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Environmental effects on corrosion properties of Alloy 22

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FINAL TECHNICAL REPORT

Environmental Effects on Corrosion Properties of Alloy 22

Prepared for the U.S. DOE/UCCSN Agreement

Task Number: ORD-FY04-014

Approvals:

Principal Investigator, Prof. Manoranjan Misra

(Approval date)
Document Format:

This document presents detailed technical report for four Subtasks that were conducted independently. All four Subtasks investigated environmental effects on corrosion properties of Alloy 22.

The four Subtasks that were investigated are as follows:

Subtask 1: Experimental Determination of Parameters for the General Corrosion Model.

Subtask 2: Corrosion under Dust Deposits Containing Hygroscopic Salts.


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Objectives and Summary of Findings Subtasks

Subtask 1: Experimental Determination of Parameters for the General Corrosion Model

Objectives of Subtask 1:

The objective of the proposed investigation of Task ORD-FY04-014, "Environmental Effects on Corrosion Properties of Alloy 22," Subtask 1, "Experimental Determination of Parameters for the General Corrosion Model," is to obtain very high-accuracy experimental data which will be used to determine model parameters that will provide accurate general corrosion modeling over the full range of temperature, pH, ionic composition, and potential anticipated over the lifetime of the repository.

Summary of Findings of Subtask 1:

Storage of High Level Nuclear Waste (HLNW) requires prediction of corrosion behavior with unprecedented accuracy over thousands of years. To support this need, high-accuracy electrochemical data are required. A laboratory with special features to support long-term electrochemical tests has been designed, built, and proven. High-accuracy electrochemical impedance spectroscopy (EIS) data and passive current densities have been measured for Alloy 22 in deaerated pH 6, 4 M NaCl and pH 3, 0.1 M Cl electrolytes at temperatures of 30°, 60°, 75°, and 90°C. Accuracy of the EIS data has been verified by checking for hysteresis of back to back scans and in data collected hundreds of hours apart, and through application of the Kramers-Kronig transforms. The data are interpreted in terms of the Point Defect Model (PDM) of growth and breakdown of passive films. Mott-Schottky analysis is applied to evaluate the semiconductor
properties of the passive film. At low potential the passive film is found to be an \( n \)-type semiconductor. The film transitions to a \( p \)-type semiconductor as potential is increased towards the transpassive potential. Impedance data collected into the transpassive range show a large drop in capacitance at low frequency. This can be interpreted as thinning of the film and weakening of the lattice structure. The observed behavior can be explained in terms of the PDM reaction mechanism as cation vacancy generation by oxidative ejection of cations at the film/solution interface. A "best guess" PDM parameter set from phase space analysis was found to provide a good match between calculated and measured impedance, current density, and film thickness. A nonlinear least squares curve fitting method to derive PDM parameters by optimizing the PDM on measured impedance data was investigated. It was found to be unconstrained and to generate multiple solutions for a single impedance spectrum. This demonstrates that the curve fitting method must be constrained by including thickness and current density equations in the model. Though unconstrained, the modeled parameters provide useful insights into the PDM reaction mechanism indicating that cation interstitials are the dominant defect over oxygen vacancies.
Subtask 2: Scientific Investigation Plan: Corrosion under Dust Deposits Containing Hygroscopic Salts

Objectives of Subtask 2

The objectives of this subtask are to model and experimentally verify the corrosion of Alloy-22 under an oxygen permeable hygroscopic dust deposit.

Summary of Findings of Subtask 2:

In order to create hygroscopic dust deposit on Alloy 22, dripping solution method was adopted. In this test, salt solutions simulating Yucca Mountain were used. Alloy 22 was maintained at a temperature of 90°C and the salt solution drops were made to drip on to it intermittently at a predetermined rate. Because of evaporation of water with time, the surface of Alloy 22 was found to become dry. Then the dripping was resumed. This process continued for 40 days. It was found that the surface slowly deposited a salt deposit on the surface of Alloy 22. Crevices were found to form between the salt deposit and the hot surface of Alloy 22. The morphology of the corrosion products formed in this test was similar to the one observed in a filiform corrosion that often found beneath a paint film. After the 40 day drip test, the specimen surface was assessed for corrosion attack, if any. No severe localized attack was noticed after the 40-day test. No pitting attack was noticed. However, very insignificant intergranular corrosion attack was noticed on Alloy 22.
Subtask 3: Heated Electrode Approach for the Study of Corrosion Under Aggressive Conditions

Objectives of Subtask 3:

The objectives of this subtask are as follows:

1. To simulate the most aggressive corrosion conditions that could be expected in repository environments and evaluate the corrosion resistance of Alloy-22 using heated electrode approach.

2. To investigate the incubation time required for passive film breakdown at different anion concentrations and pH levels

Summary of Findings of Subtask 3:

Temperature fluctuation effects on cyclic polarization, corrosion potential, and passive current density of Alloy 22 under simulated Yucca Mountain waters open to ambient air were investigated using a newly developed temperature-oscillating heated electrode technique (TOHET). Fluctuating cyclic polarization curves were obtained which show that current is sensitive to temperature variation when the temperature amplitude was greater than 2 °C. Corrosion potential and logarithmic-scale passive current density were found to be linearly proportional to temperature. Accordingly, combining typical electrochemical tests with the application of temperature-oscillating heated electrode technique provides a method to assess the temperature effect on corrosion rates within a temperature range as small as 10 °C. In addition, temperature-oscillating heated electrode technique is expected to be a useful approach for studying the effects of temperature variation on corrosion behavior of passive alloys under cyclic wet/dry conditions.
Subtask 4: Effect of Hydrogen Permeation on the Stability of the Passive Film of Alloy-22

Objectives of Subtask 4

To quantify the effect of hydrogen on the degradation of the corrosion resistance of the passive film of Alloy-22 in chloride containing environments and to understand the synergistic effect of hydrogen and chloride on the breakdown (if present) of passive film.

Summary of Findings of Subtask 4:

This part of the report deals with the results of subtask 4 of Task Number ORD-FY04-014. The objective of Subtask 4 is to study to effect of hydrogen permeation on the stability of the passive film of Alloy 22. Alloy-22 foils are studied in a Devanathan-Starchurski cell under 60°C, pH 12.5 0.1M NaOH solutions. Electrochemical impedance spectroscopy is utilized to investigate the kinetics of hydrogen absorption and effects on the general corrosion rate. Anodic polarization scans are employed to look for a synergistic pitting potential lowering effect between hydrogen and chloride as seen in type 304 stainless steels. The thickness of the passive film is estimated using a parallel plate capacitor method. Diffusivity of hydrogen in alloy-22 is estimated using ASTM standard G149-97. Electrochemical Impedance Spectroscopy is used to determine any long-term damage done to the impedance of the passive film.
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Subtask 1: Experimental Determination of Parameters for the General Corrosion Model

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Figure 1.30. Bode Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z at 50 mV (Ag/AgCl/0.1 M Cl⁻) Hysteresis between 144 hrs., 432 hrs., and 624 hrs. (Data File in Folder “Subtask1 Figures data files” File Tables 1.1-1.42-Tables 1.19, 1.20, 1.21, 1.22, 1.23, 1.24, 1.25, 1.26)

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Figure 1.44. Mott-Schottky Plot for mill-annealed Alloy 22 in deaerated, 60°C, pH 6, 4 M NaCl electrolyte, ascending voltages, nominal current density = 14 nA/cm\textsuperscript{2}.

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Figure 1.51. Schematic of the processes envisioned to take place in the barrier layer on Alloy 22 at passive potentials where the oxidation state for Cr in the barrier layer is the same as in the solution, i.e., \( \Gamma = \chi \).

Figure 1.52. Schematic of the processes envisioned to take place in the barrier layer on Alloy 22.

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Figure 1.54. Measured and calculated imaginary impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl\(^{-}\) electrolyte.

Figure 1.55. Measured and calculated real impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl\(^{-}\) electrolyte.

Figure 1.56. Measured and calculated imaginary impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl\(^{-}\) electrolyte using rate constants four orders of magnitude smaller than the phase space analysis "best guess" parameters.
Figure 1.57. Measured and calculated real impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl\textsuperscript{-} electrolyte using rate constants four orders of magnitude smaller than the phase space analysis “best guess” parameters.

Subtask 2: Scientific Investigation Plan: Corrosion under Dust Deposits Containing Hygroscopic Salts

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Figure 2.2 Temperature variations during the dripping test with different dripping intervals
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Figure 2.4 Alloy 22 at the end of the dripping test (side views)

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Figure 2.6 Optical micrograph of Alloy 22 indicating intergranular corrosion by salt deposits

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Figure 3.3  Polarization curves with different temperature variation mode. (Data file in folder “Subtask3 Figures data files”- Figure 3.3)

Figure 3.4  The effect of temperature oscillation on corrosion potential (Data file in folder “Subtask3 Figures data files”- Figure 3.4)

Figure 3.5  The effect of temperature oscillation on passive current at 150 mV vs. Ag/AgCl (Data file in folder “Subtask3 Figures data files”- Figure 3.5 & Figure 3.6)

Figure 3.6  The relationship between passive current density and temperature. (Data file in folder “Subtask3 Figures data files”- Figure 3.5 & Figure 3.6)

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Figure 4.1: Drawing of a modified Devanathan Cell

Figure 4.2 : Current density timeline for hydrogen permeation of alloy-22

Figure 4.3 Current density timeline for hydrogen permeation of alloy-22.

Figure 4.4 Current density timeline for hydrogen permeation of alloy-22 in 60°C 0.1 M NaOH solution
Figure 4.5 Alloy-22 anodic polarization curves showing transpassive initiation potentials in pH 12.5, 0.1M NaOH solutions (A) No hydrogen permeation at 60°C (B) With hydrogen permeation at 60°C (C) With hydrogen permeation at 40°C

Figure 4.6 Alloy-22 anodic polarization curves showing transpassive initiation potentials in pH 12.5, 0.1M NaOH + 0.1M NaCl solutions at 60°C (A) No hydrogen permeation (B) With hydrogen permeation (C) With hydrogen permeation (repeated) showing transpassive initiation

Figure 4.7 Galvanostatic voltage reacting to reduction in active surface area due to a growing bubble of hydrogen on alloy-22 sample surface.

Figure 4.8 EDX and Electron microscopy of the deposited arsenic compound on alloy-22

Figure 4.9: Alloy-22 passive film thickness estimation from the parallel plate capacitor method

Figure 4.10: Standard Fick’s laws flux function regression showing inability to converge.

