 \text{H}_2\text{O} \quad (3-5)$$

$$8 \text{MoO}_4^{2-} + 12 \text{H}^+ \rightarrow \text{Mo}_8\text{O}_{26}^{5-} + 6 \text{H}_2\text{O} \quad (3-6)$$

Under the constant current conditions used in our experiments, metal dissolution will be on-going at a constant rate. Since this rate is the same (at the same current) irrespective of the alloy composition, the rate of production of dissolved metal species will be constant, leading to the on-going production of acidic conditions by cation hydrolysis processes, particularly for Cr, Mo and W, e.g.,

$$\text{Mo}^{6+} + 4 \text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 8 \text{H}^+ \quad (3-7)$$

$$\text{Cr}^{6+} + 4 \text{H}_2\text{O} \rightarrow \text{CrO}_4^{2-} + 8 \text{H}^+ \quad (3-8)$$

Although some of the protons produced by these reactions will be consumed by the polymerization reactions, the modification of the local pH by molybdate formation will not be as significant as suggested previously [8,46]. Each mole of Mo will, at best, neutralize 1.5 moles of H\(^+\) (equation 3-6) while the hydrolysis of 1 mole of Mo\(^{6+}\) leads to the formation of 8 H\(^+\) (reaction 3-7). In addition, the hydrolysis of other alloy elements such as Cr and W (for C22 alloy) will also produce H\(^+\), 8 in the case of Cr\(^{6+}\) (reaction 3-8). Thus the production of H\(^+\) will far exceed its consumption by molybdate formation, and polymerization will have little effect on the pH. The more likely influence of
molybdate formation is that it stifles active alloy dissolution by formation of a protective layer. The more rapid production of large amounts of soluble Mo(VI) for the high-Mo-containing alloy (BC1) compared to the low-Mo-containing alloys (C22, C625) would then lead to the more rapid blockage of active sites. The analyses in Table 3-2 show that the Mo content of the corrosion product deposit increased with the Mo content of the alloy. However, whether this reflects a higher Mo content of the polymeric layer or a thicker molybdate layer is uncertain.

Irrespective of which of these is the case, the correlation between the Mo content of the corrosion product and the depth of penetration confirms the ability of such a layer to stifle active dissolution. Since repassivation is prevented under constant current conditions, this local site suppression leads to the lateral spread of propagation, as previously described for C22 [31], a process which requires the ongoing activation of new sites. This is sustained by the concentration of current around the periphery of the expanding damage area.

3.4 Conclusion

The effects of the alloying elements Cr, Mo and W on crevice corrosion initiation and propagation on three commercial Ni alloys were investigated under galvanostatic control in 5 M NaCl at 150°C. The galvanostatic approach was used to study activation and propagation by avoiding repassivation.

The activation step was shown to depend on the Mo content of the alloy and to involve competition between Cr(III) barrier layer breakdown and Mo(VI)/W(VI) accumulation to repair breakdown sites.

Under stable propagation conditions the $E_C$ measured is proportional to the Mo + W content of the alloy, and almost constant and independent of the applied anodic current, indicating that propagation is controlled by the crevice chemistry.
Mo content determines the distribution of corrosion damage. For C625 (9wt.% Mo) propagation leads predominantly to penetration into the alloy, whereas increased Mo content (C22 (13 wt.%) and BC1 (22 wt.%) ) causes corrosion damage to spread laterally across the creviced surface. This is attributed to formation of polymeric molybdates, which occurs more rapidly as the Mo content increases, and limits the depth of penetration into the alloy.

The primary influence of Mo is to stifle the dissolution of the alloy by accumulation at active sites. Its influence on controlling pH within the crevice is minor.

Greater than 50% of propagation is caused by proton reduction inside the crevice.

3.5 Acknowledgment

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3.6 References


Chapter 4

4 A New Approach on Crevice Corrosion Investigation of Ni-Cr-Mo Alloy Hybrid BC1


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Abstract

The initiation and propagation of crevice corrosion on the Ni–Cr–Mo Alloy BC1 (Ni-15Cr-22Mo) has been studied in concentrated chloride solutions at 120°C under galvanostatic conditions. Corrosion damage patterns were then investigated using surface analytical techniques such as scanning electron microscopy (SEM) and optical imaging and profilometry. Corrosion products were also characterized by energy dispersive X-ray spectroscopy (EDS).

The corrosion damage morphology demonstrates that applying a higher current leads to preferential propagation of crevice corrosion across the alloy surface rather than deep penetration at localized sites. When the current was applied galvanodynamically, decreasing from a higher value to zero, the crevice propagation continued even after the applied current reached zero if the creviced electrode was then coupled to the boldly exposed surface of a counter electrode of the same material. In one such case, the crevice corrosion was able to sustain itself for more than 1200 h.

Keywords: Hybrid BC1, Ni-Cr-Mo alloy, Crevice corrosion
4.1 Introduction

The ability of nickel to retain large amounts of different alloying elements in solid solution has led to the development of several binary, ternary and other complex Ni-based families of alloys [1], with each family designed for specific applications. Commercially pure Ni is widely used in caustic environments, and addition of Cu to Ni improves its corrosion resistance in reducing environments, such as hydrofluoric acid, but the corrosion resistance in oxidizing media is poor [2,3]. Ni-Mo alloys show excellent resistance to reducing acids (HCl and H$_2$SO$_4$) even at elevated temperature but the lack of Cr makes them susceptible to corrosion in the presence of oxidizing species such as ferric and cupric ions and dissolved oxygen. Ni-Cr-Mo alloys were designed to extend corrosion resistance to both reducing and oxidizing environments, with the Hybrid-BC1 developed to fill the gap between Ni-Mo and Ni-Cr-Mo alloys [4]. This alloy has a better resistance to reducing environments than the Ni–Cr–Mo alloys, but also resists corrosion under oxidizing conditions and has a high resistance to localized corrosion. These properties make the BC1 alloy suitable for a wide range of applications in the chemical processing, pharmaceutical, agricultural, food, petrochemical and power industries [5,6].

The reliable performance of Ni-Cr-Mo alloys under extreme industrial conditions is generally attributed to the presence of a passive film on the alloy surface [7,8]. However, under localized corrosion conditions when this film is breached, the alloying elements play a major role in controlling propagation and inducing repassivation. While the crevice corrosion of a range of Ni-Cr-Mo alloys has been studied [9–12], information on the crevice corrosion of the BC1 alloy is sparse. A recent comparison [4] of the C22 (Ni-22Cr-13Mo-3W) and BC1 (Ni-15Cr-22Mo) alloys in a 1 M HCl solution (90°C), simulating the conditions inside an active crevice, showed that, while the current density for active dissolution was lower, the passive current density on the high-Mo BC1 was greater than that on the high-Cr C22. Crevice repassivation potentials ($E_{R,Crev}$) for the two alloys showed that the BC1 alloy repassivated at higher potentials, indicating a beneficial effect of Mo on repassivation.
Recent studies on a wide range of Ni-Cr-Mo alloys showed that their resistance to crevice corrosion, based on breakdown and repassivation potentials and protection temperatures, improved as the Mo content increased [11,13]. In many of these studies the potentiodynamic–galvanostatic–potentiodynamic (PD–GS–PD) technique [14] was used to measure breakdown and repassivation potentials. While this technique provides fast and reliable measurements of the susceptibility to crevice corrosion, allowing the expected corrosion performance of various alloys to be ranked, it does not provide significant mechanistic information.

In this study, a combination of galvanostatic and galvanic-coupling techniques has been applied to study the various stages of crevice corrosion (initiation/activation, propagation and repassivation), with the primary goal of investigating the influence of the decreased Cr and increased Mo content of the BC1 alloy (Ni-15Cr-22Mo) compared to the well-studied C22 alloy (Ni-22Cr-13Mo-3W).

The galvanostatic technique has been used [12,15,16] to study a number of Ni-Cr-Mo alloys. The use of galvanostatic control guarantees initiation and prevents repassivation. This allows the propagation process to be investigated under conditions where both the rate of the external cathodic reaction and the total extent of electrochemically-inflicted damage can be controlled. Using the galvanic coupling technique previously used to study titanium alloys [17,18], in which a creviced electrode is galvanically coupled to a large counter electrode of the same material, all stages of the crevice corrosion process can be monitored. However, our previous studies [15,19] have shown that it is difficult to initiate crevice corrosion on Ni-Cr-Mo alloys under these natural corrosion conditions. In this study the galvanic coupling technique is used to follow the later stages of propagation (initiated galvanostatically) and repassivation.
4.2 Experimental

4.2.1 Experimental Arrangement

The composition of the Hybrid-BC1 Ni-Cr-Mo alloy is given in Table 4-1. Specimens were cut from mill annealed sheets supplied by Haynes International (Kokomo, IN, USA). The specimens had a thickness of 3.17 mm and were bent in to a V shape to produce an artificial creviced assembly. A small polytetrafluoroethylene (PTFE) wafer was used to produce a single crevice with an area of ~ 4 cm². The crevice tightness was adjusted using a PTFE “feeler” strip. The crevice electrode design and assembly have been described elsewhere [12,15]. Prior to each experiment, the crevice face and crevice former were polished with wet SiC papers from a 320 to a 1200 grit finish. All parts of the crevice assembly were rinsed in de-ionized (DI) water and sonicated in ethanol for 10 minutes.

All measurements were performed in 5 M NaCl solutions prepared using reagent grade NaCl crystals (Caledon Chemicals) and Type 1 water with a resistivity of 18 MΩ.cm. Prior to each experiment, the solution was vigorously agitated to ensure saturation with air. All experiments were performed at 120°C inside a cylindrical pressure vessel modified as an electrochemical cell. A Teflon liner was used to prevent contact of the electrolyte with the pressure vessel body. All measurements were made using a homemade Ag/AgCl electrode in saturated KCl solution (-45 mV vs. SCE) with the reference electrolyte solution contained within a PTFE container [20]. The counter electrode was of the same material as the working electrode, with a surface area ~ 50 times bigger than that of the creviced electrode to simulate the small anode/large cathode geometry generally prevailing during localized corrosion [21]. In galvanic coupling experiments, a BC1 planar electrode, 20 mm in length and 5 mm in width and thickness, was used to reveal the difference in corrosion potential ($E_{CORR}$) between the crevice/counter couple and a sample of the same material with no crevice. Before heating, the pressure vessel was tested for leaks by pressurizing it with UHP N₂ gas.
After the cell was heated to the desired temperature and the crevice electrode potential ($E_C$) had stabilized, electrochemical measurements were performed.

Table 4-1: Limiting chemical composition (wt.%) of BC1 alloy.

<table>
<thead>
<tr>
<th>Alloy/Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Fe</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>BC1</td>
<td>62</td>
<td>15</td>
<td>22</td>
<td>2</td>
<td>0.01</td>
<td>0.25</td>
<td>0.08</td>
</tr>
</tbody>
</table>

### 4.2.2 Electrochemical Measurements

Both galvanostatic and galvanodynamic polarization techniques were used to probe the crevice corrosion behaviour of the BC1 alloy. In galvanostatic experiments, a charge of 6.9 C was applied to the working electrode by passing anodic currents of 80 μA, 40 μA, 20 μA or 10 μA for 24 h, 48 h, 96 h or 192 h, respectively. The potential response was measured using a WaveDrive 20 bipotentiostat (Pine Instrument Company).

In galvanodynamic polarization experiments, $E_C$ was measured as the current was decreased from a set value (80 μA) at a constant rate of -0.464 nA/s. In other experiments, both galvanodynamic polarization and galvanic coupling were employed; after the current was ramped to zero, the creviced electrode was coupled to the counter electrode through a zero-resistance ammeter (Keithley model 6514) and the current flowing between the electrodes ($I_C$) recorded. During this coupling, $E_C$ and the potential of the planar electrode ($E_P$) were measured with a high input impedance analogue-to-digital converter (ADC) (Iotech, ADC 488/16A). After 36 days $O_2$ was added to the cell and $E_C/I_C$ measurements continued.

Potentiodynamic polarization experiments were performed in a deaerated simulated crevice solution (1 M HCl + 4 M NaCl, pH = 0) at 120°C. $E_{CORR}$ was measured for 20 min to ensure a stable surface condition. $E_{CORR}$ was measured for 20 min to ensure a stable surface condition and then a potential scan was applied at a rate of 0.167 mV/s.
Scans were started from $E_{\text{CORR}} - 50 \text{ mV}$ and extended up to a value at which an abrupt increase in anodic current density occurred.