Figure 4.11: Standard Fick’s laws flux function regression showing inability to converge.
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Subtask 1: Experimental Determination of Parameters for the General Corrosion Model

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1.1 INTRODUCTION

The proposed design of the high-level nuclear waste (HLNW) repository at Yucca Mountain, Nevada relies primarily on engineered barriers to prevent release of radioactive and toxic materials into the environment. At the time of this writing, Alloy 22 (UNS N06022, 56Ni-22Cr-13.5Mo-3W-3Fe) has been chosen as the corrosion resistant material (CRM) for the outer shell of the waste package (WP) container. The present U.S. Department of Energy (DOE) WP design has a 20-mm thick Alloy 22 outer layer surrounding a 50-mm thick type 316 nuclear grade stainless steel inner container.

The 20-mm thick Alloy 22 outer layer is intended to survive 10,000 years, breaching to the type 316 stainless steel by uniform corrosion only after 10,000 years has been passed. At the time of this writing the WP design is based on the 10,000 year regulatory lifetime originally proposed for the repository. (Note that the regulatory lifetime of the repository had been set at 10,000 years, but due to court decisions made in mid-2004 this may be increased.) This design is based on uniform corrosion rates; it considers the chance of stabilization of localized corrosion (pitting and crevice corrosion) for time periods in excess of 10,000 years to be negligible under what is believed will be the prevailing environmental conditions of the proposed repository.

Yucca Mountain is composed of fractured volcanic tuff and rhyolite. The fractured nature of the mountain results in the air in the repository drifts being in
equilibrium with the external atmospheric pressure. Considering the different ground waters present (well water, perched water, pore water), the conditions are such that relatively concentrated aerated brine solutions of near-neutral to basic pH and a wide range of ionic compositions may be present on the WP containers resulting in a variety of corrosive environments.

Alloy 22 owes its corrosion resistant properties to the formation of a thin protective film, a few nanometers thick, called the passive film or barrier layer. On metals such as Alloy 22, which contain chromium as the primary alloying element responsible for corrosion resistance, the passive film is typically between 0.5 and 4 nanometers thick depending upon the alloy and the environment. This film greatly reduces the rate of uniform corrosion under a large range of chemical conditions of the environment. Alloy 22 includes molybdenum as an alloying element to extend corrosion resistance to reducing environments and to decrease susceptibility to pitting corrosion. But in some conditions localized corrosion such as pitting and crevice corrosion still occurs as a result of destabilization of the passive film. Consequently, it is absolutely necessary to determine the chemical conditions of the material, surface, and environmental medium that affect uniform and localized corrosion behavior of the passive film and their stability with time in order to understand the behavior of a given material.

Predicting corrosion behavior for such long time periods presents an unprecedented challenge, especially since Alloy 22, which was introduced in the early 1980's, is a relatively new material with little long-term corrosion data available. To
date, predictions have been based on empirical measurements such as weight loss immersion tests \(^4\,^2^2\) and passive current density \(^3\) which are inherently limited in scope and applicability because they do not provide information about fundamental mechanisms.

At present, we have a good understanding of passive films, but not good enough to predict behavior over the 10,000+ years required for disposal of high-level nuclear waste. Corrosion resistance of a material is not an intrinsic property; it depends upon the thermal history and surface condition of the material and upon the environment to which it is exposed. Will the properties of the passive film be constant over long periods of time? The passive film can change as the environment changes over a long period of time. As the dissolution process proceeds, ions move through the film into the environment and may change the medium and also result in segregation of species in the alloy\(^2^3\) Ageing of passive films may involve various transformations such as stoichiometric changes, swelling or dehydration, further growth, recrystallization, or depletion of defects. In response to ageing processes many film properties, such as ionic and electronic conductivity and potential distribution, may change. As a consequence, film stability and corrosion resistance will be affected\(^2^4\). Therefore, film ageing is of great practical importance and our ability to predict time-dependence of properties is crucial. Because our experience with Ni-Cr alloys similar to Alloy 22 is limited to 50 years or so, a deterministic modeling approach based on time-invariant natural laws (such as conservation of mass and charge) is required to address the dynamic nature of long-
term corrosion predictions\textsuperscript{25}; predictions based on empirical measurements alone are, by their very nature, unable meet the requirements.

Many models to describe passivity of metals have been proposed\textsuperscript{26-34}. Of these, only the Point Defect Model\textsuperscript{34-37,41} (PDM), developed by D.D. Macdonald, appears to account for all of the experimental observations of the structure and behavior of passive films. The PDM is a deterministic model describing the growth and breakdown of passive films in terms of mass and charge flux across a semiconducting passive film of defective metal oxide. A chemical reaction mechanism to describe the processes is described. From this mechanism, equations describing mass and charge flux and reaction rate kinetics are derived. Further mathematical operations yield a set of equations that describe the response of the system to small, sinusoidal perturbations of applied potential as used in electrochemical impedance spectroscopy (EIS). From these equations and experimentally measured electrochemical impedance spectra, model parameters such as standard kinetic rate constants, transfer coefficients, and potential drops may be determined\textsuperscript{37}. These parameters, combined with predictions of the evolution of the repository environment, may allow accurate prediction of Alloy 22 corrosion behavior over the repository lifetime.
1.2 SCOPE AND OBJECTIVES

The purpose of this work is to collect reliable, high-accuracy electrochemical data to define the passive state of Alloy 22 for predictions of long-term corrosion damage under high-level nuclear waste geologic repository conditions. These data are evaluated using the Point Defect Model and Mott-Schottky analysis. A nonlinear least-squares curve fit model for extracting PDM parameters from experimental data has been developed and tested. Model parameters have been derived from the experimental data.

The emphasis of the work is on experimental accuracy and reliability. To that end much time was allowed for the system to attain steady state and many checks were performed to ensure stability of the system. At each potential two sets of EIS data were collected; the first was scanned from high frequency to low frequency and the second, initiated immediately after the first, was scanned in the low frequency to high frequency direction. The two scans were compared to check for hysteresis. (Hysteresis indicates non-steady state and therefore invalid data.) EIS data were also checked for validity through application of the Kramers-Kronig transforms\textsuperscript{38}. Potential was swept anodically and cathodically over the passive range, dwelling at each potential for many hours. Hysteresis of electrochemical results for ascending and descending voltages was evaluated.
1.3 EXPERIMENTAL WORK:
1.3.1 Apparatus and Procedures

1.3.1.1 Quality Assurance

Experimental work presented herein was originally performed under the control of the Nevada System of Higher Education (NSHE) Quality Assurance Program, which was approved by the U.S. Department of Energy Office of Civilian Radioactive Waste Management (OCRWM) Yucca Mountain Project (YMP). However, in accordance with direction from OCRWM, quality assurance oversight of this work was discontinued before the project activity was completed. As a result, although the technical integrity of the work is not in question, data and conclusions presented herein are unqualified and may not be used for quality affecting purposes.

1.3.1.2 Design Criteria

Because Alloy 22 displays nanoampere–level passive current densities and because these tests are designed to run continuously for times up to 2,000 hours or longer, a number of special features have been incorporated into the experimental apparatus to provide stability and increase accuracy of the experimental data. Design criteria include: dissolved oxygen at sub-ppb concentration so that oxygen reduction current is much smaller than Alloy 22 corrosion current; no reduced species generated at the counter electrode may migrate to the working electrode, which would add to the measured corrosion current; temperature stability ± 0.2 centigrade degrees; no change in electrolyte pH; and no accumulation of corrosion products.
1.3.1.3 Test Cell Design

Fresh electrolyte was continuously flowed through the test cells to prevent accumulation of corrosion reaction products and to prevent changes in electrolyte pH and chemical composition from occurring during the course of the tests. Electrolyte was discarded after one pass through the system. Figure 1.1 presents a schematic of the test cell.

Figure 1.1. Schematic of test cell. CE = counter electrode, WE = working electrode, RE = reference electrode. Note the thermowell and the port for the working electrode compartment Allihn condenser are not shown.
The cell is constructed of a 2 liter reaction flask with a Teflon top that has been machined to accommodate nylon compression fittings with Viton O-rings to seal all of the penetrations. Not shown in the schematic are the glass thermowell and thermocouple, and the fitting for the working electrode compartment vapor condenser. Each test cell is constructed with the Alloy 22 working electrode (WE) and a platinum counter electrode (CE) housed in separate compartments separated by an ultra fine (0.9-1.4 μm) porous ceramic frit. This allows electrolytic conductivity between the electrodes but largely prevents chemical species produced at the counter electrode from moving to the working electrode where they could be electrochemically oxidized resulting in an error in the measured passive current density. The risk of species migrating from counter electrode to working electrode is further reduced by providing independent electrolyte inlets and outlets to the counter electrode and working electrode compartments. Flow rates and electrode compartment volumes are such that the residence time for electrolyte in the counter electrode compartment is about 60 minutes (30 ml volume with 0.5 ml/min flow rate) and residence time in the working electrode compartment is about 300 minutes (1440 ml volume with 4 ml/min flow rate). Figure 1.2 is a photograph of the finished cell.
Figure 1.2 Photograph of test cell.
The counter electrode (CE) is a 25 mm x 25 mm platinum foil sheet connected to the potentiostat with a platinum wire, which is spot welded to the foil. Cell temperature is maintained by immersion in digitally-controlled oil baths; temperature control is ± 0.2 Celsius degrees. Temperature inside the test cells was measured using a glass thermowell immersed in the center of the test cell and National Institute of Standards and Testing (NIST)-traceable calibrated J-type thermocouples and thermocouple thermometer (Fluke Model 54 Series II).

Allihn-type vapor condensers were used to minimize concentration effects due to water vapor loss. Each counter electrode compartment has a 300 mm condenser while each working electrode compartment has a 400 mm condenser. A longer condenser is required for the working electrode compartment because the nitrogen flow rate is higher. Figure 1.3 is a photograph of the test cells, oil baths, potentiostats and associated equipment.
1.3.1.4 Test Specimen Design:

Specimens used for electrochemical testing were cut from Hastelloy C-22® plate stock obtained from Haynes International. The plate stock is from heat number 2277-1-3148.75 and was found to conform to the requirements of ASTM B 575 for Alloy N06022 by Laboratory Testing, Inc., Hatfield, PA, a vendor of the Department of Energy Yucca Mountain Project Qualified Suppliers List (QSL). Specimens used for the tests in pH 6, 4 M NaCl electrolyte were in the as-received, mill annealed condition;
specimens used for the pH 3, 0.1 M Cl\textsuperscript{−} tests were heat treated at 1200°C for 2 ½ hours followed by cold water quench before use. For heat treatment, a coupon 2 inches long by 5/8-inch diameter was used and machined into the ½-diameter test specimens after heat treatment. This was to remove the oxidized surface and the near-surface material that displayed internal oxidation from diffusion of atmospheric oxygen into the grain structure.

The Alloy 22 working electrode specimens are ½-inch diameter by 10 mm long right cylinders mounted in epoxy. The specimens are mounted so that only one flat circular face of 1.267 cm\textsuperscript{2} area is exposed to the electrolyte and the rest of the surface area is covered by epoxy. Electrical connection to the working electrode is a 12 AWG copper wire threaded into the opposite flat circular face. The copper wire is protected from the electrolyte by a ¼-inch O.D. x 8-inch long glass tube, the end of which is also embedded in the epoxy cast to protect the threaded joint from electrolyte. The specimen is mounted such that when installed in the test cell the exposed face is vertically oriented.

1.3.1.5 Nitrogen and Electrolyte Flow System

Dissolved oxygen is removed from the electrolyte by purging with ultra-high purity (UHP) nitrogen gas. The electrolyte flow system incorporates three vessels in series; a 30 gallon pumped feed tank, a 10 liter gravity feed tank, and the test cells; all three vessels are purged with UHP nitrogen. Multiple purged tanks in series allow longer deaeration time before the electrolyte enters the test cell resulting in lower dissolved oxygen concentration in the cell.
The entire system is constructed of materials that were selected to minimize oxygen diffusion into the system through component walls. Nitrogen delivery tubing and metering components are copper metal, glass, and FluoroEthylene Polymer (FEP)-lined Tygon tubing. Copper metal acts as an oxygen scavenger and is impermeable to oxygen diffusion. FEP-lined Tygon tubing is used only for connections in the N₂ delivery system; the rest of the system is copper and glass. These materials virtually eliminate oxygen diffusion into the N₂ system through tubing runs. The electrolyte flow system is constructed from FEP tubing, FEP-lined Tygon® tubing, glass, and High-Density Polyethylene (HDPE). These materials have the lowest oxygen permeability of all commercially available tubing and vessel materials that meet chemical compatibility requirements.

Electrolyte flow is by gravity to prevent pressure waves caused by metering pumps from disrupting the boundary layer of electrolyte in contact with the Alloy 22 specimen. Boundary layer disruption affects mass transport between the passive film and the bulk electrolyte and so affects the kinetics of passive film processes.

Electrolyte flow through the cell is maintained by pressurizing the inside of the cell to 14 inches of water (0.5 psig). Pressurization is accomplished by placing the nitrogen outlet in a graduated cylinder under a 14-inch column of water. Nitrogen gas and electrolyte flows are controlled with needle valves and monitored with rotameters to ensure long-term stability of flow rates.
1.3.1.6 Reference Electrode Fabrication

Reference electrode elements were fabricated in-house by thermal decomposition of a silver oxide/silver chlorate paste ball on the end of a silver wire after Ives and Janz. The Ag/AgCl reference electrode is placed inside a Luggin probe tube which is positioned so the reference element is inside the test cell at the same temperature as the working electrode. This eliminates the salt bridge and attendant errors associated with correcting potential to account for the salt bridge and thermal gradient. Dimensions of the Luggin probe tip are 4 mm O.D. by 2 mm I.D. The tip was placed 4 mm from the working electrode face. Examination of working electrode faces after cyclic polarization measurements showed minimal shadowing due to the Luggin probe. Some tests were conducted with the reference electrode element in a 16-in. long x ¼ in O.D. x 3/16 in. I.D. polyethylene barrel filled with 4 M KCl or saturated KCl solution saturated in AgCl separated from the working electrode solution by a porous Vicor™ frit. Reference electrodes prepared with saturated KCl solution had a small amount of solid KCl added to the barrel to ensure saturation. Other tests were conducted with the Ag/AgCl sensing element placed directly in the working electrode solution. Then, the test solution functioned as the reference solution. This works well as long as the test solution contains an amount of chloride greater than the maximum solubility of AgCl. The configuration used for specific test conditions is specified in Table 1.1.

1.3.1.7 Corrections to Standard Hydrogen Electrode (SHE)

Silver/silver chloride reference electrodes were used with a variety of temperatures and filling solutions as shown in Table 1.1. Potential measured with the
Ag/AgCl electrodes were corrected to the Standard Hydrogen Electrode (SHE) scale at the operating temperature for use in the modeling calculations presented in Section 5. An additional correction factor to convert to the SHE scale at 25°C for is presented for readers who wish to have this information. Corrections to the Standard Hydrogen Electrode (SHE) scale at the operating temperature were made using the Nernst equation. Chloride activities for the various combinations of solution and temperature were calculated by George Englehardt of OLI Systems\textsuperscript{41} The half-cell reaction for silver/silver chloride is:

\[ \text{AgCl} + e^- = \text{Ag} + \text{Cl}^- \quad (1.1) \]

The Nernst equation gives the half-cell electrode potential vs. SHE at temperature \( T \) as\textsuperscript{42}

\[ E_{\text{AgCl}}(T) = E_{\text{AgCl}}^\circ(T) - \frac{RT}{F} \ln(a_{\text{Cl}}^-) \quad (1.2) \]

where \( E_{\text{AgCl}}^\circ(T) \) is the standard potential for the AgCl half-cell reaction at temperature \( T \), \( a_{\text{Cl}}^- \) is the chloride ion activity in mol/L, \( R \) is the universal gas constant, 8.3144 J/mol·K,
$T$ is the absolute temperature in Kelvin, and $F$ is Faraday's constant, 96,487 C/equivalent. For $T$ between 0 – 95 °C, the standard potential, $E^\circ_{\text{AgCl}}(T)$, is given by:

$$E^\circ_{\text{AgCl}}(T) = 0.23659 - 4.8564 \times 10^{-4} T - 3.4205 \times 10^{-6} T^2 + 5.869 \times 10^{-9} T^3. \quad (1.3)$$

where $T$ is given in Celsius degrees for the calculation.

To correct potentials measured with Ag/AgCl reference electrodes to the SHE scale the corrections shown in Table 1.1 are added to the measured potentials. Liquid junction potential corrections are neglected for the 4 M KCl and saturated KCl cases. In the 4 M KCl case the junction potential is negligibly small because the reference and test solutions are both 4 M in chloride and at the same temperature. Junction potential for the saturated KCl case is larger, but is still considered negligible because the passive film is relatively insensitive to applied potential. For all other cases the reference sensing element is in direct contact with the working electrode solution resulting in the absence of a liquid junction potential between the reference and test solutions.

Potential versus SHE is zero at all temperatures by definition, but there is a potential difference between SHE at different temperatures. Therefore the measured potential may be further corrected to SHE(25°C) by applying an additional correction factor, $T \Delta E_{\text{SHE}}$. The correction $T \Delta E_{\text{SHE}}$ may be determined using the "linear ionic heat
capacity approximation" method of Taylor\textsuperscript{44}. Using tabulated data summarized in Bosch et al\textsuperscript{40}, the correction factor for the temperature range 25-100°C may be calculated from:

\begin{equation}
 T_{25} \Delta E_{\text{SHE}} = -2.383 \times 10^{-2} + 1.006^{-3} T - 2.143 \times 10^{-6} T^2 + 1.905 \times 10^{-9} T^3
 \end{equation}

where $T$ is given in Celsius degrees.

The test performed in pH 3, 0.1 M Cl$^-$ electrolyte at 60°C used a reference electrode filled with saturated KCl solution with a small amount of solid KCl added to the barrel. The intent was that the solid KCl would ensure saturated KCl electrolyte for the duration of the test. This was not the result. The experimental behavior indicated that the reference electrode potential had drifted over the course of the test due to ionic diffusion across the porous frit separating the reference solution from the working solution. An experiment to measure the potential of the drifting electrode vs. time was performed. A bare reference electrode was immersed in the working solution and installed in the test cell in place of the working electrode. A reference electrode with barrel and frit was prepared with saturated KCl solution and solid KCl as before. The potential difference between the two was measured for 350 hours. Knowing the potential of the bare reference element in the working electrolyte (-0.2706 V vs. SHE from Table 1.1) allowed a simple correction for the drifting RE potential to the SHE scale. The results are presented in Figure 1.4. In the absence of more accurate information, the data presented in Figure 1.4 are taken to represent the potential of the saturated KCl RE used in the 60°C test at any given time.
Table 1.1. Silver/silver chloride reference electrode: electrolyte solutions, temperatures, chloride activities, and corrections to the Standard Hydrogen Electrode (SHE) scale.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temperature, °C</th>
<th>Chloride Activity, M</th>
<th>Potential Correction to SHE(T), V</th>
<th>Potential Correction to SHE(25°C), V</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 M KCl</td>
<td>30</td>
<td>2.58900</td>
<td>0.1942</td>
<td>0.1986</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>2.65600</td>
<td>0.1684</td>
<td>0.1977</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>2.59000</td>
<td>0.1397</td>
<td>0.1905</td>
</tr>
<tr>
<td>Saturated KCl</td>
<td>30</td>
<td>2.79900</td>
<td>0.1921</td>
<td>0.1966</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>3.58800</td>
<td>0.1598</td>
<td>0.1890</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>4.03400</td>
<td>0.1259</td>
<td>0.1766</td>
</tr>
<tr>
<td>pH 3, 0.099 M NaCl + 0.001 M HCl</td>
<td>30</td>
<td>0.07670</td>
<td>0.2861</td>
<td>0.2906</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.07570</td>
<td>0.2706</td>
<td>0.2998</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.07500</td>
<td>0.2611</td>
<td>0.3015</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.07420</td>
<td>0.2509</td>
<td>0.3016</td>
</tr>
<tr>
<td>pH 11, 0.10 M NaCl + 0.001 M NaOH</td>
<td>30</td>
<td>0.07731</td>
<td>0.2859</td>
<td>0.2903</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.07638</td>
<td>0.2703</td>
<td>0.2996</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0.07574</td>
<td>0.2608</td>
<td>0.3012</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>0.07500</td>
<td>0.2506</td>
<td>0.3013</td>
</tr>
</tbody>
</table>
Figure 1.4. Potential vs. time for drifting Ag/AgCl/saturated KCl reference electrode in 60°C, pH 3, 0.1 M Cl⁻ electrolyte test.

1.3.1.8 Potentiostats

Four identical PC-based programmable Gamry PC4/750mA potentiostats running DC105 electrochemical corrosion and EIS300 electrochemical impedance spectroscopy software were used. Accuracy of the data was ensured by checking the calibration of the potentiostats using NIST-traceable electrical resistors and a NIST-traceable calibrated multimeter. It was found that a large electrostatic charge accumulates in the electrolyte
flow circuit because all the components in contact with the solution are dielectric. The potentiostats are subject to electrostatic discharge (ESD) damage and so a platinum ground wire was placed in the overflow tanks and run to building ground to protect the instruments. (This was learned only after several potentiostat input buffers had been destroyed.) The connection was checked for ground loop between the electrolyte and potentiostat by placing a zero resistance ammeter in the ground wire and checking for current flow while the potentiostat was controlling the test cell. No ground loop was found.

1.3.1.9 Specimen Preparation

Specimens used for anodic cyclic polarization measurements were wet-polished with 240 grit followed by 600 grit SiC paper according to ASTM standards. Specimens used for passive current density and EIS measurements were polished to a 0.05 μm mirror finish. The sequence used was to wet polish using 240 grit, 400 grit and 600 grit SiC papers followed by polishing on a lapping wheel using 1 μm, 0.3 μm and 0.05 μm Al₂O₃ aqueous suspensions followed by 20 minutes in an ultrasonic cleaning bath. All specimens were wet-polished and not allowed to dry at any time between beginning the polishing process and being mounted in the test cell.