### 4.2.3 Post-corrosion Surface Analysis

When each experiment was completed, the creviced specimen was rinsed in deionized water and ethanol, and dried using UHP Ar gas. The specimen was then photographed using a digital camera and image analysis software (Image Pro Plus) was used to analyze the creviced surface. A Hitachi S-4500 field emission scanning electron microscope (SEM) equipped with an EDAXM energy-dispersive X-ray spectroscopy (EDS) system was used to examine the surface features and analyze the composition of the corroded sample.

Surface profilometry was used to obtain a 3 dimensional (3D) image of the corroded area and to measure the penetration depth in the corroded region. A mechanical stylus profilometer with a diamond tip (~2 μm in radius) was scanned over the surface at a speed of 50 μm/s. By stitching together the profiles obtained from a series of line scans over the surface, a 3D topographic image of the corroded area was reconstructed [11].

### 4.3 Results and Discussion

#### 4.3.1 Crevice Corrosion under Galvanostatic Polarization

Figure 4.1 shows $E_C$ for the first 25 h of experiments at 4 different values of applied current. As noted in chapter 3 [16], these curves exhibit 3 distinct regions; (i) an initial rise in $E_C$ as the passive film, comprising an inner Cr(III)/Ni(II) barrier layer and an outer Mo(VI) layer [22,23], is forced to grow by the applied current; (ii) a rapid decrease in $E_C$ as the passive-to-active transition occurs; and (iii) the establishment of a steady-state $E_C$ once active propagation conditions are established within the crevice. While these curves are similar in overall form to those previously recorded on C22 [15], they differ quantitatively. Though noisy, $E_C$ does not exhibit the major potential excursions observed on C22. This can be attributed to the high Mo content in BC1 which suppresses
the attempted activation events, observed as large transitory decreases in $E_C$ on C22, by the rapid formation of molybdates at the film breakdown sites. The ability of Mo to repair attempted breakdown sites rapidly would also explain the longer times required to initiate the passive-to-active transition on BC1 (e.g., ~22 h at an applied current of 10 µA, compared to ~7 h for C22 at the same current) [12,15]. These observations are consistent with the metastable behaviour on Ni-Cr-Mo alloys observed by others [24,25].

Except for the largest applied current (80 µA), the passive-to-active transition occurs once $E_C$ reaches a value in the range 200 mV to 300 mV vs. Ag/AgCl. This is consistent with previous results for C22 which showed the initiation of crevice corrosion requires the onset of the transpassive conversion of the passive Cr(III) layer to Cr(VI), leading to the destruction of the passive film barrier layer. A combination of electrochemical impedance spectroscopy [15,26], X-ray photoelectron spectroscopy, and time-of-flight secondary ion mass spectrometry [23] showed this occurs for potentials $\geq$ 200 mV, as indicated by the dashed line in Figure 4.1.

![Figure 4.1: First 25 h of the $E_C$ vs. time plots recorded on the BC1 alloy at various applied currents.](image)

The dashed line shows the 0.2 V thresholds for the onset of the passive-to-active transition [17].
Once the passive-to-active transition has occurred the noise associated with $E_C$ effectively disappears, indicating that once active conditions have been established, the applied current is used in propagation not the initiation of additional active sites. This is consistent with previous observations on a number of alloys, which exhibit only one propagating site \[16\], and with the results of this study (see below).

Although not shown in Figure 4.1, $E_C$ eventually reaches a steady-state value, $(E_C)_{SS}$, when stable propagation conditions are achieved within the creviced region, indicating the establishment of the critical crevice solution \[27,28\] and potential. $(E_C)_{SS}$ is the potential at the mouth of the crevice, the actual potential at active locations within the crevice being lower as a consequence of the IR drop associated with the crevice \[29\]. Figure 4.2 shows $(E_C)_{SS}$ is independent of the applied current over the range used in this study.

![Figure 4.2: The steady-state crevice potential, $(E_C)_{SS}$, (from Figure 4.1) as a function of applied current.](image)
This independence indicates that the propagation process is not electrochemically controlled by the external current. This is probably the consequence of internal proton reduction as discussed before in chapter 3. In our previous study on the effects of alloying elements on crevice corrosion [16], \((E_c)_{SS}\) was shown to depend on the Mo content of a number of Ni-Cr-Mo alloys (including BC1), a feature which was shown to control the depth of corrosion penetration while making it effectively independent of the applied current for alloys with a sufficiently high Mo content.

### 4.3.2 Surface Analyses of the Corroded Region

Figure 4.3 shows optical images of the alloy corroded at different applied currents. The area covered with corrosion products is marked in red, and the dashed white lines indicate the edges of the crevice former.

![Figure 4.3](image)

**Figure 4.3:** Optical images of the surfaces after corrosion at different applied currents; (a) 10 μA, (b) 20 μA, (c) 40 μA, and (d) 80 μA: the corroded region is coloured red, and the white dashed lines show the edge of the crevice.

At some locations, particularly at an applied current of 10 μA, the red area extends to locations outside the creviced region. However, this is due to the transport and
deposition of molybdate corrosion products from within the crevice and not due to corrosion at these external locations. At all currents, corrosion started close to the crevice edge and propagated both along the edge and towards the centre of the creviced area. As the current was increased, propagation along the edge dominated, as shown by the increase in the corroded region expanded along the crevice edge, while propagation into the crevice became independent of the applied current, Figure 4.4, the latter indicating the external current is ineffective at these locations.

![Graph showing length of corroded edge and maximum depth of propagation into the crevice as function of the applied current.](image)

**Figure 4.4:** The length of the corroded edge and the maximum depth of propagation into the crevice as function of the applied current.

The total extent of crevice corrosion damage resulting from a constant applied charge in the form of different anodic currents is defined by the area of the surface corroded and the depth of penetration within that area.

Table 4-2 shows the corroded areas, determined using Image Pro® software on optical images, as a function of applied current, the tendency for corrosion to spread as the applied current was increased being clearly apparent.
Table 4-2: Corroded surface area for different applied currents.

<table>
<thead>
<tr>
<th>Applied current (µA)</th>
<th>Corroded surface area (mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>10.43</td>
</tr>
<tr>
<td>20</td>
<td>19.66</td>
</tr>
<tr>
<td>40</td>
<td>34.18</td>
</tr>
<tr>
<td>80</td>
<td>62.55</td>
</tr>
</tbody>
</table>

Figure 4.5 shows a 3D image of the alloy surface after corrosion at an applied current of 20 µA (Figure 4.3 (b)). According to the IR drop model [30], to obtain an IR drop sufficiently large to place the surface in the active region, a short distance into the crevice from the crevice mouth should remain uncorroded. Beyond this depth the maximum penetration should be achieved at the location where the anodic dissolution current achieves a maximum.

Figure 4.5: 3D image obtained by profilometry on the BC1 crevice sample corroded at 20 µA. The scale shows the relationship between colour and depth.
The location of maximum penetration can be seen as the blue valley in the image, Figure 4.5. However, the inner perimeter of the crevice does not exhibit a regular front easily interpretable according to the IR drop model. The images obtained for other applied currents show similar features, although the geometry tends to become more regular at the higher applied currents. As will be discussed in more detail below, these features reflect the redistribution of current as crevice propagation proceeds and corrosion product accumulates.

To obtain a measure of the depth of penetration, profilometry line scans were performed on samples that were corroded at the different applied currents, Figure 4.6. In some cases, as shown in Figure 4.3, the corrosion product was deposited outside the creviced region, and this deposit could not always be removed after the experiment, making it difficult to locate the uncorroded alloy surface by profilometry. This is particularly obvious in the line scans recorded at applied currents of 40 and 80 μA, Figure 4.6 ((c) and (d)). This "offset" was taken into account when calculating penetration depths.

The depth profiles recorded as line scans are similar for samples corroded at all applied currents, Figure 4.6. In all depth profiles, the depth of damage increases with increasing distance from the crevice mouth, up to a maximum depth at a distance $x_{\text{Max}}$. Farther from the crevice mouth the depth decreases. However, a single line scan may not locate the actual point of maximum depth in the entire crevice, making the values only estimates. While $x_{\text{Max}}$ is only qualitative, it is worth noting that it occurs closer to the crevice mouth as the applied current is increased, consistent with the expectations of the IR drop model [31–33].
Figure 4.6: Line scans obtained by profilometry, showing the maximum penetration depth \((x_{\text{Max}})\) at (a) 10 \(\mu\)A, (b) 20 \(\mu\)A, (c) 40 \(\mu\)A, and (d) 80 \(\mu\)A. All depth measurements were made with respect to the crevice mouth, at which the depth was set to zero.

Figure 4.7 shows plots of the creviced areas and the maximum penetration depths obtained from images and profiles such as those in Figure 4.3 and Figure 4.6. As observed previously for alloy C22 [19], the area corroded increases and the penetration depth decreases as the applied current increases. However, for BC1 the area corroded is considerably larger (10 mm\(^2\) to 65 mm\(^2\)) than C22 (1 mm\(^2\) to 35 mm\(^2\)) over the same current range for the same total charge (6.9 C). Correspondingly, the penetration depths are considerably smaller for BC1 (65 \(\mu\)m to 5 \(\mu\)m) than for C22 (82 \(\mu\)m to 20 \(\mu\)m). These results support our previous claim [16,19] that the redistribution of corrosion over a wider area is driven by the accumulation of Mo oxides at the corroding location. This
insulates that location and forces the current to relocate to areas unprotected by the presence of a molybdate deposit. As expected, this indication is more readily achieved for BC1 than for C22, due to the higher Mo content.

![Graph showing crevice area and maximum penetration depth as a function of applied current.](image)

**Figure 4.7:** Crevice area and maximum penetration depth as a function of applied current.

The presence of a Mo deposit is confirmed by the SEM image and EDS spectrum in Figure 4.8. The flaky nature of the deposit and its high Mo content are consistent with previous observations [16,34] on crevice-corroded Ni-Cr-Mo alloys. At locations closer to the centre of the crevice where the deposit either detached or was removed, the pitted nature of the alloy surface can be seen (location 2, Figure 4.8 (c)). These pits are detected in the line scans shown in Figure 4.6. Selective grain boundary attack has been shown to occur more readily on the random grain boundaries on Ni-Cr-Mo alloys, which have a large fraction of more corrosion resistant $\Sigma 3$ boundaries [35,36]. The deep penetration at triple points has been shown to be due to the higher susceptibility to corrosion of triple points between random boundaries. This will be discussed in more detail in chapter 6.
Figure 4.8: SEM images recorded after corrosion at an applied current of 20 µA: (a) the crevice mouth and corroded regions within the crevice; (b) the corrosion product accumulated near the crevice mouth (area 1); (c) the intergranularly corroded alloy surface (area 2) and (d) EDS analysis of the corrosion products at the location marked with an X.

4.3.3 Crevice Repassivation

In galvanodynamic experiments, crevice corrosion was initiated at an initial applied current of 80 µA and then the applied current was continuously decreased at a rate of 1.67 µA/h until the current reached 0. In this manner the same amount of charge (6.9 C) was injected as in the experiment at a continuously applied current of 80 µA. The rates of charge injection are compared in Figure 4.9. By steadily decreasing the applied current in this manner, we might expect the rate of propagation to slowly decrease to zero, at which point the crevice would be expected to repassivate.
Figure 4.9: The charge injection profiles for crevices corroded either galvanostatically or galvanodynamically.

Figure 4.10 shows the response of $E_C$ to the decreasing current. Once the current reached zero, $E_C$ was measured for a further period of 50 h. The inset in the figure shows that the passive-to-active transition occurred in 10 to 12 min as observed for a constant applied current of 80 µA (Figure 4.1). Figure 4.11 shows a polarization curve recorded in a simulated crevice solution (deaerated 1 M HCl + 4 M NaCl) from $E_{CORR} -50$ mV to 1.1 $V_{Ag/AgCl}$. The active, passive and transpassive regions are clearly delineated. This curve shows that under the acidic conditions anticipated in the crevice the alloy can be considered to be in the active region for potentials $\leq 0.1$ V and should have an $E_{CORR} \sim -0.1$ V. The corrosion current can be estimated with reference to the polarization curve by matching observed values of $E_C$ to the polarization curve (Figure 4.11) and estimating the associated current value. The current shows that crevice remains active showing no tendency to repassivate. However, the corrosion current values determined by this approach can only be considered estimates because the polarization curve represents the overall current only (i.e. sum of anodic and cathodic contributions at any potential).
Figure 4.10: $E_C$ vs. time and current for galvanodynamic polarization starting at $I = 80 \, \mu A$ with the current subsequently decreasing at a rate of $-1.667 \, \mu A/h$, followed by a measurement of $E_C$ on open circuit after the applied current reached 0. The insert shows the details of the first hour of applied current.
As the current was decreased, $E_C$ became significantly noisier, Figure 4.10. This can be appreciated by comparing the minor fluctuations in the current range 68 µA to 58 µA, Figure 4.12 (a), with those in the current range 8 µA to 0 µA, Figure 4.12 (b). As the current approached zero, 10-12 mV excursions were observed. Expansion of the scale shows that these excursions lasted 3 to 5 minutes, suggesting that they involved small local chemical changes within the crevice. Once the current reached zero, $E_C$ began to increase, achieving a steady-state value for the remaining 20 h of the experiment, Figure 4.10. Additionally, the potential excursions that developed as the applied current approached zero persisted, Figure 4.12 (c), until the steady-state $E_C$ was achieved, Figure 4.12 (d). Even over this final steady-state period, $E_C$ fluctuated over a 10 to 12 mV range but on a much longer time scale. This minimal increase in $E_C$ over the 50 h open circuit period ($t > 48$ h, Figure 4.12 (c) and (d)) suggests that some potential-determining locations within the crevice remained active despite the absence of an external current.