1.3.1.10 Electrolyte Preparation

Electrolyte was prepared using deionized water of 12 MΩ/cm resistivity, A.C.S. Reagent Grade chemicals, Class A volumetric flasks and pipettes conforming to ASTM standards, and an NIST-traceable calibrated balance (Ohaus model N1H110).
Two electrolytes were used: pH 3, 0.1 M Cl\textsuperscript{-} and pH 6, 4 M NaCl. The 4 M NaCl electrolyte was buffered to pH 6 using a sodium acetate/acetic acid buffer system. The buffer system was a 40:1 molar ratio of sodium acetate to acetic acid. The total acetate concentration was 6.83x10\textsuperscript{-3} molar. The pH 3 electrolyte was prepared using 0.001 M HCl in 0.099 M NaCl; no buffer was used.

1.3.1.11 Anodic Cyclic Polarization and Range of Passivity

To determine the passive potential range to be used for each set of test conditions, anodic cyclic polarization curves were measured according to ASTM standards\textsuperscript{46}. Specimens were prepared as described above and installed in the test cell at room temperature. The electrolyte was deaerated with UHP nitrogen for \( \frac{1}{2} \) hour before turning on the heat bath. Open circuit potential (corrosion potential) was measured overnight to allow the system to reach a steady state. Temperature was measured and open circuit potential was checked to verify that the specimen surface preparation was good. (OCP is generally several hundred millivolts negative vs. Ag/AgCl; an OCP that is near zero or positive indicates an oxide film on the specimen surface either from inadequate grinding and polishing or allowing the specimen to dry before installing it in the test cell; allowing the specimen to dry results in an air-formed oxide film.) The cyclic polarization test was started at the open circuit potential and scanned in the anodic direction at 600 mV/hr (0.1667 mV/sec) to a maximum current of 1 mA. The scan direction was reversed when the maximum current was reached and the cathodic scan was performed at the same rate. The test was terminated at a potential about equal to the open circuit potential.
The passive range was estimated by examining the forward (anodic) scan for the region over which current changes little or not at all with increasing potential. The curves were plotted and straight lines were drawn tangent to the lower, middle and upper regions of the curve. Where the tangent lines intersect are considered to be the limits of passivity. This is shown in Figures 1.5 – 1.10. The passive ranges determined for all test conditions are shown in Table 1.2. These results show that passive range is about 600 mV depending upon temperature, chloride and pH. Also, the transpassive potential decreases systematically with temperature and is lower at high chloride concentration.

Table 1.2. Estimated passive potential ranges for Alloy 22 under various conditions of electrolyte composition and temperature.

<table>
<thead>
<tr>
<th>Electrolyte (deaerated)</th>
<th>Temperature (°C)</th>
<th>Estimated Passive Potential Range (mV vs. SHE)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 M NaCl, pH 6, 7x10⁻³M acetate buffer</td>
<td>30</td>
<td>150 to 750</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>-115 to 650</td>
</tr>
<tr>
<td>0.1 M Cl⁻, pH 3 (NaCl + HCl)</td>
<td>30</td>
<td>350 to 950</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>120 to 850</td>
</tr>
<tr>
<td></td>
<td>75</td>
<td>0 to 825</td>
</tr>
<tr>
<td></td>
<td>90</td>
<td>190 to 650</td>
</tr>
</tbody>
</table>
Figure 1.5  Cyclic polarization curve and passive potential range for Alloy 22 in deaerated pH 6, 4 molar NaCl electrolyte at 30°C.
Figure 1.6 Cyclic polarization curve and passive potential range for Alloy 22 in deaerated pH 6, 4 molar NaCl electrolyte at 60°C.
Figure 1.7  Cyclic polarization curve and passive potential range for Alloy 22 in deaerated pH 3, 0.1 molar Cl\(^-\) electrolyte at 30°C.
Figure 1.8 Cyclic polarization curve and passive potential range for Alloy 22 in deaerated pH 3, 0.1 molar Cl\(^-\) electrolyte at 60°C.
Figure 1.9  Cyclic polarization curve and passive potential range for Alloy 22 in deaerated pH 3, 0.1 molar Cl\textsuperscript{−} electrolyte at 75°C.
Figure 1.10  Cyclic polarization curve and passive potential range for Alloy 22 in deaerated pH 3, 0.1 molar Cl⁻ electrolyte at 90°C.
1.3.1.12 Electrochemical Impedance Spectroscopy

In order for EIS data to be valid the system must conform to the following requirements of linear systems theory: The system must be stable, i.e., passive current must be at steady state; the current response to an applied alternating voltage must be linear; and the system response must be causal and finite valued. The conditions of causality and finite valued response are assumed to be valid. Linear response was ensured by limiting the amplitude of the applied alternating voltage signal to 10 mV RMS. Steady state was determined by observing the passive current versus time over a period of many hours until the rate of change was judged to be insignificant over the approximately 45 minutes required to run two EIS scans, which were compared to check for hysteresis; significant hysteresis indicates non-steady state. To check for hysteresis, two impedance scans were performed sequentially at each potential, the first scan in the high-frequency to low-frequency direction and the second scan in the low-frequency to high-frequency direction. For this work, the frequency range was 10 kHz to 10 mHz with ten points per decade being measured (60 points total). Validity of EIS results was also verified by applying the Kramers-Kronig transforms\textsuperscript{38,48}.

1.3.2 Results and Discussion-Experimental work

Experimental results consist of potentiostatic current densities, current density transients in response to step changes in potential and electrochemical impedance spectroscopy data. It is seen that impedance is relatively insensitive to applied potential in the range of passivity. The general trend is that impedance increases with increasing potential for the
lower potentials and decreases with increasing potential for higher potentials. (The potential where impedance begins to decrease with increasing potential and the semiconductor character changes to p-type is defined as the pre-transpassive potential.) The largest increase in low frequency impedance with potential over the passive range is a factor of 2 with an average of 1.5. Current density effects are about the same, i.e., current density is nearly independent of applied potential, as predicted by the Point Defect Model. Low frequency impedance increases with increasing pH/chloride concentration. Because pH and chloride were not varied independently, the cause for this behavior cannot be determined. Overall, however, the impedance and current density change little over the range of conditions tested with temperature having the largest effect.

1.3.2.1 Results in pH6, 4 M NaCl Electrolyte

1.3.2.1.1 EIS Results

All the EIS data share the same basic characteristics. The Nyquist plots all show real and imaginary impedance to increase in magnitude with decreasing frequency. The greatest magnitude occurs at the lowest frequency (0.01 Hz) in all cases with decreasing impedance corresponding to increasing frequency.

The data shown in Figures 1.11 and 1.12 were collected to check the validity of the EIS results by comparing two back-to-back impedance scans to check for hysteresis; hysteresis would indicate the system was not at steady state over the time required to collect the data. Figure 1.11 shows the Nyquist plot for back-to-back scans performed
after the specimen had been held potentiostatically at –250 mV vs. Ag/AgCl for 113 hours at 60.5°C. In the Nyquist plot representation of impedance, the frequency used to collect each data point is not shown explicitly. The plot has been labeled with some of the frequencies; the highest impedance magnitudes correspond to the lowest frequency with magnitude of impedance decreasing with increasing frequency. This is seen explicitly on the Bode plot shown in Figure 1.12. These figures show no hysteresis. In fact, the data for these scans are so close as to be practically indistinguishable. The very small hysteresis at 10 mHz (about 0.5%) is an instrument artifact that was seen upon reversing scan direction; the instrument has to “hunt” for the appropriate current-potential (IE) range at low frequency, which slightly perturbs the steady state resulting in a small low-frequency hysteresis.

After it was determined that 113 hours of potentiostatic conditioning at 60.5°C allowed the system to come to a sufficiently steady state to collect valid EIS data, the effect of time at a specific potential was investigated. The Nyquist plot and Bode plot shown in Figures 1.13 and 1.14, respectively, present impedance and phase shift versus time data for a specimen held at –200 mV vs. Ag/AgCl at 30°C. EIS scans were run at 71 hours, 214 hours, and 352 hours and it is seen that impedance increases with increasing time. For each data set back-to-back scans were performed and checked for hysteresis, which was absent in all cases. The magnitude of change seen between 71 hours and 214 hours and between 214 hours and 352 hours is frequency dependent. At high frequency, the rate of change decreases with increasing time. At low frequency, the rate of change increases with increasing time. This indicates that although the quasi-
steady state attained after 71 hours is sufficiently stable to generate valid EIS data a true steady state had not been attained even after 352 hours. No further attempt was made to establish how long it takes to reach a true steady state.

The effect of potential on impedance is shown in Figures 1.15 - 1.18 for two different specimens in pH 6, 4 M NaCl electrolyte at 60°C. Nyquist plots are shown in Figures 1.15 and 1.17 while the corresponding Bode plots are shown in Figures 1.16 and 1.18. Figures 1.15 and 1.16 show EIS results for a specimen with 14 nA/cm² passive current density and Figures 1.17 and 1.18 show EIS results for a specimen with passive current density of 62 nA/cm². In both cases, impedance increases with increasing anodic potential. It is also seen that impedance is dependent upon passive current density; impedance increases with decreasing passive current density. Also note the 62 nA/cm² test (Figures 1.17 and 1.18) shows an unusual feature in the low frequency region between 0.1 Hz to 0.01 Hz; the phase shift plot has upturned tails and shows dispersion with potential. The rest of the frequency range does not show dispersion with potential. No other data show dispersion with potential in the low frequency range; this indicates some significant difference in the passive film on this particular specimen that is likely related to grain boundary precipitates. There are discontinuities in the slopes of the impedance versus frequency plots, corresponding to the upturned tails, which can be seen in the Bode and Nyquist plots. Upturned tails are seen at high frequency (1,000 Hz to 10,000 Hz) in Figures 1.13 and 1.14 (time dependence of impedance in pH 6, 4 M NaCl electrolyte at 30°C), but there is no dispersion with potential. These features may indicate mechanisms demonstrating relaxations at frequencies lower or higher than those
measured. Similar behavior has been seen on carbon steel, chromium steel, and high speed steel in bicarbonate solutions\(^{42}\).

### 1.3.2.1.2 Variability of Mill-Annealed Alloy 22

Figures 1.15–1.18 show a large variability in electrochemical behavior of as-received, mill annealed Alloy 22. In Figures 1.15 and 1.16, the specimen shows a passive current density of 14 nA/cm\(^2\) and a low frequency (10mHz) impedance of about 530,000 ohm-cm\(^2\) at 118 mV SHE (-50 mV Ag/AgCl). In Figures 1.17 and 1.18 the specimen shows passive current density of 62 nA/cm\(^2\) and 10 mHz impedance at 118 mV SHE of about 110,000; there is about a five-fold difference in current density and impedance between the two specimens. It can also be seen, as noted above, that there is a significant difference in the shape of the impedance vs. frequency curve between the two specimens.

Variability of the as-received, mill-annealed Alloy 22 is further illustrated by cyclic polarization results for two different mill-annealed Alloy 22 specimens in deaerated pH 1, 4 M Cl\(^-\) at 80°C. Figure 1.19 shows grain boundary sensitization and susceptibility to intergranular corrosion while Figure 1.21 does not show this tendency. These data indicate significant variability of microstructure and electrochemical and corrosion behavior among mill-annealed specimens.

Figures 1.20 and 1.22 are photomicrographs of the Alloy 22 specimens which generated the cyclic polarization scans in Figures 1.19 and 1.21, respectively. Both specimens were in the mill-annealed state and were cut from the same parent plate (same heat) of C-22. Both specimens were polished to a mirror finish and subjected to cyclic
polarization. These specimens were etched only by the cyclic polarization process in pH 1, 4 M Cl\textsuperscript{-} electrolyte; no additional etching was performed to reveal the microstructure. Significant grain boundary precipitation is seen in Figure 1.20 while Figure 1.22 shows much less, accounting for the difference in cyclic polarization scans. Also, both specimens show slip lines. These differences in microstructure have a significant impact on corrosion behavior.

Variability of as-received, mill annealed Alloy 22 is an important observation. Since high-accuracy data is the main objective of this work, these results indicate the need for solution-annealed specimens and thorough metallographic examination so that the data generated are internally consistent. Also, this observation is important because many measurements reported in the literature have been made on as-received, mill-annealed Alloy 22\textsuperscript{20,49,50} , evaluation of such data must include awareness of this variability.

1.3.2.1.3 Potentiostatic Current Transients

Figure 1.23 shows a potentiostatic current transient measured at 60°C in pH 6, 4 M NaCl solution for the step change from –50 mV to 50 mV. Notice that the slope of the time vs. current curve on the log-log plot is nearly zero at –50 mV before the increase in potential is applied. The near-zero slope indicates that the system is very near true steady state and therefore confidence in the accuracy of impedance data collected under these conditions is great. Also note that the current density at 50 mV returns to the same value (62 nA/cm\textsuperscript{2} ) that was measured at –50 mV, validating the Point Defect Model prediction that passive current density is independent of potential for n-type defective
chromic oxide films such as that which forms on Alloy 22. The transients (not shown) measured for \(-250\) mV to \(-150\) mV and \(-150\) mV to \(-50\) mV also prove this result, returning to 62 nA/cm\(^2\) about 48 hours after the potential step-change was applied.

### 1.3.2.1.4 Localized Corrosion

Figure 1.24 shows the potentiostatic current density data for an Alloy 22 specimen as it developed stable localized corrosion at 60°C in pH 6, 4 M NaCl solution. The specimen had been in the test cell continuously for about 525 hours (22 days) before the localized corrosion became stable resulting in greatly increased current density. Notice the occurrence of small current spikes likely indicating metastable pitting for many hours before the baseline current density deviated from the established steady state value. This behavior has been found to be typical in 4 M NaCl at pH 6 maintained by a sodium acetate/acetic acid buffer system \((6.83 \times 10^{-3} \text{ M acetate anion})\) at all temperatures tested. Every specimen tested under these conditions has developed localized corrosion in about three weeks.

Figure 1.25 is a photomicrograph of one of the localized corrosion pits on the Alloy C-22 specimen which was used to generate the data in Figure 1.24. Figure 1.26 a and Figure 1.26 b are scanning electron micrographs of the same Alloy C-22 specimen shown in Figure 1.25. Magnification is 500x for Figure 1.26 a and 2500x for Figure 1.26 b. It is seen that the porous, precipitated, upper layer film of the bilayer passive film (seen on the right hand side of the image) has been removed by the localized attack (left hand side of the image).
A complete set of data covering the entire passive potential range has not been collected because stable localized corrosion developed after about three weeks in all cases preventing completion of the pH 6, 4 M NaCl tests.
Figure 1.11. Nyquist plot showing absence of hysteresis in EIS data after the specimen was held for 113 hr. potentiostatically at -82 mV SHE (-250 mV vs. Ag/AgCl) in pH 6, 4 M NaCl at 60.5°C. Passive Current Density was 14 nA/cm². Note that only one curve is easily discernible because forward and reverse scans overlap.
Figure 1.12. Bode plot showing absence of hysteresis in EIS data after the specimen was held for 113 hr. potentiostatically at -82 mV SHE (-250 mV vs. Ag/AgCl) in pH 6, 4 M NaCl at 60.5°C. Passive Current Density was 14 nA/cm². Note that only one curve is easily discernible because forward and reverse scans overlap.
Figure 1.13 Nyquist plot showing time dependence of impedance for a specimen held potentiostatically at -6 mV vs. SHE (-200 mV vs. Ag/AgCl) in pH 6, 4 M NaCl at 30° C.
Figure 1.14. Bode plot showing time dependence of impedance and phase shift for a specimen held potentiostatically at -6 mV vs. SHE (-200 mV vs. Ag/AgCl) in pH 6, 4 M NaCl at 30°C.
Figure 1.15 Nyquist plot for potential dependence of impedance for a specimen with 14 nA/cm² passive current density in pH 6, 4 M NaCl at 60.5°C.
Figure 1.16  Bode plot for potential dependence of impedance and phase shift for a specimen with 14 nA/cm² passive current density in pH 6, 4 M NaCl at 60.5°C.
Figure 1.17. Nyquist plot for potential dependence of impedance for a specimen in pH 6, 4 M NaCl at 60°C with 62 nA/cm² passive current density.
Figure 1.18. Bode plot for potential dependence of impedance and phase shift for a specimen in pH 6, 4 M NaCl at 60°C with 62 nA/cm² passive current density.
Figure 1.19. Cyclic polarization of Alloy 22 in pH 1, 4 M Cl\textsuperscript{-} at 81.7°C showing grain boundary sensitization.

Figure 1.20. Photomicrograph of specimen used to generate cyclic polarization scan shown in Figure 1.19
Figure 1.21. Cyclic polarization of Alloy 22 in pH 1, 4 M Cl\textsuperscript{-} at 81.9°C showing absence of grain boundary sensitization.

Figure 1.22. Photomicrograph of specimen used to generate cyclic polarization scan shown in Figure 1.21
Current Transient, -50mV to +50mV (SSC), 60°C, pH6, 4M NaCl
0.1s Sample Rate to 2.2E+03 s, 20s Sample Rate Thereafter

Figure 1.23. Current transient in response to step change in potential from -50 mV to 50 mV vs. Ag/AgCl.
Figure 1.24. Potentiostatic transient for Alloy 22 in pH 6, 4 M NaCl solution at 60°C obtained on stepping the potential from 50 mV to 150 mV vs. Ag/AgCl, 4 M KCl, showing the onset of localized corrosion between the alloy and the mounting material.

Figure 1.25. Photomicrograph showing localized corrosion at the interface between the Alloy 22 specimen and the mounting epoxy - Potentiostatic transient generated is shown in Figure 1.24
Figure 1.26 a. Scanning electron micrograph of localized corrosion on Alloy 22 showing removal of porous, precipitated upper layer film of the bilayer passive film (magnification 500x).
Figure 1.26 b. Scanning electron micrograph of localized corrosion on Alloy C-22 showing removal of porous, precipitated upper layer film of the bilayer passive film (magnification 2500x).
1.3.2.2 Results in pH 3, 0.1 M Cl\textsuperscript{-} Electrolyte

Upon evaluation of the results in pH 6, 4 molar NaCl electrolyte it was determined to change the conditions before proceeding. The electrolyte was changed to 0.1 molar Cl\textsuperscript{-} to reduce the probability of failure by crevice corrosion. The Alloy 22 specimens were cut from coupons that had been heat treated at 1200°C for 2 1/2 hours. The heat treatment was intended to eliminate grain boundary precipitates and relieve internal stress, which are responsible for the variability in electrochemical behavior of the observed in the as-received, mill annealed material.

1.3.2.2.1 EIS Results

Decreasing the chloride concentration to 0.1 molar proved to allow completion of testing over the entire passive range for temperatures up to 75°C; tests at 90°C still failed due to crevice corrosion. Data at four potentials at 90°C were collected. The most extensive data set was collected at 75°C. Potential was stepped ascendingly from the low (cathodic) end of the passive region to the upper (anodic) end, then stepped descendingly back to the cathodic limit, and ascendingly again to the anodic limit. This test ran continuously for 31 days (744 hours).

Figures 1.27 and 1.28 show the Nyquist and Bode plots, respectively, for data collected for the first ascending voltages at 75°C. Low frequency (0.01 Hz) impedance increases with increasing potential starting at 94,000 ohm·cm\textsuperscript{2} and reaches a maximum of 160,000 ohm·cm\textsuperscript{2} at 511 mV SHE then decreases slightly to 149,000 ohm·cm\textsuperscript{2} at 611 mV SHE. The Nyquist plot is labeled with current density at each potential. Current
densities were calculated from last 200 seconds of potentiostatic current vs. time data that were collected just before running the impedance spectrum at each potential. Generally, current density increases with increasing potential. The Bode plot shows two well-defined time constants at 0.1 Hz and 100 Hz. Impedance becomes independent of frequency at about 5,000 Hz and 9 ohm-cm$^2$, which is the resistance of the test cell, $R_s$. High frequency phase shift is small, -7 degrees at 10,000 Hz, indicating little double layer capacitance due to the diffuse, weakly polarized interface. This is consistent with the relatively low ionic strength of the 0.1 M Cl$^-$ solution. Compare this to the high frequency phase shift of -70 degrees in 60°C, pH 6, 4 M NaCl electrolyte, which indicates large capacitance of the double layer due to a compact, strongly polarized double layer resulting from high chloride concentration. Low frequency phase shift is large, -80 degrees at 0.01 Hz, indicating that low frequency impedance is dominated by the capacitance of the passive film. Low frequency phase shift in 0.1 M Cl$^-$ and 4 M NaCl electrolytes is nearly identical at about -80 degrees, indicating that the passive film is affected little or not at all by chloride concentration.