**Figure 4.11** Potentiodynamic polarization curve obtained in deaerated 1M HCl + 4 M NaCl solution at 120°C.
This is not surprising since it was previously shown [16] that > 50% of crevice propagation is supported by the reduction of protons within active crevice locations. This was attributed to the extensive hydrolysis of the highly charged cations (Cr(VI), Mo(VI)) produced by anodic dissolution, yielding a critical crevice solution with an extremely low pH. Under these conditions even low concentrations of O₂ reduced on the external surface of the crevice could maintain the critical chemistry at a number of small locations within the crevice.

Figure 4.12: (a) and (b), $E_C$–time plots recorded over various time periods of the galvanodynamic experiment (Figure 4.10); (c) and (d) $E_C$–time plots recorded over two time periods during the open circuit period of the experiment (Figure 4.10).
4.3.4 Galvanically Coupled Experiment

To determine whether the crevice remained active once the applied current was reduced to zero, a similar galvanodynamic experiment was conducted, starting at 80 µA with the current slowly decreased to zero (achieved after 48 h). Then, the creviced electrode was galvanically-coupled to a large counter electrode through a zero resistance ammeter, and the crevice current, $I_C$, and $E_C$ recorded. Simultaneously, the potential, $E_P$, of a planar electrode was also monitored. $E_P$ increased steadily to a value of ~ 0.26 V over the first 120 h, Figure 4.13 (a), before finally achieving a long term value (up to 920 h) of ~0.3 V confirming the establishment of passivity on this electrode.

The galvanodynamically activated crevice electrode had a $E_C$ value of ~ -0.11 V on first coupling to the large counter electrode, which increased to ~ -0.095 V over the subsequent period of galvanic coupling (up to 920 h, Figure 4.13 (a)). That the crevice was active and still able to propagate is confirmed by the value of $I_C$ which rapidly established a value of ~ 8 µA at the beginning of the galvanic coupling period and was sustained, decreasing only to 6 µA after 920 h, Figure 4.13 (a). The support of crevice propagation by O$_2$ reduction on the coupled electrode was demonstrated by the addition of O$_2$ to the cell after 920 h, which led to an increase of $I_C$ to ~11 µA and of $E_C$ by 10 mV to -0.105 V. The planar electrode also sensed the addition of O$_2$, $E_P$ increasing to ~ -0.33 V, Figure 4.13 (a).
Figure 4.13 (a) $E_C$, $E_p$, and (b) $I_C$ as functions of time during a galvanodynamic crevice experiment (up to 48h) followed by a subsequent period with the crevice galvanically-coupled to a large counter electrode. The time at which the applied current reached zero is indicated.

Closer inspection of the $E_C$ and $I_C$ –time plots during the galvanically-coupled period reveals the presence of coupled excursions, with rapid decreases in $E_C$ being accompanied by sudden increases in $I_C$, Figure 4.14. This behaviour suggests the initiation of new active locations, expected to be located around the propagating
perimeter of the damaged area. However, an initial surge in $I_C$ lasted only ~1 min while $E_C$ took ~ 6 to 10 min to return to the value prevailing prior to the excursion; i.e., the demand for current from the external cathode is short but leads to a rapid local disturbance in electrochemical conditions.

![Graph showing transients on $I_C$ and $E_C$](image)

**Figure 4.14:** An expanded view of transients on $I_C$ and $E_C$ during galvanic coupling experiment between 210-212 h.

Figure 4.15 illustrates the probable mechanism behind the current-potential response observed in Figure 4.14. In chapter 3 [16] it was shown that $E_C$ is a function of the Mo content of a series of Ni-Cr-Mo alloys and almost independent of the external current supply. Thus, the most likely explanation for the coupled short $I_C$-long $E_C$ excursions is that the initiation of a new active location leading to exposure of the substrate alloy initially demands external current for metal dissolution to occur. This external current is provided by the oxygen reduction reaction, as shown in stage 1 in Figure 4.15. Subsequently, local acidity develops as the metal cations hydrolyze, allowing a switch from external current demand (causing the decrease in $I_C$) to internal cathodic support by $\text{H}^+$ reduction (stage 2). As metal dissolution continues soluble Ni and Cr diffuse out of
the corroding site and molybdate accumulates, leading to the increase in $E_C$ and the suppression of active dissolution (stage 3). Such small events would account for the observation that crevice corrosion damage on these alloys inevitably accumulates as small pits, often linked along grain boundaries, Figure 4.8 [34,36], and containing molybdate deposits [34]. It should be noted the internal $H^+$ reduction cannot diminish the critical chemistry solution inside the crevice due to the extent of hydrolysis of metal cations especially Cr(VI) and Mo(VI) as discussed in chapter 3.

![Diagram](image)

**Figure 4.15:** Schematic showing the stages of (1) initiation of an active site at the periphery of the already crevice-corroded area; (2) propagation; and (3) stifling, and their corresponding $I_C$ and $E_C$ responses observed on a galvanically coupled crevice specimen.

When the $O_2$ concentration is decreased the occurrence of these individual coupled events continues, as illustrated in Figure 4.16, which shows $I_C$ and $E_C$ recorded over the time interval 812 to 813 h. The constancy of the current confirms that these individual active locations are stifled by molybdate accumulation and do not lead to an expansion of the area within the crevice undergoing active propagation, which would be expected to lead to an increased demand for external current support.
Figure 4.16 An expanded view of transients in $I_c$ and $E_c$ during a galvanic coupling experiment, after 812 h.

4.4 Conclusions

In this study the initiation and propagation of crevice corrosion on BC1 alloy at 120°C in 5 M NaCl solution were studied under galvanostatic and galvanodynamic polarization.

Under galvanostatic polarization, a constant columbic charge of 6.9 C was applied in the form of different currents of 10, 20, 40 or 80 µA. The electrochemical behaviour during initiation varied with applied current. However, in cases where sustained propagation occurred, the $E_C$ was relatively constant and similar in value over a range of applied currents.

Optical microscopy and 3D imaging of the corroded area using profilometry demonstrated that damage morphologies vary with applied current. Higher currents lead to a shallower and broader creviced area, causing the current density to stay almost constant. This is because at higher applied currents the formation of proton-consuming
polymeric molybdate products happens faster. Since these oxides block the progress of crevice corrosion, propagation is forced to spread laterally.

When the same 6.9 C charge is applied galvanodynamically, starting from a current of 80 µA and decreasing steadily to 0, the same passive-to-active potential response as observed during galvanostatic polarization was obtained. However, the size and frequency of active going transients in $E_c$ were increased by decreasing the current.

Coupling the crevice sample to a counter electrode through a zero resistance ammeter immediately after galvanodynamic polarization demonstrated very clearly that the negative-going transients in $E_c$ are linked to anodic spikes in $I_c$. This confirms that metastable film breakdown and repair happens in the creviced region even after 900 h. The response of $E_c$ and $I_c$ to the addition of oxygen to the system shows that the oxygen reduction reaction is one of the cathodic reactions supporting the corrosion. The other cathodic reaction is the hydrogen evolution reaction occurring inside the creviced region.

### 4.5 Acknowledgements

The authors would like to thank Haynes International, Kokomo, Indiana, for their generous donation of material, and the Western Nanofabrication facility for SEM and EDS analyses. This project received funding from the natural sciences and engineering research council of Canada (NSERC).
4.6 References


Chapter 5

5 Assessment of the Role of Alloying Elements on the Oxide Film Properties of Ni-Cr-Mo alloys

5.1 Introduction:

Ni-Cr-Mo alloys are well known for their corrosion resistance in both oxidizing and reducing environments [1–3]. While Ni itself readily forms a protective passive oxide when exposed to air, the oxide is thermodynamically unstable in oxidizing environments [4]. To overcome this shortcoming Ni is alloyed with Cr giving the oxide stability at oxidizing potentials [5]. Further alloying with Mo and W not only improves passivity but also helps suppress localized corrosion purportedly by rapid oxide reformation within active sites [6]. Efforts to optimize the Cr and Mo contents have resulted in significant improvements in the corrosion resistance of these alloys in aggressive media.

Many studies have focused on the passive film properties of Ni-Cr-Mo alloys. Lloyd et al. [7–9] studied the influence of the key alloying elements, Cr, Mo and W, on the passive film behavior of a series of Ni-Cr-Mo (W) alloys in acidic conditions. The oxide film thickness was reported to be only a few nanometers (< 5 nm), and was dependent on the Cr content of the alloy. Alloys with higher Cr content maintained passivity even at pH = 1 and 75°C. At lower pH values ranging from 2 to -1 the passive film on C22 became thinner before eventually destabilizing at pH ≤ 0.

The oxide film was found to have a multi-layered structure with Ni, but especially Cr, enriched at the inner metal/oxide interface and Mo-W concentrated at the outer oxide/solution interface. McDonald et al. [10,11] studied the growth of the passive oxide film on C22 at pH = 3 and 80°C over a wide range of potentials using electrochemical impedance spectroscopy (EIS). Analyzed according to the point defect model (PDM), the oxide formed at passive potentials $E < 0.6 \text{V(SHE)}$ is a defective Cr oxide with n-type
semiconducting properties, while for \( E > 0.6 \) V(SHE), the oxide changes to p-type due to cation vacancies created by dissolution of Cr (VI) into the electrolyte.

Zhang et al. [12] studied the effect of temperature on the passive film on C2000 (Ni-23Cr-16Mo-1.6Cu) at neutral pH, a layered oxide being formed at low and mild temperatures with high levels of hydroxide in the outer layer compared to oxide in the inner layer. On increasing the temperature up to 90°C, a growth in Ni content was accompanied by a drop in Cr and Mo content and a segregation of Cu to the outer regions of the film. Jakupi et al. [13] studied the oxide film formed on Alloy C22 in neutral pH at applied potentials from -600 mV to 600 mV (vs. saturated Ag/AgCl). Three distinct potential regions were identified: from -600 mV ≤ \( E \) ≤ -300 mV both film resistance \( (R_{\text{film}}) \) and \( \text{Cr}_2\text{O}_3 \) content (region 1) increased; from -300 mV ≤ \( E \) ≤ 300 mV, the oxide film stabilized and \( R_{\text{film}} \) and the \( \text{Cr}_2\text{O}_3 \) content reached a maximum (region 2). By further increasing \( E \) to > 300 mV, the passive film degraded with \( R_{\text{film}} \) decreasing and most of the \( \text{Cr}_2\text{O}_3 \) converting to \( \text{Cr(OH)}_3 \) (region 3). Besides \( \text{Cr(OH)}_3 \), Mo(VI) and W(VI) were also enriched in the outer layer of the film [14]. A more recent study on C2000 showed the passive film formed at neutral pH and different applied potentials [16], increased in thickness and Cr content from -0.4 V (Sat Ag/AgCl) to 0.6 V. Angle-resolved X-ray photoelectron spectroscopy (AR-XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) confirmed that the inner passive layer was enriched with \( \text{Cr}_2\text{O}_3 \) while transpassive dissolution at high \( E \) was due to the conversion of Cr(III) to Cr(VI).

In this study the properties of the passive oxide films on BC1 and C22 are compared using potentiostatic and EIS experiments at pH 7 and 9. The composition of the films was subsequently analyzed by XPS and AES. The influence of a period of corrosion under the conditions anticipated during crevice propagation is simulated by excursions into the transpassive region followed by a return to the passive and prepassive regions, with the primary goal of determining whether true repassivation can be achieved.

In addition our previous studies have shown that Ni-Cr-Mo alloys [14,15] are extremely clean with no intermetallic precipitates, a homogeneous composition, and a large
proportion of symmetrical ($\sum 3$) low energy grain boundaries. As a consequence, the onset of crevice corrosion requires that the potential exceeds that at which the Cr(III) oxide can be further oxidized to Cr(VI); i.e., the initial stages of transpassivity. Subsequently, as crevice corrosion propagates, Ni and Cr dissolve and are transported out of the active region while the molybdate is deposited on the active locations as Mo(VI) oxide/gel. This deposit was shown to suppress active dissolution forcing the active corrosion process to migrate to molybdate-free locations [16]. Since these experiments were conducted with a constant applied current, repassivation was prevented. This leaves unanswered the question of whether the molybdate surface layer could be considered passive and protective or whether it was permanently degraded. A key reason why molybdates are deposited in actively corroding crevices is their insolubility in acidic solutions. Experiments on planar surfaces under alkaline conditions or in the presence of a HCO$_3^-$/CO$_3^{2-}$ buffer show molybdates do not form for pH $\geq 9$ [17,18].

5.2 Experimental

5.2.1 Sample Preparation

C22 and BC1 discs with a diameter of 1 cm (Table 5-1) were cut from mill annealed plates supplied by Haynes International, Kokomo, Indiana (USA). The discs were then mounted in a heat-resistant epoxy resin (Dexter Hysol resin EE4183; hardener HD3561) to ensure only a single disc face, 0.78 cm$^2$ in surface area, was exposed to the electrolyte. A rod of the same material was connected to the back of the specimen to maintain electrical connectivity. Before each experiment the surface of specimens was wet polished with SiC papers from 180 grit to 1200. They were then ultrasonically cleaned for 10 min in a 50/50% mixture of ethanol and water, rinsed with deionized water, and dried using Ar gas.
Table 5-1: Chemical composition (wt.%) of the BC1 and C22 alloys.

<table>
<thead>
<tr>
<th>Alloy/Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>C</th>
<th>Co</th>
<th>Mn</th>
<th>Si</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>BC1</td>
<td>62</td>
<td>15</td>
<td>22</td>
<td>-</td>
<td>2</td>
<td>0.01</td>
<td>-</td>
<td>0.25</td>
<td>0.08</td>
<td>-</td>
</tr>
<tr>
<td>C22</td>
<td>56</td>
<td>22</td>
<td>13</td>
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<td>2.5</td>
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</tr>
</tbody>
</table>

5.2.2 Electrochemical Analysis

A three electrode cell placed in a grounded Faraday cage was used for electrochemical measurement with a 99.95% pure Pt plate (2.4 cm²) as the counter electrode (CE) and a home-made Ag/AgCl electrode immersed in a saturated KCl solution (0.197 V vs. NHE) as the reference electrode (RE). 5 M NaCl solutions were prepared using NaCl crystals (Caledon Ltd, GR ACS grade) and type I deionized water with a resistivity of 18 MΩ.cm. To obtain the desired pH = 7, 0.5 M HCl and NaOH solutions were used. To prepare a buffered basic (pH = 9) solution, 0.05 M NaHCO₃ + 0.05 M Na₂CO₃ was added to the chloride solution. An Orion Model 250A pH meter was used to measure pH. Solutions were purged with ultra-high purity Ar gas for 1 h before an experiment to minimize the O₂ concentration in the electrolyte. Purging was continued throughout an experiment. All measurements were performed at room temperature.

Prior to an experiment, the working (WE) electrode was cathodically cleaned by applying a potential of -1 V for 1 hour. Films were grown at constant potentials applied to the WE for 2 h using a Solartron 1287 potentiostat while the current response was recorded. The potential was then increased and the procedure repeated at 0.1 V intervals from -0.8 V up to a potential of 0.6 V (Sat.Ag/AgCl). After polarization at each potential, an EIS measurement was performed using a Solartron 1255 frequency response analyzer. EIS measurements were performed using a sinusoidal input potential with an amplitude of ±10 mV at 11 individual frequencies per frequency decade over the range 10⁵ Hz to 10⁻³ Hz. To ensure the validity of the EIS data K-K (Kramers-Kronig) transformations were performed [19]. In some experiments the potential was then reversed from 0.6 V
and similar measurements performed at 0.1 mV intervals down to -1 V to investigate the reformation of the passive film after transpassive dissolution.

In experiments to determine film compositions as the potential was either increased or decreased, films were grown for 8 h at potentials of 0 V, 0.5 V as the potential was increased and 0 V and -0.4 V as the potential was decreased. To minimize the effect of air exposure on the oxide composition, specimens were cleaned ultrasonically for 1 min and rinsed in water and dried by Ar gas immediately after growth. They were then stored in a small container in a desiccator before performing XPS and AES analyses.

5.2.3 Surface Analysis

XPS analyses were performed with a Kratos Axis Ultra XPS at surface science Western (SSW) using an Al Kα (1486.8 eV) radiation source. The Au 4f\textsubscript{7/2} metallic Au binding energy (83.95 eV) was used as a reference point for calibration of the instrument work function. Survey spectra and high resolution spectra were recorded on all samples for the Ni 2p, Cr 2p, Mo 3d, C 1s and O 1s spectral regions. Commercial CasaXPSTM software was used to fit the spectra. If required, charging in XPS spectra was corrected by fixing the C binding energy in the C 1s spectrum at 284.8 eV.

Auger analyses were performed with a PHI 660 Auger electron spectrometer instrument with excitation energy of 5 keV. An area of 100 μm by 100 μm was bombarded with an electron beam with a current of 500 nA. The sputtering source used for depth profiling was an Ar+ ion beam with an energy of 3 keV. The ion beam, with a current of 125 nA, was rastered over a 2 μm by 2 μm area as the signal strengths for Ni, Cr, Mo and O were recorded as a function of sputtering time. To convert sputtering times to penetration depths, a reference value of 32 nm/min was used [20].
5.3 Results and Discussion

5.3.1 Potentiostatic Polarization

Figure 5.1 shows the current density ($i$) response to applied potentials ($E$) of -0.7 V, 0 V and 0.6 V for BC1 in a deaerated solution with pH = 7 recorded for 2 hours. The three potentials cover the range from inadequate passivation (−0.7 V) to protective passivity (0 V) and transpassivity (0.6 V) [7]. At all potentials, $i$ is initially anodic due to oxide growth. However, at -0.7 V, the current switches to cathodic after 800 s, indicating the film is defective enough to support $\text{H}_2\text{O}/\text{H}^+$ reduction. At 0 V, the steady decrease in $i$ with time to a value of 40 nA.cm$^{-2}$ indicates the growth of a protective passive oxide. The current density at 0.6 V is initially much higher at 15 μA.cm$^{-2}$ and decreases to only 4 μA.cm$^{-2}$ consistent with transpassive oxide dissolution. Since at all three applied potentials $i$ becomes either very small or constant after 2 h, this duration was selected for film growth as it is sufficient to achieve steady-state conditions.

![Figure 5.1: Current response vs. time measured on BC1 at three applied potentials in pH = 7 solution.](image-url)
Figure 5.2 shows the current density ($i_{\text{Final}}$) recorded on BC1 at the end of the polarization period at pH = 7 as a function of applied $E$. The current response to the applied potential can be divided into three distinct regions as indicated in the figure.

![Figure 5.2: $i_{\text{Final}}$ as a function of applied $E$ recorded on BC1 at pH = 7. The (-) sign indicates the potentials at which a cathodic current was obtained and the (+) sign is the potential at which the current changed from cathodic to anodic.](image)

(1) For $E < -0.6\, \text{V}$, $i_{\text{Final}}$ is negative, with the value decreasing as $E$ increased. In this region, anion vacancies created during film formation result in a donor-type (n-type) behaviour [21]. As the potential is increased, the number/density of these vacancies decreased leading to an improvement in passive behaviour [22].

(2) For potentials in the range -0.6 V to 0.2 V, $i_{\text{Final}}$ becomes positive. The passive current is ~ 60 nA.cm$^{-2}$ and is independent of $E$ as expected for a passive layer with a low concentration of defects.

(3) For $E > 0.2\, \text{V}$, $i_{\text{Final}}$ begins to increase with $E$ which is indicative of the onset of transpassivity, when the oxidation of Cr(III) to Cr(VI) and Mo (IV) to Mo (V) and
(VI) results in the production of cation vacancies [7]. As a result, the passive film exhibits acceptor-type (p-type) behaviour [21,22].

5.3.1.1 Positive and Negative Potential Scans

The initiation of crevice corrosion requires an excursion into the transpassive region. Consequently, repassivation effectively involves the recovery from a period of transpassive dissolution. To investigate the reformation of the passive film after transpassive dissolution, $i_{\text{final}}$ values were recorded for both alloys at pH = 7, first from -0.9 V to 0.6 V at 100 mV intervals (positive scan) and then recorded again at the same potentials as $E$ was decreased (negative scan), Figure 5.3. For the increasing potential direction, the values recorded on BC1 are slightly larger than those measured on C22 consistent with the higher Cr content of the latter. For the negative scan the currents measured on both alloys are lower. For C22 the current is reduced by a factor of 3 while for BC1 the current is up to 50 times smaller. This suppression of anodic current on BC1 compared to C22 commences in the transpassive region 3 (i.e., from 0.5 V to 0.2 V) suggesting that the molybdate deposit formed on the high-Mo BC1 is more protective than that formed on the low-Mo C22, consistent with expectations based on crevice electrodes (chapter 3). Although not measured, the formation of Cr(VI)/Mo(VI) species in the transpassive region (region 3) would lower the pH considerably due to their hydrolysis leading to molybdate formation. On decreasing the potential to the passive region (region 2) the substantial decrease in $i_{\text{final}}$ suggests either this deposited molybdate does provide a passive film or the Cr(III) oxide barrier layer is readily reformed beneath the molybdate layer.
Figure 5.3: $i_{Final}$ recorded on BC1 and C22 for applied potentials from -0.9 V to 0.6 V at pH = 7 recorded as the potential was increased (positive scan) and then decreased (negative scan) from 0.6 V to -0.9 V at pH = 7 solution.

This experiment was repeated in buffered carbonate/bicarbonate solution at pH = 9. Figure 5.4 shows $i_{Final}$ recorded on BC1 and C22 as the potential is increased and decreased over the range -0.9 V to 0.6 V at pH = 9. As the potential is increased the currents in the passive region (-0.6 V to 0.2 V) are the same as at pH = 7 with the values recorded for BC1 being larger than those for C22, as expected from their respective Cr contents.

As the potential is decreased the currents recorded on both alloys in the passive region are low but the difference in current between the two alloys, observed in both the transpassive and passive regions at pH = 7, was not observed and identical passive currents being observed. The key difference between pH = 7 and pH = 9 is the lower
passive current measured on the reverse scan for C22, suggesting that passivity is more readily re-established on this alloy at pH = 9 than at pH = 7.

![Figure 5.4](image)

*Figure 5.4: $i_{\text{Final}}$ recorded on BC1 and C22 for applied potentials from -0.9 V to 0.6 V at pH = 9 recorded as the potential was increased and then decreased.*

Previously, Mishra et al. [17,18] used XPS and AES to show that the deposition of molybdates was prevented in $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffered solution (pH = 9) since the acidic conditions required for its deposition were prevented in slightly alkaline buffered solutions. The lower values of $i_{\text{Final}}$ recorded on C22 at pH = 9 (compared to pH = 7) suggests that the re-establishment of passivity on this alloy is assisted by the removal of Mo. For BC1 the $i_{\text{Final}}$ observed at pH = 9 in the negative scan is a factor of 4 higher than recorded at pH = 7. Since, due to the buffering at pH = 9, molybdate formation on the alloy surface will be prevented, or at least significantly reduced, the lower currents at pH = 7 indicate an influence on passivity of the transpassively-formed molybdate. Irrespective of this influence of pH, the low $i_{\text{Final}}$ value recorded on BC1 on the negative
scan compared to the positive scan at both pH values confirms that molybdate deposition is not the only contributor to the enhanced passivity on BC1 observed on the negative scan.

In region 1 \((E, -0.6V)\) no difference in \(i_{final}\) is observed between the two alloys although the currents recorded as the potential is decreased are again lower than those recorded on the forward scan. These currents indicate that an excursion into the passive and transpassive regions as the potential was increased led to a significant suppression of \(\text{H}_2\text{O}\) reduction.

### 5.3.2 EIS Analyses

EIS measurements were performed on both alloys (at \(\text{pH} = 7 \text{ and } 9\)) over the range -0.9 V to 0.6 V as the potential was increased and then decreased. Figure 5.5 shows Bode plots measured at selected potentials on BC1 (\(\text{pH} = 7\)) as the potential was first increased and then decreased. The three selected potentials are representative of the behaviour observed in the three regions defined above. The spectra are similar at the same potential on both the increasing and decreasing scans. At -0.8 V (region 1), 2 distinct time constants are observed, but only one time constant is observed at 0 V in the passive region (region 2). At positive potentials (0.5 V (Region 3)) 2 time constants are required to fit the data although they are less distinct than in region 1. In region 1 the low frequency response is attributed to the dielectric processes within a thin defective film (i.e., an incompletely formed passive oxide) and the high frequency response to charge transfer processes at the film/electrolyte interface due to \(\text{H}_2\text{O}\) reduction.