Data collected for descending voltages and the second set of ascending voltages are presented by comparing impedance results for the same potentials to show hysteresis of the system after many hours and many potential steps up and down. Figures 1.29 and 1.30 show the Nyquist and Bode plots, respectively, for long term hysteresis at 311 mV SHE and first ascending, descending, and second ascending voltages at 144 hours, 432 hours, and 624 hours, respectively. These data show a 1.35% hysteresis at 10 mHz between the first and second ascending voltage sweeps (144 hours and 624 hours) and a
4.8% difference between the ascending sweeps and the descending sweep. The higher impedance with the descending sweep is accompanied by a decrease in current density from 25 nA/cm$^2$ to 15 nA/cm$^2$. Figures 1.31 and 1.32 show the Nyquist and Bode plots, respectively, for long term hysteresis at 211 mV SHE and ascending and descending voltages at 96 and 480 hours, respectively. The difference in impedance is 1% over 384 hours showing the system is remarkably stable. Figures 1.33 and 1.34 show the Nyquist and Bode plots, respectively, for long term hysteresis at 111 mV SHE and ascending and descending voltages at 48 hours and 528 hours, respectively. These data show a quite large difference in impedance: 94,360 ohm·cm$^2$ at 48 hours and 73,150 ohm·cm$^2$ at 528 hours. I believe the discrepancy here can be resolved by discounting the 48 hour value as representing the passive film before it was fully developed. Examination of the data in Figure 1.18 shows that the 528 hour value for 111 mV SHE impedance fits the general trend for low frequency much better than the 48 hour value, giving a 100 mV potential step difference in impedance of about 20,000-25,000 ohm·cm$^2$. Behavior of the phase shift (Figure 1.) for the 48 hour data point is also a poor fit to the rest of the data. Considering this along with the very small hysteresis shown at higher potentials for longer times, it is reasonable to discard the 48 hour impedance value for 111 mV SHE. Figures 1.35 and 1.36 show the Nyquist and Bode plots, respectively, for the full passive range using the 528 hour value for 111 mV SHE instead of the 48 hour value; these are the data that I believe most accurately define the low frequency behavior of Alloy 22 in 75°C, pH 3, 0.1 M Cl$^-$ electrolyte.

EIS data collected at 30°C in pH 3, 0.1 M Cl$^-$ electrolyte are presented in Figures 1.37 and 1.38, which are the Nyquist and Bode plots, respectively. This test was begun at
low potential and potential was stepped in the ascending direction only; no descending potential steps were made so there is no long term hysteresis information. It is seen that impedance increases with increasing potential for the first three potential steps (486, 546, and 606 mV SHE) then decreases for the next three increasing potential steps (666, 726, and 786 mV SHE). The two highest potentials show lower impedance than the lowest potential. An increase in current density accompanies the decrease in impedance at higher potential. Current densities were calculated by dividing the dc current recorded by the potentiostat at 0.01 Hz by the surface area of the specimen. Using the dc current from the EIS data file was judged to be more accurate than the potentiostatic current vs. time data, though no significant difference between the two was observed; the dc current densities are about 10% greater at each potential than those from potentiostatic data. The Bode plot shows the phase shift as -7 degrees at high frequency (10,000 Hz) and increasing with decreasing frequency to about -85 degrees at 10 Hz. The phase shift at the highest frequency is the same as the 75°C data (-7 degrees) and is a little greater at the lowest frequency (-85 degrees compared to -80 degrees at 0.01 Hz.), but is virtually independent of frequency between 10 Hz and 0.01 Hz. There is only one time constant apparent compared to the two well-defined peaks measured at 75°C. Phase shift for the highest three potentials decreases with increasing potential corresponding to the decrease in impedance with increasing potential. Phase shift at the highest potential is about -80 degrees compared to -85 degrees for the lowest potential. Cell resistance (impedance at 10,000 Hz) is about 10 ohms·cm², which is substantially the same as the 75°C result.

EIS data collected at 90°C in pH 3, 0.1 M Cl⁻ electrolyte are presented in Figures 1.39 and 1.40, which are the Nyquist and Bode plots, respectively. The Nyquist plot
shows increasing impedance with increasing potential for the first two potential steps and
decreasing impedance with increasing potential for the next two potential steps. The
current densities shown on the Nyquist plot legend were obtained from the dc current
recorded by the potentiostat at 0.01 Hz divided by the surface area of the specimen. The
dc current data from the EIS data were used because the potentiostatic data were noisy
from the many current spikes due to metastable pitting events, as shown in Figure 1.41.
Crevice corrosion became stable at 541 mV SHE (290 mV Ag/AgCl) resulting in
continuously increasing current similar to Figure 1.24. The onset of stable crevice
corrosion prevented collection of data at potentials more positive than 481 mV SHE.

Figures 1.42 and 1.43 show the Nyquist and Bode plots, respectively for EIS data
collected at 60°C in pH 3, 0.1 M Cl− electrolyte. This test stepped potential into the
transpassive region. Increasing impedance with increasing potential is seen for the first
three potential steps (200 mV, 280 mV, 360 mV Ag/AgCl). The following three
potential steps show decreasing impedance with increasing potential. Low frequency \(f <\
10 \text{ Hz}\) phase shift and impedance over the entire frequency range drop markedly at the
highest potential, 600 mV Ag/AgCl. Phase shift decreases significantly at transpassive
potential at frequencies lower than about 40 Hz. Phase shift decreases by 12 degrees
from -83 to -71 degrees at 0.01 Hz. Smaller phase shift means the imaginary component
of impedance is less important meaning capacitance has decreased. This can be
interpreted as thinning of the film and weakening of the lattice structure. The observed
behavior can be explained in terms of the reaction mechanism of the PDM as cation
vacancy generation by oxidative ejection of cations at the film/solution interface.
High frequency (10,000 Hz) real impedance drops by 10 ohms·cm$^2$ from 22.2 ohms·cm$^2$ to 11.9 ohms·cm$^2$. High frequency impedance converges to the same value in all the tests except this one. These changes are much greater than similar changes seen in other tests and appear as two distinct bands. They can be interpreted as the result of transpassive dissolution of the passive film increasing ion concentration at the film/solution interface resulting in decreased faradic resistance. Thinning of the passive film also decreases resistance.
Figure 1.27. Nyquist Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z vs. E (Ag/AgCl/0.1 M Cl⁻), 1st Ascending Voltages.
Figure 1.28. Bode Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z vs. E (Ag/AgCl/0.1 M Cl⁻) 1st Ascending Voltages.
Figure 1.29. Nyquist Plot, Alloy 22, 75°C, pH3, 0.1 M Cl, Z at 50 mV (Ag/AgCl/0.1 M Cl) Hysteresis between 144 hrs., 432 hrs., and 624 hrs.
Figure 1.30. Bode Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z at 50 mV (Ag/AgCl/0.1 M Cl⁻) Hysteresis between 144 hrs., 432 hrs., and 624 hrs.
Figure 1.31. Nyquist Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z at -50 mV (Ag/AgCl/0.1 M Cl⁻) Hysteresis between 96 hrs. and 480 hrs.
Figure 1.32. Bode Plot, Alloy 22, 75°C, pH3, 0.1 M Cl, Z at 50 mV (Ag/AgCl/0.1 M Cl) Hysteresis between 144 hrs. and 624 hrs.
Figure 1.33. Nyquist Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z at -150 mV (Ag/AgCl/0.1 M Cl⁻) Hysteresis between 48 hrs. and 528 hrs.
Figure 1. Bode Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z at -150 mV (Ag/AgCl/0.1 M Cl⁻) Hysteresis between 48 hrs. and 528 hrs.
Figure 1. Nyquist Plot, Alloy 22, 75°C, pH3, 0.1 M Cl\textsuperscript{-}, Z vs. E (Ag/AgCl/0.1 M Cl\textsuperscript{-}), 1\textsuperscript{st} Ascending Voltages, but using the descending value for -150 mV Ag/AgCl instead of 1\textsuperscript{st} ascending value. These are the best low frequency ($f < 100$ Hz) data for Alloy 22 at 75°C in pH 3, 0.1 M Cl\textsuperscript{-}.
Figure 1.36. Bode Plot, Alloy 22, 75°C, pH3, 0.1 M Cl⁻, Z vs. E (Ag/AgCl/0.1 M Cl⁻), 1<sup>st</sup> Ascending Voltages, but using the descending value for -150 mV Ag/AgCl instead of 1<sup>st</sup> ascending value. These are the best low frequency (f < 100 Hz) data for Alloy 22 at 75°C in pH 3, 0.1 M Cl⁻.
Figure 1.37. Nyquist Plot, Alloy 22, 30°C, pH3, 0.1 M Cl\(^-\), Z vs. E (SHE 30°C), Ascending Voltages.
Figure 1.38. Bode Plot, Alloy 22, 30°C, pH3, 0.1 M Cl\textsuperscript{-}, Z vs. E (SHE 30°C) Ascending Voltages.
Figure 1.39. Nyquist Plot, Alloy 22, 90°C, pH3, 0.1 M Cl⁻, Z vs. E (SHE 90°C) Ascending Voltages.
Figure 1.40. Nyquist Plot, Alloy 22, 90°C, pH3, 0.1 M Cl⁻, Z vs. E (SHE 90°C) Ascending Voltages.
Figure 1.41. Current vs. time at 230 mV Ag/AgCl in 90°C, pH 3, 0.1 M Cl\textsuperscript{-} electrolyte. These data show current spikes followed by repassivation of metastable pitting events. Crevice corrosion became stable at 290 mV Ag/AgCl resulting in continuously increasing current.
Figure 1.42. Nyquist Plot, Alloy 22, 60°C, pH3, 0.1 M Cl⁻, Z vs. E, Ascending Voltages.
Figure 1.43. Bode Plot, Alloy 22, 60°C, pH3, 0.1 M Cl⁻, Z vs. E, Ascending Voltages.
1.3.2.3 Mott-Schottky Analysis

The space-charge region of the semiconductive passive films was characterized by evaluating capacitance. Assuming that the capacitance of the Helmholtz layer is large compared to that of the space-charge region of the passive film, which is polarized as the depleted state, the capacitance of the semiconductor layer follows the Mott-Schottky relationship.\(^1\)

\[
\frac{1}{C_{sc}^2} = \frac{2}{\varepsilon_0 e N} \left( E - E_{fb} - \frac{kT}{e} \right)
\]

where \(C_{sc}\) is the space charge capacitance, \(\varepsilon\) is the dielectric constant of the film, \(\varepsilon_0\) is the vacuum permittivity (8.85 x 10-14 F/cm), \(e\) is the elementary charge (1.60218 x 10-19 C), \(E\) is the applied potential, \(E_{fb}\) is the flatband potential, \(k\) is the Boltzmann constant (1.380650\(^{23}\) J/K), and \(T\) is the absolute temperature. \(N\) is either the donor density, \(N_D\), for \(n\)-type semiconductors, or \(N_A\), the acceptor density for \(p\)-type semiconductors. The constant, \(kT/e\) has the value of 0.0261 V at 30°C and 0.0313 V at 90°C and so for this work is ignored with respect to \(E\) and \(E_{fb}\). Equation 1.5 depends upon the assumption that \(C_{dl}\) is much greater than \(C_{sc}\). Thus, when writing the term for series capacitances,

\[
\frac{1}{C_{cl}} + \frac{1}{C_{sc}}
\]

the term for \(C_{sc}\) dominates when \(C_{sc}\) is much smaller than \(C_{dl}\). Since \(C_{sc}\) is usually on the order of pF and \(C_{dl}\) is \(\mu\)F this assumption is justifiable. From Equation 1.5, a plot of \(1/C^2\) vs. \(E\) is predicted to be linear with a slope of \(2/\varepsilon_0 e N\) from which the
donor or acceptor density may be derived, provided the dielectric constant is known. Moffatt and Latanision \textsuperscript{13} found the dielectric constant for chromic oxide passive films on pure chromium to be about 25 assuming the double layer capacitance, $C_{dl}$, to be 32 $\mu$F/cm$^2$, and 20 assuming $C_{dl} >> C_{film}$. In the absence of other information for the dielectric constant of passive films on Cr-bearing alloys, this work assumes $\varepsilon = 25$.