In region 2, Figure 5.5 (c) and (d), only one time constant is required to fit the spectra demonstrating that the interfacial impedance is dominated by the properties of the passive oxide film. In region 3, Figure 5.5 (e) and (f), the passive layer is destabilized in the transpassive region. Although the spectra are not shown, a similar series of experiments was performed on C22.
Figure 5.5: (a)-(f) Selected impedance spectra recorded on BC1 at three potentials in a pH = 7 solution: (a) (c) and (e) were recorded as the potential increased; (b), (d) and (f) were recorded as the potential was decreased. The points indicate the experimental data and the black lines indicate the fit.

Depending on whether one or two time constants are required, the equivalent circuits shown in Figure 5.6 were used to fit the data. To account for the non-ideality of the
capacitative response, constant phase elements (CPE) rather than capacitances were used when fitting the data.

![Diagram of electrical equivalent circuits](image)

**Figure 5.6**: Electrical equivalent circuits used to fit impedance spectra. (a) one time constant circuit consisting of a solution resistance \( R_s \), a film resistance \( R_f \) and film capacitance (CPE\(_f\)) in parallel representing a passive film: (b) a two time constant circuit including a charge transfer resistance \( R_{ct} \) and an interfacial capacitance (CPE\(_{ct}\)) for charge transfer processes at either the film/electrolyte or the alloy/film interface.

The CPE for the surface film, CPE\(_f\), was > 0.8 in regions 1 and 3 and > 0.9 in region 2. The second CPE, CPE\(_{ct}\), for the interfacial charge transfer process (required in regions 1 and 3) is generally in the range 0.59 to 0.83. These lower values are not surprising since charge transfer involves many cations with a wide range of often large oxidation states (Cr (III and VI), Mo (III, IV, V, and VI) and W (III, IV, V, VI) which would lead to large pseudo capacitances accounting for the very large apparent capacitance values. Also, visual inspection of the spectra in Figure 5.5 ((e) and (f)) suggests a contribution from diffusive transport at low frequencies (< 10\(^{-1}\) Hz), which would be consistent with the presence of a molybdate layer at transpassive potentials through which dissolving cations would need to diffuse. Since our primary interest is in the properties of the surface film, only the values of \( R_f \) and CPE\(_f\) are considered further. Also, the exponent “\( n \)” is large for this CPE allowing us to assume it can be approximated to a capacitance using the Hsu-Mansfeld conversion [23]. This conversion has been suggested previously to obtain effective capacitance \( C_f \) values for chromium-rich passive films [24] using the equation below,
\[ C_f = CPE_f \left( \frac{1}{n} \right) R_f \left( \frac{1-n}{n} \right) \] (5-1)

The values of \( R_f \) and \( C_f \) are plotted in Figure 5.7 for the two alloys as the potential was first increased and then decreased at pH = 7 and 9. As the potential was increased, \( R_f \) for BC1 was considerably lower than for C22. The rapid rise in \( R_f \) on C22 compared to BC1 can be attributed to the more rapid formation of the passive film at the higher Cr content.

Figure 5.7: Film resistance (\( R_f \)) and film capacitance (\( C_f \)) as a function of applied potential recorded on BC1 and C22 as the potential was increased and then decreased: (a) and (b) pH = 7, (c) and (d) pH = 9.
In region 2, the $R_f$ values are similar with $R_f$ (C22) being slightly greater than $R_f$ (BC1) consistent with the steady-state $i_{\text{Final}}$ values (Figure 5.3), and expected due to the higher Cr-content. In the transpassive region (3), the $R_f$ values for both alloys are again similar.

While the absolute values of $C_f$ are difficult to interpret (as discussed above), the steep decrease in $C_f$ which accompanies the rapid rise in $R_f$ on C22 is the expected behaviour for the potential-driven formation of a passive oxide. By contrast, the independence of $C_f$ and the much slower increase in $R_f$ with increasing potential on BC1 confirms that the passive film is less readily formed on this low-Cr alloy. The very high value of $C_f$ for C22 at low potentials may reflect the consequences of the prolonged cathodic cleaning treatment which has been shown to lead to the accumulation of Cr(OH)$_3$ on this alloy [14].

The passive film, reformed at pH = 7 as the potential is reduced from the transpassive region, had a higher resistance on both alloys than that formed as the potential was increased, Figure 5.7, again consistent with the low values of $i_{\text{Final}}$, Figure 5.3 and Figure 5.4. For BC1 the passive film remained stable to potentials as negative as -0.5 V. The value of $R_f$ on C22 decreases markedly over the potential range -0.2 V to -0.7 V compared to the value on BC1, Figure 5.7 (a). This suggests a more defective film is present on this alloy or one which is made more defective by the reduction of a species within the film possibly allowing the reduction of trace amounts of dissolved O$_2$ remaining in the solution. That this decrease in $R_f$ (C22) can be attributed to a film reduction process would be consistent with the difference in behaviour of $C_f$ for the two alloys as the potential is decreased. The steep increase in $C_f$ (C22) which accompanies the decrease in $R_f$ (C22) suggests a larger pseudo capacitance due to polarizable species in the film. The absence of a similar large increase in $C_f$ (BC1) would be consistent with the passive layer on the latter alloy being more stable and/or less readily reduced.

At pH = 9, Figure 5.7 ((c) and (d)), the two alloys exhibit almost identical values of $R_f$ on both the sequence of increasing and decreasing potentials. The $R_f$ values remain very
large on both alloys for $E \leq 0.2$ V, the decrease in value of $R_f$ (C22) for $E$ in the potential range -0.2 V to -0.5 V being minor.

Since the difference in behaviour at pH = 7 and 9 are thought to reflect the ability to retain molybdate on the surface at pH = 7 but not at pH = 9, the maintenance of high $R_f$ values to potentials $\leq -0.5$ V (on the BC1 especially) suggests the presence of molybdate is not the key feature of the repassivation process. For both alloys, $C_f$ at positive and negative potentials is considerably lower than at pH = 7, consistent with a reduced pseudo-capacitance due to the lower accumulation of molybdate at this pH.

### 5.3.3 XPS/AES Results

Based on the polarization and EIS results, 4 potentials of 0 V and 0.5 V on the positive scan representing passive and transpassive potentials, and 0 V and -0.4 V on the negative scan representing the regrown passive oxide were selected for surface analyses. The oxide film was grown for 8 h in a pH = 7 solution prior to XPS and AES analyses.

![Figure 5.8: XPS survey spectrum recorded on C22 after polarization at 0 V (+) in a pH = 7 solution.](image-url)
Figure 5.8 shows an example of a survey scan recorded on C22 at 0 V (+). The Ni 2p, Cr 2p, Mo 3d, O 1s and C 1s are the main peaks detected in the spectrum. Since the C 1s peak is due to surface contamination it was not included when determining the surface composition.

Figure 5.9 shows the elemental compositions (at.%) of the electrode surfaces determined from the relative intensities of the peaks in the survey spectra for both alloys. As expected, the composition is dominated by the O content at all potentials. In the passive region (0 V (+)) both alloys have a high Cr content especially C22. In the transpassive region (0.5 V (+)), a decrease in Cr and an increase in Mo of the film is observed. In the passive region (0 V (+)), the Cr content of both alloys is high, especially that of C22 consistent with the lower $i_{\text{final}}$ and higher $R_f$ measured on this alloy at this potential compared to BC1.

In the transpassive region (0.5 V (+)), the Cr content of both alloys is reduced especially that of the high-Cr C22, indicating destruction of the barrier layer, at least locally, Zhang et al. having shown that transpassive oxidation proceeds non-uniformly on the surface of Ni-Cr-Mo alloys [25]. The decrease in the Cr content on oxidation in the transpassive region is accompanied by an increase in Mo content of the surface. This increase is particularly marked on the high-Mo BC1, the increase in C22 being marginal.
Figure 5.9: Surface composition (normalized) obtained from the survey spectra of (a) C22 and (b) BC1 alloy after polarization at 0 V and 0.5 V (positive scan) and 0 V and -0.4 V (negative scan) at pH = 7 solution.

On reversing the potential to the passive region (0 V (-)) after a period of transpassive oxidation (0.5 V (+)), to simulate a period of crevice propagation, the Cr content of the surface on both alloys is increased. This increase in relative Cr content and accompanying decrease in relative Ni and Mo occurs on both alloys and suggests the regrowth of a Cr(III) barrier layer. This reformation would be consistent with the lower
$i_{\text{Final}}$ and higher $R_f$ values observed at this potential on both alloys after an excursion into the transpassive region (Figure 5.3 and Figure 5.7). This relative increase in Cr content, coupled with a decrease in Ni and Mo content, is particularly marked on the BC1 alloy, Figure 5.9 (b). In fact, the Cr-content of the surface is increased significantly compared to that of the oxide grown at this potential prior to the transpassive period (0 V (+)). This increased Cr content offers a possible explanation for the markedly lower $i_{\text{Final}}$ and higher $R_f$ values on this alloy (Figure 5.3 and Figure 5.7). On C22 the relative content of Mo on the surface is essentially the same for all potentials. However, its relative content on the BC1 surface is reduced by the excursion to transpassive conditions. This is most likely due to an increase in Cr-content rather than a real decrease in Mo content.

High resolution spectra were collected for both alloys at pH = 7 at the same 4 potentials. The spectra were corrected using a Shirley background subtraction, and deconvoluted according to the procedures developed by Biesinger et al. [26–28] and Spevac and McIntyre [29]. An example of high-resolution deconvoluted XPS spectra for the O 1s, Ni 2p, Cr 2p and (d) Mo 3d peaks recorded on C22 at 0 V (+) is shown in Figure 5.10. The O 1s spectra were fitted with three component peaks: the peaks at 529-530 eV, 531-532 eV, and ~533 eV are attributed to O$^{2-}$ in an oxide, OH$^-$ species or defective sites in the oxide and adsorbed H$_2$O, respectively [27]. Both the Ni 2p and Cr 1s spectra were fitted with three main components of metallic (Ni and Cr), oxide (NiO and Cr$_2$O$_3$) and hydroxide (Ni(OH)$_2$ and Cr(OH)$_3$) species. Fitting of the Mo 3d spectra required the inclusion of peaks for metallic Mo and several Mo oxidation states of (IV), (V) and (VI). The deconvolution of these spectra yields the distribution (%) of each component for the main alloying elements.
Figure 5.10: High-resolution deconvoluted XPS spectra for (a) O 1s, (b) Ni 2p, (c) Cr 2p and (d) Mo 3d collected on C22 at 0 V (+) and pH = 7. The red line shows the fitted spectra envelope.

Multiplying this by the normalized relative amounts of the main alloying elements on the surface obtained from survey scans e.g., Figure 5.9 yields the percentage distributions of the various surface components, Figure 5.11.

The surface oxide/hydroxide was sufficiently thin that the underlying metallic components of the alloy could be detected at all polarization potentials. The film thicknesses were estimated based on the relative sizes of the metal and oxide/hydroxide contributions and the AES data collected on the same samples after XPS measurement. For the passive film formed at 0 V (+), the film thickness on the two alloys was very similar (2.6 nm (C22)) and (2.3 nm (BC1)). Increasing the potential into the transpassive
region (0.5 V (+)) lead to an increase in thickness particularly for BC1 (6.4 nm (C22) and 13 nm (BC1)).

Figure 5.11: Normalized relative film composition (%) of Ni, Cr and Mo and their relative metal, oxide, hydroxide components present in films polarized at specific potentials for (a) C22 and (b) BC1.

The AES profiles recorded in the passive region (0 V (+)) (Figure 5.13 (a) and Figure 5.12 (a)) show that the barrier layer is much more sharply defined for C22 than for BC1, with the characteristic enrichment of Ni in the alloy surface. For BC1 the segregation of Cr to the barrier layer and accompanying retention of Ni in the alloy
surface is not particularly well defined consistent with the lower Cr content of the oxide and the higher $i_{\text{Final}}$ and lower $R_f$ values. The very high Cr(OH)$_3$ content observed in the XPS data at (0 V (+)) Figure 5.11 can be attributed to the prolonged cathodic treatment required to produce a reproducible surface prior to performing anodic oxidation [14].

After oxidation in the transpassive region (0.5 V (+)), the Cr$_2$O$_3$ content on C22 is considerably reduced, as expected, and accompanied by a major increase in the Ni(OH)$_2$ and Cr(OH)$_3$ contents of the surface, both of which have been shown previously to accumulate in the outer region of the film [14]. The absence of Cr(VI) can be attributed partially to the loss of CrO$_4^{2-}$ by dissolution but also to its reduction back to Cr(III) (accounting for the increase in Cr(OH)$_3$) by one or both of two processes; reduction of Cr(VI) when the electrode is removed from the cell and transferred to the ultra-high vacuum system of the XPS [30] and/or reduction induced by the X-ray beam when the XPS analyses were performed. Although the relative amount of Mo(V)/Mo(VI) does not increase, previous studies [14] showed that some accumulation of Mo species did occur in the outer region of the film. For BC1, oxidation in the transpassive region effectively destroys the barrier layer, negligible amounts of Cr$_2$O$_3$ being detected by XPS, Figure 5.11 (b), while extensive accumulation of Mo(V)/Mo(VI) occurs on the electrode surface. As discussed in chapter 3 and 4, this is consistent with the observed behaviour in galvanostatically propagated crevices. These features are accompanied by a large increase in the relative Cr(OH)$_3$ content of the film (presumably present as Cr(VI) prior to analyses). This accumulation of Mo(V)/Mo(VI) and Cr(VI) would account for the much thicker film present on BC1 (13 nm) compared to C22 (6.4 nm).

Reforming the oxide after the transpassive treatment (0 V (-)) leads to a decrease in oxide thickness (6.4 nm to 3.8 nm for C22) especially for BC1 (13 nm to 5.4 nm), consistent with the loss of Ni and Mo as indicated by the relative surface compositions, Figure 5.9. This indicates that the enhanced passivity of BC1 (i.e., increased $R_f$, decreased $i_{\text{Final}}$) cannot simply be attributed to a thick molybdate film formed under transpassive conditions.
Reducing the potential from 0.5 V (+) to 0 V (-) leads to the reformation of Cr$_2$O$_3$ barrier layer on C22 as indicated by the significant Cr$_2$O$_3$ content of the thicker oxide, Figure 5.11 (a). This repassivation process proceeds by a similar process to that which governed the growth of the original passive film (0 V (+)) as confirmed by comparison of the AES profiles recorded at 0 V before and after the transpassive treatment, Figure 5.12 (a) and (c), which are effectively identical. The enrichment of Ni in the alloy surface indicates that the reformation of the barrier layer proceeds by regrowth not by reduction of species formed transpassively. The improved passivity may reflect some contribution from the residual molybdate deposited during oxidation at 0.5 V (+).

![Figure 5.12: AES profiles measured on films grown on C22 at (a) 0 V (+), (b) 0.5 V (+), (c) 0 V (-) and (d) -0.4 V (-).]
By contrast the reformation of the Cr$_2$O$_3$ barrier layer is not so clearly marked on BC1 and there is no evidence for Ni enrichment in the surface of the alloy at 0 V (-). This last observation suggests that the barrier layer did not regrow in a similar manner to the regrowth observed on C22. Despite this, both XPS (Figure 5.11 (b)) and AES (Figure 5.13(c)) indicate an increase in the amount of Cr in the passive film, with AES profiles indicating retention of Cr close to the alloy/film interface. Despite this ambiguity concerning the chemical state of the Cr, the $i_{\text{Final}}$ and $R_f$ values confirm passivity is achieved. The relatively high Mo content on the surface, Figure 5.11, suggests passivity may be at least partially sustained by the retention of the molybdate film formed transpassively.

Figure 5.13: AES profiles measured on films grown on BC1 at (a) 0 V (+), (b) 0.5 V (+), (c) 0 V (-) and (d) -0.4 V (-).
5.4 Conclusions

Potentiostatic polarization and EIS measurements conducted at different potentials show that both alloys exhibit generally similar passive behaviour. EIS measurements indicate that while the passive film may form less readily on BC1 than on C22 at pH = 7, the repaired film formed after transpassive breakdown is more resistive on BC1. The higher resistance of the reformed film on BC1 was diminished at pH = 9 solution indicating that transpassively-formed molybdate contributes to the enhanced passivity.

Upon transpassive film breakdown the Cr$_2$O$_3$ undergoes oxidative dissolution for both alloys and the overall film thickness is increased while the relative Mo(VI)/Mo(V) of the film increases.

Upon reformation of the passive layer after transpassive dissolution, C22 regrows an effectively identical Cr$_2$O$_3$ barrier layer and the improved passivity (i.e. higher $R_f$ and lower $i_{Final}$) on the negative scan may reflect some contribution to enhance passivity from the residual molybdate deposited during oxidation. The XPS and AES profiles recorded on the reformed passive film on BC1 alloy show an increase in the amount of Cr in the passive film but only a minor contribution from a reformed Cr$_2$O$_3$ barrier layer. Despite this uncertainty concerning the state of the Cr, passivity is strongly enhanced suggesting this state is at least partially sustained by the transpassively-formed molybdate.
5.5 References


Chapter 6

6 Sigma and Random Grain Boundaries and their Effect on the Corrosion of Ni-Cr-Mo Alloys


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Abstract:

The corrosion behaviors of Ni-Cr-Mo alloys have been compared using corrosion potential measurements, electron backscatter diffraction techniques and confocal scanning laser microscopy. The corrosion resistance of the alloys was linked to the crystallographic properties of their grains and grain boundaries. Grain boundaries exhibiting coincidence site lattices, especially $\Sigma 3$, were the most resistant to intergranular corrosion. Transmission electron microscopy (TEM) of the $\Sigma$ and random boundaries was used to investigate the origin of this increased corrosion resistance. Scanning transmission electron microscopy (STEM) of the boundaries showed needle shaped inclusions on a random boundary, but not on the $\Sigma 3$ boundary, and electron energy loss spectroscopy (EELS) analysis confirmed that these inclusions are enriched in oxygen and depleted in nickel.
6.1 Introduction:

Nickel superalloys are a group of materials with excellent elevated-temperature strength, resistance to creep and resistance to degradation in corrosive environments [1,2]. The Face center cubic (FCC) structure of the γ phase of Ni, tolerates high alloying element solubility with Cr (35 wt.%), Mo (20 wt.%) and W (20 wt.%) [3]. It is this ability to accommodate extensive alloying without the formation of precipitates that is responsible for the high performance properties of Ni alloys. These alloys are widely used in aerospace and power generation turbines, rocket engines and other challenging environments including chemical and petrochemical processing plants and oil and gas industry applications [1,4]. A key feature in their exceptional corrosion resistance is the ability to form a thin protective (passive) oxide film, which protects the underlying alloy [5–7], and prevents failure by uniform corrosion in aggressive environments, but not necessarily localized corrosion processes such as pitting, intergranular corrosion and crevice corrosion [8–13].

Many material properties depend on the transmission of forces and stress fields across grain boundaries and are sensitive to the grain boundary structure, chemistry, and morphology [14]. Localized corrosion at grain boundaries is influenced by the 3-dimensional grain boundary structure, and reduced susceptibility to intergranular corrosion is associated with low energy grain boundaries [15]. The coincidence site lattice (CSL) model [16,17] is commonly used to describe the crystallographic relationship between adjacent grain crystal lattices. Each boundary is assigned a number, sigma (Σ), corresponding to the reciprocal number density of lattice sites that are common to both crystals. “Special boundaries” are characterized by a particular misorientation (Δθ), the difference in crystallographic orientation between two crystallites, and high degree of atomic matching; they can be described geometrically by a low Σ number (1 ≤ Σ ≤ 29), with an allowable angular deviation from the Brandon criterion of Δθ ≤ 15° [1]. These boundaries possess extraordinary properties compared to high angle (> 15°) “random” boundaries with Σ ≥ 29 [16,18].
In recent years, grain boundary engineering (GBE), the deliberate manipulation of grain boundary structure, has been widely applied in the development of high performance structural and functional polycrystalline materials [19–22]. For FCC metals and alloys with low stacking fault energy, GBE has been used to generate a very high fraction of \( \Sigma \) 3-related \( (\Sigma = 3^n) \) CSL boundaries coupled with the formation of annealing twins [19]. The generation of a structure with low \( \Sigma \) CSL boundaries is thermodynamically favorable since they constitute a low energy configuration [23], and many material properties are enhanced. Jakupi et al. [18] reported that the intergranular corrosion of alloy-C22 (Table 6-1), stimulated galvanostatically in 5.0 M NaCl, mostly propagated along random rather than \( \Sigma \) boundaries. Kobayashi et al. found that high-energy random boundaries play a key role as the preferential crack path way during intergranular stress corrosion cracking with the crack length decreasing as the special boundary fraction increased [19]. Many other studies have observed that \( \Sigma \), compared to random boundaries, are often more resistant to degradation reactions such as stress-corrosion cracking [24,25], creep [26], fatigue [27], segregation and precipitation [28].

The primary goal of this study is to determine whether compositional differences exist between \( \Sigma \) and random grain-boundaries in Ni-Cr-Mo alloys, and whether the differences in corrosion behaviour in solutions similar to those encountered in active corrosion can be explained by such differences. Three commercial Ni alloys differing in Cr and Mo content were investigated. The materials were corroded in acidic chloride solutions similar to those likely to be encountered in active corrosion. The electrode surfaces were characterized both before and after corrosion using electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM).

6.2 Experimental

6.2.1 Materials and Specimen Preparation

The chemical compositions of the alloys used in this study are given in Table 6-1. The main difference between these alloys is in their Cr and Mo contents. Electrodes (1 cm\(^2\) in
surface area) were cut from as-received, mill-annealed bulk sheets supplied by Haynes International (Kokomo, IN, USA). The specimens were prepared for EBSD using the following procedure: Specimens were ground with a series of SiC papers (from 320 to 4000 grit) using water as a lubricant, and then polished on a Struers DP-Dur pad using a diamond paste (3 to 1 µm) as an abrasive. A final 0.05 µm polish was performed on a Struers OP-Chem pad using a solution mixture containing 50/50% ethylene glycol/0.05 µm colloidal silica as an abrasive and ethylene glycol as a lubricant. The specimens were then sonicated in a 50/50% water/ethanol mixture for 5 minutes to remove any polishing residue. The polished surface was marked with a hardness indenter so that the characterized area could be relocated and reanalyzed after corrosion. SE (Secondary electron) and BSE (Back scatter electron) images were recorded on the polished surface to identify any surface defects or polishing artefacts.

Table 6-1: Alloy chemical compositions (wt.%).

<table>
<thead>
<tr>
<th>Alloy/Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>W</th>
<th>Fe</th>
<th>Co</th>
<th>C</th>
<th>Mn</th>
<th>S</th>
<th>Si</th>
</tr>
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<tbody>
<tr>
<td>C22</td>
<td>56</td>
<td>22</td>
<td>13</td>
<td>3</td>
<td>3</td>
<td>2.5</td>
<td>0.01</td>
<td>0.5</td>
<td>0.02</td>
<td>0.08</td>
</tr>
<tr>
<td>C625</td>
<td>62</td>
<td>21</td>
<td>9</td>
<td>-</td>
<td>5</td>
<td>1</td>
<td>0.10</td>
<td>0.5</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>BC1</td>
<td>62</td>
<td>15</td>
<td>22</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>0.01</td>
<td>0.25</td>
<td>-</td>
<td>0.08</td>
</tr>
</tbody>
</table>

6.2.2 Electrochemical Procedure

For electrochemical measurements, a small hole was machined in the top of the specimens to connect to a cylindrical rod which provided a connection to external circuitry. A standard three-electrode, glass electrochemical cell was used for all experiments. The cell contained the specimen as the working electrode and a Pt counter electrode and saturated calomel (SCE) reference electrode (244 mV vs. SHE at 25°C). The cell had an outer jacket through which water was circulated from a thermostatic bath.
(Isotemp 3016H, Fisher Scientific) to maintain the temperature of the solution to within 1°C. In corrosion experiments, electrodes were exposed to a corrosive solution (3 M NaCl + 1.5 M HCl) for 8 hours at 75°C and the corrosion potential \( E_{\text{CORR}} \) recorded. Potentiodynamic polarization measurements were performed in the same solution at a scan rate of 0.5 mV/s. Before applying the scan, \( E_{\text{CORR}} \) was measured for 15 min to ensure a stable surface condition. Scans were started from a potential 50 mV below \( E_{\text{CORR}} \) and extended up to a value at which an abrupt increase in anodic current density occurred. All electrochemical measurements were conducted using a Solartron 1480 MultiStat, and Corrware software (Scribner and Associates).