From impedance theory the relationship for capacitance, $C$, is:

$$Z'' = \frac{1}{j\omega C} = \frac{1}{2\pi f C}$$

(1.6)

where $Z''$ is the imaginary component of impedance, $\omega$ is the angular frequency, and $f$ is the frequency in Hz. During the course of these tests, the specimens were polarized at potentials covering the passive range in steps of 100 mV, 80 mV or 60 mV depending upon the anodic polarization curve. At each potential an impedance spectrum was measured over the frequency range 10,000 HZ to 0.01 Hz. For use in Mott-Schottky analysis, the capacitance was calculated at each applied potential from the impedance measured at 3,163 Hz. Using a high frequency limits the contribution of ionic processes\textsuperscript{37,53-57} and is the method commonly employed.

One of the key problems in the application of Mott-Schottky analysis is that $1/C^2$ vs. $E$ profiles must be measured under conditions that do not result in a change in the dimensions of the passive film\textsuperscript{55}. This is ordinarily accomplished by polarizing the specimen to a high potential, allowing the passive film to develop, and then very quickly
stepping potential cathodically measuring impedance at each applied potential over a

time period that is so short the film does not have time to change dimensions. The work

presented here uses a different method that allows the passive film to attain a steady state

at each potential before measuring impedance (capacitance). This method results in a
different film thickness for each potential, but has been used with success by Macdonald

et al. In this work, the validity of this method is demonstrated by comparison of
calculated carrier densities with the results of other researchers, by evaluating internal

consistency of the results, and by comparison of the two methods for the 75°C, pH 3, 0.1
M Cl⁻ electrolyte test performed here. We believe that the requirement that scans for
Mott-Schottky analysis must be fast enough to prevent change in the passive film
dimensions is not one of semiconductor behavior. This is because if the film is allowed
to begin changing dimensions it is no longer at steady state, a condition which violates
linear systems theory and invalidates the impedance data.

The Mott-Schottky plot shown in Figure 1.44, which was constructed for mill-annealed
Alloy 22 in 60°C, pH 6, 4 M NaCl electrolyte displaying 14 nA/cm² current density,
shows clearly defined linear behavior. The slope of the plot is \( m = 1.885 \times 10^{10} \ \text{cm}^4 \text{F}^{-2} \text{V}^{-1} \) and the regression line has a correlation coefficient of \( R^2 = 0.99 \). The positive slope
indicates \( n \)-type semiconductor behavior, so the donor density (cation interstitials and/or
oxygen vacancies) may be calculated from:

\[
N_p = \frac{2}{m \epsilon \varepsilon_0 e}
\]

(1.7)
Using the values given above, the donor density for the 14 nA/cm\(^2\) current density test is \(3.0 \times 10^{20}\) cm\(^{-3}\). In comparison, Figure 1.45 shows the Mott-Schottky plot for mill-annealed Alloy 22 in 60°C, pH 6, 4 M NaCl electrolyte displaying 62 nA/cm\(^2\) current density. The slope is \(m = 7.709 \times 10^9\) cm\(^4\) F\(^{-2}\) V\(^{-1}\) and the regression coefficient is \(R^2 = 1.00\). The donor density in this case is found to be \(7.3 \times 10^{20}\) cm\(^{-3}\), which is more than twice that found for the 14 nA/cm\(^2\) current density case. The higher donor density is consistent with higher current density. These results are also consistent with typical values determined by other researchers\(^{48,66-76}\).

Figure 1.46 shows the Mott-Schottky plot for solution annealed Alloy 22 in 75°C, pH 3, 0.1 M Cl\(^-\) electrolyte derived from long-term EIS data. Capacitance values calculated from both ascending and descending voltages are shown. The slope of \(1/C^2\) vs. \(E\) is positive, indicating \(n\)-type semiconductor. The donor density is calculated as \(7.4 \times 10^{20}\) cm\(^{-3}\) for ascending voltages and \(8.0 \times 10^{20}\) cm\(^{-3}\) for descending voltages. Correlation coefficients are \(R^2 = 0.99\) and 0.96 for ascending and descending voltages, respectively. Figure 1.47 shows \(1/C^2\) vs. \(E\) for the same specimen, but these data were collected at one time in the conventional manner, that is, the specimen was polarized to 350 mV Ag/AgCl and allowed to come to steady state. Then the potential was stepped cathodically in 100 mV steps measuring 3,000 Hz impedance at each step. The total time required was too short to allow the dimensions of the passive film to change. The results of this test \((N_D = 7.4 \times 10^{20}\) cm\(^{-3}\)) are identical to the results obtained by allowing the film to come to steady state at each potential step before measuring impedance. The correlation coefficient is \(R^2 = 0.94\), which is a little less accurate than the long-term data.
This comparison, along with the agreement between these data and those of other researchers, and the internal consistency of the 60°C, pH 6, 4 M NaCl data, validates the use of the long-term test method for collecting impedance data for Mott-Schottky analysis.

Figures 1.48, 1.49, and 1.50 present Mott-Schottky results for solution-annealed Alloy 22 in pH 3, 0.1 M electrolyte at 30°, 60°, and 90°C, respectively. Each of these plots show two regions of linearity for $1/C^2$ vs. $E$; a region with positive slope at lower potential ($n$-type semiconductor) and a region with negative slope at high potential. The transition to negative slope indicates a transition to $p$-type semiconductor. The barrier layer is found to be $n$-type at lower potentials. As potential is increased, at some potential the semiconductor character changes to $p$-type, i.e., the dominant defect becomes cation lattice vacancies. The potential at which the transition from $n$-type to $p$-type occurs corresponds to the pre-transpassive potential, which occurs at a lower potential than the transpassive potential. The change in electronic character is most likely due to generation of cation lattice vacancies at the film/solution interface by oxidative ejection of Cr cations. This process can be represented as:

$$Cr_{Cr} + 4H_2O \rightarrow CrO_4^{2-} + V_{Cr}^{3+} + 8H^+ + 3e^-$$ (1.8)
These Mott-Schottky plots present $1/C^2$ and current density vs. applied potential. It is seen that in the $n$-type region current density usually increases slightly, and linearly, with increasing potential. At the transition to $p$-type the current is seen to increase at a faster rate. This is seen on the plots for pH 3, 0.1 M Cl$^-$ at 30° and 60°C; passive current density changes slope and increases at a greater rate at the potential where the transition to $p$-type occurs. The effect is more pronounced at lower temperature and is not evident at 90°C. This is explained by the contribution of the process described by Equation 1.8 adding to the total current density. The relative contribution of the current from Equation 1.8 decreases with increasing temperature because the baseline current density in the $n$-type region increases with increasing temperature.

The acceptor concentration, $N_A$, can be determined from the slope, $m$, according to:

$$N_A = -\frac{2}{m \varepsilon_0 e}$$  \hspace{1cm} (1.9)$$

Values for $N_A$ are the same order of magnitude as $N_D$, slightly greater than $N_D$ at 30°C and about three times less at 60°C and 90°C. Many researchers have published data that show a transition to $p$-type at higher potentials, but none has drawn attention to it. This is likely because Gerischer's model for band structure on classical semiconductors is assumed to represent the data and it is not valid for the condition of degeneracy that is seen in passive films.
Table 1.3 summarizes the results of Mott-Schottky analysis. The trends shown illustrate the accuracy and internal consistency of the data. For mill-annealed Alloy 22 in 60°C pH 6, 4 M NaCl electrolyte, \(N_D\) is larger at higher current density. For solution-annealed Alloy 22 in pH 3, 0.1 M Cl\(^-\) electrolyte, \(N_D\) increases with increasing temperature. Correlation coefficients for linear regression are 0.99 or better for all ascending voltage data, indicating high accuracy. The results for 60°C data show a pH/chloride concentration effect on \(N_D\). \(N_D\) for the 60°C, pH 3, 0.1 M Cl\(^-\) condition is more than twice that for 60°C, pH 6, 4 M NaCl with 14 nA/cm\(^2\) current density (the 62 nA/cm\(^2\) test is not considered because it is believed that specimen contained grain boundary precipitates); lower pH/chloride concentration appears to increase donor density and decrease low frequency impedance, which is correspondingly 2.6 times smaller for the 60°C, pH 3, 0.1 M Cl\(^-\) condition.
Table 1.3. Mott-Schottky analysis for carrier densities.

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Temperature (°C)</th>
<th>Average Current Density (nA/cm²)</th>
<th>N_D (cm⁻³)</th>
<th>Correlation Coefficient R²</th>
<th>N_A (cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH 6, 4 M NaCl</td>
<td>60</td>
<td>14</td>
<td>3.0 x 10²⁰</td>
<td>0.99</td>
<td>Not applicable</td>
</tr>
<tr>
<td>pH 6, 4 M NaCl</td>
<td>60</td>
<td>62</td>
<td>7.3 x 10²⁰</td>
<td>1.00</td>
<td>Not applicable</td>
</tr>
<tr>
<td>pH 3, 0.1 M Cl⁻</td>
<td>30</td>
<td>1.8</td>
<td>5.1 x 10²⁰</td>
<td>1.00</td>
<td>6.2 x 10²⁰</td>
</tr>
<tr>
<td>pH 3, 0.1 M Cl⁻</td>
<td>60</td>
<td>18</td>
<td>6.3 x 10²⁰</td>
<td>1.00</td>
<td>1.8 x 10²⁰</td>
</tr>
<tr>
<td>pH 3, 0.1 M Cl⁻</td>
<td>75</td>
<td>29</td>
<td>7.4 x 10²⁰</td>
<td>0.99</td>
<td>Not applicable</td>
</tr>
<tr>
<td>pH 3, 0.1 M Cl⁻</td>
<td>90</td>
<td>83</td>
<td>7.6 x 10²⁰</td>
<td>1.00</td>
<td>2.3 x 10²⁰</td>
</tr>
</tbody>
</table>
Figure 1.44. Mott-Schottky Plot for mill-annealed Alloy 22 in deaerated, 60°C, pH 6, 4 M NaCl electrolyte, ascending voltages, nominal current density = 14 nA/cm².
Figure 1. 45. Mott-Schottky Plot for mill-annealed Alloy 22 in deaerated, 60°C, pH 6, 4 M NaCl electrolyte, ascending voltages, nominal current density = 62 nA/cm².
Figure 1.46. Mott-Schottky plot for solution-annealed Alloy 22 in deaerated, 75°C, pH 3, 0.1 M Cl⁻ electrolyte, ascending and descending voltages.
Figure 1.47. Mott-Schottky plot for solution-annealed Alloy 22 in 75°C, pH 3, 0.1 M Cl-electrolyte. Capacitance data were collected at one time, not allowing the passive film to change dimensions. Impedance was collected at 3,000 Hz. Comparison of these data to those collected from the long-term tests shows that both methods produce the same results, validating the use of long-term steady state data for Mott-Schottky analysis.
Figure 1.48. Mott-Schottky plot for solution-annealed Alloy 22 in deaerated, 30°C, pH 3, 0.1 M Cl⁻ electrolyte, ascending voltages.
Figure 1.49. Mott-Schottky plot for solution-annealed Alloy 22 in deaerated, 60°C, pH 3, 0.1 M Cl⁻ electrolyte, ascending voltages.
Figure 1.50. Mott-Schottky plot for solution-annealed Alloy 22 in deaerated, 90°C, pH 3, 0.1 M Cl⁻ electrolyte, ascending voltages.
1.3.3 MODELING WORK