### 6.2.3 Surface Characterizations

EBSD analyses were performed on specimens before and after corrosion in the ZAPlab laboratory at Western University. A Hitachi SU6600 field emission gun scanning electron microscope (FEG-SEM) operated at 20 kV was used to obtain grain orientation data. A step size of 1 µm was used to map the surface. HKL Channel 5 Tango software was used to obtain crystal orientation EBSD maps and electron backscatter patterns were indexed according to the FCC structure. Image-Pro Plus software was used to statistically analyze the corroded sites on grain boundaries and inside grains. A cleaning level 2 was performed on EBSD images on un-corroded samples while no cleaning was done on post corrosion EBSD images.

The distribution of surface damage on the C22 alloy was imaged using an LSM 510 confocal laser scanning microscope (CLSM) in the Biotron facility at Western University. Samples for TEM analysis were prepared as follows: Orientation map obtained from EBSD identified a network of \( \Sigma \) (red) and random (yellow) grain boundaries, Figure 6.1(a). Two adjacent \( \Sigma 3 \) and random grain boundaries were selected to avoid possible lateral differences in composition caused during solidification. A line across one of each type of boundary was then marked with Pt, Figure 6.1(b), and a section cut out using a focused ion beam, Figure 6.1(c). Finally, one of each type of boundary was thinned down for TEM analysis (Figure 6.1(d)). The FIB section was
analyzed using a FEI Titan 80-300 microscope (FEI Company, Eindhoven, The Netherlands), equipped with a CEOS image corrector (CEOS GmbH, Heidelberg, Germany), an Oxford INCA x-sight system (Oxford Instruments, Abingdon, United Kingdom) and a Gatan Tridium energy filter (Gatan Inc., Pleasanton, CA). The microscope was operated at 300 kV.

Energy-dispersive X-ray spectroscopy (EDS) point analysis was performed in scanning transmission electron microscopy (STEM) mode, with a beam current of 150 pA and an acquisition time of 50 s. The dispersion per channel was 10 eV, and the process time was set to 4.

Figure 6.1: Preparation of a TEM sample using a focused ion beam. (a) sigma (red) and random (yellow) grain boundaries identified by EBSD. $\Sigma 3$ and random grain boundary were chosen and (b) marked with a line of Pt across selected $\Sigma 3$ and random grain boundaries: (c) the cut specimen with the two grain boundaries at the two ends, (d) the final TEM specimen with thinned $\Sigma$ and random boundaries.
Electron energy loss spectroscopy (EELS) maps were acquired in STEM mode with a step size of 1.5 nm and an exposure time of 20 ms per pixel. The convergence semi-angle of the beam was set to 8 mrad. Diffraction patterns were acquired in STEM mode with a beam convergence semi-angle of 1 mrad and an exposure time of 100 ms. The illuminated area per diffraction pattern was approximately 2 nm. 2D maps of diffraction patterns were recorded in order to analyze the interface region.

6.3 Result and Discussion

6.3.1 Surface Imaging of the Uncorroded Alloys

After polishing the surface, the areas of interest were selected and marked for analysis before and after corrosion. The Inverse pole figure (IPF) EBSD maps for the three alloys are shown in Figure 6.2. The $\Sigma$ and random grain boundary maps were superimposed on the IPF map in red and black, respectively. The percentage of $\Sigma$ and random grain boundaries were calculated using Tango EBSD software and are presented with the corresponding IPF maps. All three alloys have a large number of $\Sigma$ boundaries (more than 60%). The total ratio of $\Sigma$ to random boundaries being almost the same (ca. 69% $\Sigma$ to 31% random), while the fraction of $\Sigma^3$ boundaries was in the order, BC1 (67.8%) > C625 (63.2%) > C22 (59%).

Additionally, Annealing twins are well-developed in all the alloys, particularly the BC1 alloy. The IPF maps show a wide distribution of crystallographic orientations with the C22 alloy exhibiting a preference for the \{101\} orientation, and the BC1 and C625 alloys possessing a large number of grains with orientations distinct from the three main orientations.
Figure 6.2: Crystallographic plane-normal orientation (IPF) maps for (a) C22; (b) BC1; and (c) C625 alloys with $\Sigma$ (red) and random (black) grain boundaries superimpose on the map. The accompanying graphs show the percentage of each type of boundary for the three alloys.
The histograms of the size distributions are shown in Figure 6.3. A total of 184, 220 and 259 grains were analyzed for the BC1, C22 and C625 alloys, respectively, using Tango EBSD software to determine the size distribution.

Figure 6.3: Grain diameter distributions for the three alloys.

Estimation of grain size using EBSD is more precise than traditional methods, such as light microscopy of the etched surface, and allows twin boundaries to be disregarded in grain size estimations [29]. ASTM E112 [30] is used for grain size measurement in this analysis. All histograms show the same trend with a large number of small grains and a decreasing number of grains as their size increases. The C22 and BC1 alloys have
relatively large grains with average grain diameters of 38.1 μm and 42.8 μm, respectively.

The maximum grain size detected in BC1 was 158.7 μm and in the C22 alloy, 192.1 μm. By contrast, the grain size in the C625 alloy is found to be 3.4 μm, which is ~ 10 times smaller than for the other two alloys, with a maximum grain size of 16 μm.

6.3.2 Corrosion and Electrochemical Measurements

Figure 6.4 shows potentiodynamic polarization curves recorded in the 3 M NaCl + 1.5 M HCl solution at 75°C. Both the high-Cr alloys, C22 and C625, exhibit an active region with critical current \(i_{\text{crit}}\) values for the active to passive region of 0.002 A/cm\(^2\) (C22) and 0.030 A/cm\(^2\) (C625) while the low-Cr alloy (BC1) does not exhibit an active peak. This decrease in \(i_{\text{crit}}\) with Mo content is consistent with published data. Also consistent with expectations, the passive current density is higher for the low-Cr BC1 than for the high Cr C22 and C625, and the onset of transpassivity occurs at a slightly lower potential for the low Cr BC1 alloy.

Figure 6.4: Potentiodynamic polarization curves for BC1, C22 and C625 alloys in 3 M NaCl + 1.5 M HCl at 75°C solution at a scan rate of 0.5 mV/s.
The passive current for the C625 alloy is slightly less stable than for the other two alloys, consistent with an influence of Mo in maintaining passivity, this alloy having the lowest Mo content. Current density fluctuations observed in the passive region for C625 can be attributed to metastable pitting. No such behavior was observed for the other two alloys. The absence of metastable current fluctuations in C22 and BC1 alloy is likely due to their higher Mo content. By increasing the potential to 0.9 V all the alloys show a rapid rise in current due to the onset of transpassivity.

Figure 6.5 shows the $E_{\text{CORR}}$ values recorded over 7 h. For all 3 alloys, $E_{\text{CORR}}$ initially decreases rapidly eventually achieving a steady-state value. The initial decrease can be attributed to dissolution of the native oxide film present on first immersion. The steady-state $E_{\text{CORR}}$ values increase in the order

\[ \text{C625 (-230 mV) < C22 (-200 mV) < BC1 (-130 mV)} \]

as observed in the polarization curves.

![Figure 6.5: Corrosion potential ($E_{\text{CORR}}$) recorded on Alloy 22, BC1 and C625 over 7 hours of immersion in 3 M NaCl + 1.5 M HCl at 75°C.](image)
The steady-state $E_{\text{CORR}}$ values are clearly in the active region for C625 and C22 indicating these alloys would be susceptible to crevice corrosion if the critical crevice solution achieved these acidic saline conditions. The absence of an active region suggests the BC1 alloy would not be susceptible to crevice corrosion for these conditions.

### 6.3.3 Post-Corrosion Surface Imaging

Secondary Image (SE) micrographs of selected areas of the corroded C22 and BC1 alloys are shown in Figure 6.6 (a) and Figure 6.6 (b).

![Secondary Image (SE) micrographs of selected areas of the corroded C22 and BC1 alloys](image1)

Figure 6.6: SE images of (a) C22 and (b) BC1 surfaces after exposure to the acidic solution and their corresponding orientation map images (c) and (d). All $\Sigma$ and random grain boundaries are in red and yellow, respectively. Non-indexed points (mostly due to localized corrosion) are in green.
Of the three alloys, C625 alloy was the most heavily corroded, Figure 6.7 (d), as expected from the $E_{\text{CORR}}$ and polarization scans. Since there is literature to suggest the corrosion rate should decrease as the grain size decreases [31,32], and this alloy has a significantly lower grain size than the other two, grain size is not the dominant feature in controlling the corrosion rate.

This leaves two possible explanations for the enhanced corrosion of this alloy: the grain orientation and grain boundary properties, and the alloy composition. According to Horton and Scully [31], based on a study of crystal orientation on the corrosion of FCC FePd, the corrosion rate is expected to be lowest on the three low index orientations of {111}, {100} and {110} and increases when the grain orientation diverges from the {100} and {111} orientations. Inspection of the IPF map for C625, Figure 6.2, shows this is the case for this alloy. However, given the polarization behaviour (Figure 6.4) it seems more likely that the determinant of corrosion behaviour is the low Mo content [32].

By contrast, the BC1 and C22 alloys exhibited considerably less corrosion and maintained their crystal orientations after corrosion, Figure 6.6 (a) and (b). The most visible signs of corrosion are the intergranular trenches and the small etch pits on the grain surfaces, with a slightly higher density of the latter on the BC1 alloy. This latter observation may reflect the larger number of grains with orientations which deviate from the more corrosion resistant low index planes. High interfacial energies commonly make grain boundaries preferred sites for corrosion. However, for both alloys some grain boundaries are corroded while others are not, as shown clearly in Figure 6.7 (a) and (b). Orientation maps obtained by EBSD for the surface areas shown in Figure 6.6 (a) and (b) are presented in Figure 6.6 (c) and (d), respectively. Red and yellow lines indicate $\Sigma$ and random grain boundaries, respectively, with non-indexable locations shown in green. The inability to index certain sites can be attributed to corrosion as clearly indicated by the correlation between their location in these maps with the etch pits on the grain surface shown in Figure 6.6 (a) and (b). For the grain boundaries, the non-indexable points are
located along the random boundaries and at some of the triple point junctions, many of which are preferentially corroded, Figure 6.7 (c).

![Figure 6.7: A corroded random grain boundary in (a) BC1 and (b) C22 alloy; (c) triple points corroded in the C22 alloy; (d) general corrosion on C625.](image)

Close inspection enabled the characterization of four distinct groups of triple point junctions: junctions linking three $\sum$ boundaries ($\sum \sum \sum$), two $\sum \sum$ and one random boundary ($\sum \sum \ R$), one $\sum$ and two random boundaries ($\sum \ RR$), and three random boundaries (RRR), for which the last type proved most susceptible to corrosion.

A statistical analysis was performed to compare the corrosion resistance of $\sum$ and random boundaries. A total of 156 (C22) and 159 (BC1) grain boundaries were analyzed. The length of all the $\sum$ and random boundaries, and also the length of corroded regions on each type of grain boundary were measured using Image Pro software. The linear proportion corroded percent was calculated as the ratio of the corroded length over the total length of each characterized boundary (Figure 6.8). For both alloys the $\sum$ boundaries were considerably more resistant than the random boundaries: 16% (random)
and 1.7% ($\Sigma$) for C22, and 7% (random) and 1.7% ($\Sigma$) for BC1. These results are consistent with previous observations [18].

Figure 6.8: Fraction of $\Sigma$ and random grain-boundaries that undergo corrosion.

4.3.4 Confocal Laser Microscopy

Besides intergranular corrosion and grain defect etching the alloys also exhibited different rates of grain surface dissolution depending on the crystallographic orientation of the grain. Figure 6.9 shows 3D CLSM images of the areas circled in the inverse pole figure maps.

These images show that the corrosion rates of individual grains correlates with their orientation in the surface normal direction. The least corroded grains have a $\{111\}$ orientation. This is the most densely packed plane in the FCC crystal lattice and would be expected to have the slowest corrosion rate, Gray et al. [33] having reported that the corrosion rate of C22 decreases with the plane normal crystallographic orientation in the order $\{111\} \geq \{110\} > \{100\}$.
The intergranular corrosion can be seen in Figure 6.9 (c) and a closer look at individual grains shows that some grains are high relative to adjacent grains, the difference in height being due to general corrosion. The dissolution behavior of the grains was found to correlate to the orientation in the surface normal direction. The majority of high grains are blue on the EBSD map meaning they exhibit a $\{111\}$ orientation. These grains dissolve at a slower rate and are more corrosion resistant than grains in other orientations. Greater corrosion resistance is attributed to the growth of a more compact, coherent oxide on grains with $\{111\}$ orientations.

### 6.3.4 TEM Analysis

To investigate the reasons for the enhanced corrosion resistance of $\Sigma$ boundaries, TEM specimens were prepared from $\Sigma$ and random grain boundaries on the C22 alloy. The specimens cut using a focussed ion beam were characterized using a scanning transmission electron microscope (STEM) equipped with an electron energy dispersive
X-ray analyzer (EDS). The EDS analyses were performed at a number of locations across the $\Sigma$ and random grain boundaries as indicated in Figure 6.10.

Figure 6.10: EDS data points recorded across $\Sigma$ (a) and a random (b) grain boundaries as indicated by numbers.

Figure 6.11 summarizes the compositions obtained from this analysis and shows uniform composition of the material on both sides of the boundary the location of which is shown with a dashed line. No significant change in elemental composition is observed across either grain boundary. Table 6-2 shows the mean, minimum and maximum and standard deviation of the EDS data points across the $\Sigma$ and random grain boundaries. The homogeneity in composition is demonstrated by the small standard deviation ($< 0.6\%$). Due to the weak detection limit for EDS these minor differences are not significant.
Figure 6.11: Chemical composition (wt.%) of C22 alloying elements at locations across a $\Sigma$ and a random grain boundary.

Table 6-2: The mean, minimum, maximum and standard deviation of the EDS data points measured across $\Sigma$ and random grain boundaries.

<table>
<thead>
<tr>
<th>Elements /Points</th>
<th>Sigma Boundary</th>
<th>Random Boundary</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ni  Cr  Mo  Fe  W</td>
<td>Ni  Cr  Mo  Fe  W</td>
</tr>
<tr>
<td><strong>Mean</strong></td>
<td>57.7 25.3 11.2 4.4 1.4</td>
<td>58.2 25.5 10.2 4.6 1.3</td>
</tr>
<tr>
<td><strong>Std. Dev</strong></td>
<td>0.3 0.3 0.3 0.2 0.2</td>
<td>0.6 0.4 0.3 0.2 0.1</td>
</tr>
<tr>
<td><strong>Min</strong></td>
<td>57.2 24.8 10.7 4.2 1.1</td>
<td>57.3 24.9 9.8 4.3 1.2</td>
</tr>
<tr>
<td><strong>Max</strong></td>
<td>58.4 25.7 11.5 4.6 1.7</td>
<td>59.0 26.2 10.8 5.0 1.6</td>
</tr>
</tbody>
</table>
The boundaries were also examined by Annular Dark Field (ADF) STEM. Bright needle inclusions were detected in random boundaries in close proximity to the grain boundary and protruding into the grain, Figure 6.12 (b). The length of these inclusions was ~ 20-40 nm. No similar inclusions were detected on ∑ boundaries, Figure 6.12 (a). Subsequently, EELS analysis was performed to investigate the nature of these inclusions.

ADF-STEM micrographs of the regions on either side of the grain boundaries are shown in Figure 6.13 along with the corresponding EELS maps for the same locations. For the random boundary the inclusions detected in the ADF STEM images are shown to be depleted in Ni and slightly enriched in O. No changes in Fe and Cr content were detected. For the ∑ boundary no Ni depletion/O enrichment was observed, all elements (O, Ni, Fe, Cr) being uniformly distributed within both grains and along the grain boundary. No Mo EELS map could be obtained by this method as the specimen thickness was too large and thus the signal background generated by multiple scattering events was higher than the anticipated Mo peak at the given Mo concentration.

Figure 6.12: ADF STEM images of (a) ∑ and (b) random grain-boundaries. The arrows on figure (b) show the line shaped inclusions.
Figure 6.13: EELS maps of (a) random and (b) ∑ grain boundaries and the related elemental composition of the same area; the arrows show the location of needle shaped inclusions.

The diffraction pattern recorded in the same regions was analysed for both grain-boundaries, Figure 6.14. The transition in diffraction pattern from one grain to the other is abrupt for a random boundary, as expected for the high degree of mismatch between the orientations in the two grains. Analysis of the diffraction patterns recorded in adjacent grains, confirms the nature of these inclusions is different from that of other locations in the grain-boundary. The identity of these inclusions remains to be confirmed. In contrast, the ∑ 3 grain boundary shows no distinct diffraction peaks, the interface between the grains yielding the sum of the diffraction patterns of both grains. This is not surprising since the chosen grain boundary is a ∑ 3 boundary with one in each three lattice points coincident within the boundary.
Figure 6.14: the $\Sigma$ (S) and random (R) grain boundaries and the diffraction patterns of the two adjacent grains (B) and (D) and the grain boundaries (C) and the needle shape inclusion (E).

6.4 Conclusions

Corrosion analysis on both alloys showed that $\Sigma$ grain boundaries are less susceptible to corrosion compared to random grain boundaries for both C22 and BC1 alloy. Based on confocal microscopy and EBSD analysis, some grains appear higher than adjacent grains. The majority of these grains exhibit a \{111\} orientation suggesting these planes are more corrosion resistant than the \{001\} and \{101\} planes and all the other orientations between the low-index planes.
The TEM analysis of a selected random grain boundary shows O-rich inclusions in close proximity to the boundary. These inclusions have a crystalline nature, are 20-40 nm long and only a few nanometers wide. They form needle shaped structures which would act as initiation locations for corrosion, weakening the grain boundary in the process. The diffraction patterns collected from areas near, and on, the \( \Sigma \) and random grain-boundaries show abrupt changes in crystal orientation on random grain boundaries confirming the higher energy at these locations. This higher degree of lattice mismatch would be another reason for the lower corrosion resistance of these boundaries. The general corrosion resistance of C625 is considerably lower indicating that the composition of the alloy, in particular the low Mo content, controls the corrosion.

### 6.5 Acknowledgment

This research was supported by the Canadian natural sciences and engineering council (NSERC). The Nanofab facility at University of Western Ontario is acknowledged for use of their equipment. TEM research was performed at the Canadian centre for electron microscopy at McMaster University, which is supported by NSERC and other government agencies. Haynes International (Kokomo, Indiana, USA) supplied the alloys.
6.6 References


Chapter 7

7 Conclusions and Future Work

7.1 Conclusions

This thesis investigated the effect of alloying elements on the corrosion behaviour of Ni-Cr-Mo alloys, especially crevice corrosion. The primary focus was on the mechanism controlling propagation of crevice corrosion especially the factors controlling the propagation of corrosion damage.

The effects of the alloying elements Cr, Mo and W on crevice corrosion initiation and propagation on three commercial Ni alloys were investigated under galvanostatic control in 5 M NaCl at 150°C. The galvanostatic approach was used to study activation and propagation while avoiding repassivation. The activation step was shown to depend on the Mo content of the alloy and to involve competition between Cr(III) barrier layer breakdown and Mo(VI)/W(VI) accumulation to repair breakdown sites. Under stable propagation conditions the crevice potential ($E_C$) measured is proportional to the Mo + W content of the alloy, and almost constant and independent of the applied anodic current, indicating that propagation is controlled by the crevice chemistry.

Mo content determines the distribution of corrosion damage. For C625 (9wt.% Mo) propagation leads predominantly to penetration into the alloy, whereas increased Mo content (C22 (13 wt.%) and BC1 (22 wt.%)) causes corrosion damage to spread laterally across the creviced surface. This is attributed to formation of polymeric molybdates which stifles the dissolution of alloy by accumulation at active sites. By increasing the Mo content of the alloy, the stifling and blocking of the active sites occurs more rapidly and limits the depth of penetration into the alloy.
The crevice initiation and propagation on BC1 (the alloy with the highest Mo content) were investigated by applying a constant charge of 6.9 C in the form of different currents of 10, 20, 40 or 80 μA. The electrochemical behaviour during initiation varied with applied current. However, in cases where sustained propagation occurred, $E_C$ was relatively constant and similar in value over a range of applied currents.

Optical microscopy and 3D imaging of the corroded area using profilometry demonstrated that damage morphologies vary with applied current. Higher currents lead to a shallower and broader creviced area, causing the current density to stay almost constant. This is because at higher applied currents the formation of proton-consuming polymeric molybdate products happens faster. Since these oxides block the progress of crevice corrosion, propagation is forced to spread laterally.

When the same 6.9 C charge is applied galvanodynamically, starting from a current of 80 μA and decreasing steadily to 0, the same passive-to-active potential response as observed during galvanostatic polarization was obtained. Coupling the crevice sample to a counter electrode through a zero resistance ammeter immediately after galvanodynamic polarization demonstrated clearly that the negative-going transients in $E_C$ are linked to anodic spikes in crevice current ($I_C$). The response of $E_C$ and $I_C$ to the addition of oxygen to the system shows that the oxygen reduction reaction is one of the cathodic reactions supporting the corrosion. The other cathodic reaction is the hydrogen evolution reaction occurring inside the creviced region. Weight change measurements during crevice corrosion shows that greater than 50% of propagation is caused by proton reduction inside the crevice.

To answer the question of whether the molybdate surface formed inside a creviced region could be considered passive and protective or whether it was permanently degraded, a series of EIS analyses followed by XPS and AES were conducted on oxide films grown electrochemically on BC1 and C22 at different potentials at pH = 7 and 9 solutions. EIS measurements indicate that while the passive film may form less readily on BC1 than on C22 at pH = 7, the repaired film formed after transpassive breakdown is more resistive on
BC1. The higher resistance of the reformed film on BC1 was diminished at pH = 9 solution indicating that transpassively-formed molybdate contributes to the enhanced passivity.

Upon reformation of the passive layer after transpassive dissolution, C22 regrows an effectively identical Cr₂O₃ barrier layer and the improved passivity may reflect some contribution to enhanced passivity from the residual molybdate deposited during oxidation. The XPS and AES profiles recorded on the reformed passive film on BC1 show an increase in the amount of Cr in the passive film but only a minor contribution from a reformed Cr₂O₃ barrier layer. Despite this uncertainty concerning the state of the Cr, passivity is strongly enhanced suggesting this state is at least partially sustained by the transpassively-formed molybdate.

The corrosion damage observed beneath the corrosion product was intergranular with more corrosion occurring on random grain boundaries compared to special Σ boundaries. TEM analysis of a selected random grain boundary shows O-rich inclusions in close proximity to the boundary. These inclusions have a crystalline nature, are 20-40 nm long and only a few nanometers wide. They form needle shaped structures which would act as initiation locations for corrosion, weakening the grain boundary in the process. The diffraction patterns collected from areas near, and on, the Σ and random grain-boundaries show abrupt changes in crystal orientation on random grain boundaries confirming the higher energy at these locations. This higher degree of lattice mismatch would be another reason for the lower corrosion resistance of these boundaries.

7.2 Future Work

In this study, an attempt was made to draw a correlation between corrosion resistance of Σ and random grain boundaries and the in composition differences, between the two grain boundaries. While TEM and EELS analyses show some oxygen-rich inclusion on random grain boundaries, the exact composition of these features was not determined. Atom probe tomography on these grain boundaries could be used to determine whatever
compositional differences associated with these inclusions can explain the susceptibility of random boundaries.

The morphology of corrosion propagation has been investigated by examining the cross sections of creviced specimens and performing surface profilometry of the corroded area. These techniques have provided significant insight on damage propagation. However, a more complete imaging of the damage sustained for a wider range of conditions is required. The application of additional techniques such as X-ray imaging should be considered.

Based on weight loss measurements on BC1 for a constant applied charge and a knowledge of the anodic charge applied, it was shown that > 50% of crevice propagation is driven by internal proton reduction. How this balance between internal and external corrosion is influenced by a range of parameters (alloy composition, temperature, and duration of propagation) should be determined.

The results presented indicate that the conditions inside an active crevice are dominantly determined by alloy composition. This makes it difficult to see how the process can be described by the IR drop model. The investigation of a wider range of alloys and exposure conditions should be undertaken to enable the development of a model to describe crevice propagation on these alloys and to determine the conditions under which it might be expected.
Curriculum Vitae

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Working Experiences

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Material Engineer (Oct 2010- Aug. 2011)

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Supervisor: Dr. David Shoesmith


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Thesis: Role of dichromate ions on critical pitting temperature of 2205 duplex SS.

Supervisor: Dr. Hadi Moayed


Ferdowsi University of Mashhad

Publications


**Conferences Presentations**


**Awards**

1. NACE Northern Area Western conference student poster award (2015)

2. NACE corrosion 2014 student travel award (2014)

3. NACE corrosion 2013 student travel award (2013)

4. NACE Northern Area Eastern conference student poster award (2012)

5. EBSD 2012 conference student scholarship (2012)

6. Western graduate research scholarship (2011-2015)

8. Ferdowsi University of Mashhad talented students award (2007).