1.3.3.1 Impedance Model

The following mathematical development of the impedance model is after Macdonald et al\textsuperscript{37} and is included to support the model parameter derivation method. Reaction 1, Figure 1.51 describes the injection of the metal interstitial, \( Cr_i^{x^+} \), into the barrier layer.

\[
\begin{align*}
\text{Alloy 22} & \quad \text{Cr}_2\text{O}_3 \text{ Barrier Layer} & \quad \text{Solution} \\
(1) \quad Cr \xrightarrow{k_1} Cr_i^{x^+} + v_{Cr} + \chi e^- & \quad (3) \quad Cr_i^{x^+} \xrightarrow{k_2} Cr^{x^+} + (\Gamma - \chi)e^- \\
(2) \quad Cr \xrightarrow{k_3} Cr_{cr} + \frac{\chi}{2} V_o + \chi e^- & \quad (4) \quad V_o + H_2O \xrightarrow{k_i} O_2 + 2H^+ \\
(5) \quad CrO_{\frac{\chi}{2}} + \chi H^+ \xrightarrow{k_i} Cr^{x^+} + \frac{\chi}{2} H_2O + (\Gamma - \chi)e^- \\
Cr_i^{x^+} & \rightarrow \\
V_o & \rightarrow \\
x = L & \quad x = 0
\end{align*}
\]

Figure 1.51. Schematic of the processes envisioned to take place in the barrier layer on Alloy 22 at passive potentials where the oxidation state for Cr in the barrier layer is the same as in the solution, i.e., \( \Gamma = \chi \). These are the processes considered in the development of the impedance model for passive potentials and do not consider cation vacancies.
The chromium interstitial is then transmitted through the barrier layer and ejected into the solution, as described by Reaction 3, Figure 1.51. Reaction 2, Figure 1.51 results in the growth of the barrier layer into the bulk Alloy-22 via the generation of oxygen vacancies ($V_o^{2-}$), and Reaction 5, Figure 5.1 leads to the destruction of the barrier layer by dissolution. Reaction 4, Figure 1.51 represents the annihilation of oxygen vacancies at the film/solution interface, which are produced by Reaction 2, Figure 1.51 at the metal/film interface. Note that Reactions 1, 3, and 4, Figure 1.51 are lattice conservative processes, in that their occurrence does not result in the movement of the corresponding interface with respect to a laboratory frame of reference, while Reactions 2 and 5, Figure 1.51 are lattice non-conservative processes. A steady state must involve a balance between at least two non-conservative reactions, since only one non-conservative reaction would lead to monotonic growth or thinning of the passive film. Considering our findings that the dominant defects in the barrier layer on Alloy-22 within the passive state must be oxygen vacancies or chromium interstitials, with the latter being most likely, the reactions regarding the consumption (at the metal/film interface) and production (at the film/solution interface) of chromium (III) vacancies are not included in the impedance model. However, cation vacancies (Reactions 1 and 4, Figure 1.52) appear to be the dominant defect in the transpassive state.
Figure 1.52 Schematic of the processes envisioned to take place in the barrier layer on Alloy 22. This mechanism includes cation vacancies (Reactions 1 and 4), which are considered significant only at pre-transpassive and transpassive potentials.
The rate of change of barrier layer thickness involves two lattice non-conservative reactions, as follows:

$$\frac{dL}{dt} = -\frac{2\Omega}{\chi} J_o - \Omega k_s C_H^n$$  \hspace{1cm} (1.10)

where the first term on the right hand side corresponds to barrier layer generation at the alloy/film interface [Reaction 2, Figure 1.51] and the second term corresponds to the dissolution of the barrier layer at the barrier layer/solution interface. The parameter \( \Omega = 14.59 \text{ cm}^3\text{mol}^{-1} \) is the molar volume per cation of the barrier layer, \( \chi = 3 \) is the oxidation state of chromium in the barrier layer in the passive state, \( J_o \) is the flux of oxygen vacancies within the barrier layer, \( C_H^n \) is the hydrogen ion concentration in the solution at the film/solution interface, \( n \) is the kinetic order of the film dissolution reaction with respect to \( C_H^n \), and \( k_s \) is the rate constant for Reaction 5, Figure 1.51. Table 1.4 displays the functional forms of the rate constants for the five interfacial reactions identified in Figure 1.51; the definition of standard rate constants will be given later in this section.

All interfacial reactions that produce or consume electrons contribute to the total current density, which is described as:

$$I = F[-\chi J_{t/f}^{m/f} - 2J_o^{m/f} - (\Gamma - \chi)J_{t/s}^{f/s} + (\Gamma - \chi)k_s C_H^n]$$  \hspace{1cm} (1.11)

in which \( F = 96487 \text{ C/equiv} \) is Faraday's constant, and \( \Gamma = 3 \) is the oxidation state of chromium in solution in the passive range. At sufficiently high potentials, chromium may enter the solution in the +6 state (as chromate, \( \text{CrO}_4^{2-} \)), either by
ejection of cation interstitials (Reaction 3, Figure 1.51) or by barrier layer dissolution (Reaction 5, Figure 1.51), or both. In that case, \( \Gamma = 6 \).

The fluxes of the point defects in the barrier layer may be written as

\[
J_i = -D_i \left( \frac{\partial C_i}{\partial x} \right) - \chi K D_i C_i \quad \text{and} \quad J_o = -D_o \left( \frac{\partial C_o}{\partial x} \right) - 2 K D_o C_o
\]

for chromium interstitials and oxygen vacancies, respectively, where \( D \) and \( C \) are the diffusivity and concentration, respectively, and subscripts \( i \) and \( o \) designate chromium interstitials and oxygen vacancies, respectively. Additionally, \( K = \varepsilon F / RT \), \( R = 8.314 \, J \, mol^{-1} K^{-1} \) is the gas constant, \( T \) is the absolute temperature in Kelvins, and \( \varepsilon \) is the electric field strength in \( V \, cm^{-1} \), which is considered to be a constant, according to the PDM. The continuity equations \( \frac{\partial C}{\partial t} = -\nabla J \) then become:

\[
\frac{\partial C_i}{\partial t} = D_i \frac{\partial^2 C_i}{\partial x^2} + \chi D_i K \frac{\partial C_i}{\partial x}
\]

and

\[
\frac{\partial C_o}{\partial t} = D_o \frac{\partial^2 C_o}{\partial x^2} + 2 D_o K \frac{\partial C_o}{\partial x}
\]

These equations are then solved for the initial conditions \( t = 0 \) of \( C_i(x) = C_i^0(x) \) and \( C_o(x) = C_o^0(x) \) and for the boundary conditions \( t > 0 \) of: \( x = 0 \) (the film/solution interface), \( J_i(0) = -k_i^0 e^{-\beta C_i}(0) \, (k_2^0, \, cm/s) \), \( J_o(0) = -\left( \chi / 2 \right) k_4^0 e^{a' \rho C_o}(0) \, (k_4^0, \, cm/s) \); at \( x = L \) (the metal/film interface), \( J_i(L) = -k_i^0 e^{a' \rho} e^{-bL} \, (k_1^0, \, mol/s/cm^2) \), \( J_o(L) = -\left( \chi / 2 \right) k_2^0 e^{a' \rho} e^{-bL} \, (k_2^0, \, mol/s/cm^2) \). Note that the fluxes of cation interstitials and oxygen vacancies are negative when the species move from the metal/film (m/f)
interface to the film/solution (f/s) interface in the coordinate system adopted in Figure 1.51.

Combined with the rate constants shown in Table 1.4, the rate of change of the barrier layer thickness [Equation (1.14)] and the current density [Equation (1.15)] then become:

\[
\frac{dL}{dt} = -\Omega k_1^0 e^{\alpha VT} e^{-hL} - \Omega k_s^0 e^{\beta VT} C_H^n
\]  

(1.14)

and

\[
I = F[\chi k_1^0 e^{\alpha VT} e^{-hL} + \chi k_s^0 e^{\beta VT} e^{-hL} + (\Gamma - \chi') k_1^0 e^{\alpha VT} C_s(0) + (\Gamma - \chi') k_s^0 e^{\beta VT} C_H^n] \tag{1.15}
\]

where \(C_H^n\) has units of \(\text{mol/cm}^3\). Note that the current density [Equation (1.15)] is a function of \(V\), \(L\), and \(C_s(0)\). Accordingly, for any arbitrary changes \(\delta V\), \(\delta L\), and \(\delta C_s(0)\) we have:

\[
\delta I = \left(\frac{\partial I}{\partial V}\right)_{L,C_s(0)} \delta V + \left(\frac{\partial I}{\partial L}\right)_{V,C_s(0)} \delta L + \left(\frac{\partial I}{\partial C_s(0)}\right)_{V,L} \delta C_s(0) \tag{1.16}
\]

The variations in \(V\), \(L\), and \(C_s(0)\) are sinusoidal in an EIS measurement, so that we write \(\delta V = \Delta V e^{j\omega t}\), \(\delta L = \Delta L e^{j\omega t}\), and \(\delta C_s(0) = \Delta C_s(0) e^{j\omega t}\); note that \(\Delta X\) is the amplitude of the variation in \(X\) at a frequency \(\omega = 0\). From Equation (1.16), the faradic admittance is then defined as:

\[
Y_f = \frac{\delta I}{\delta V} = I^V + I^L \frac{\Delta L}{\Delta V} + \frac{\Delta C_s(0)}{\Delta V} \tag{1.17}
\]

where \(I^V = (\partial I/\partial V)_{L,C_s(0)}\), \(I^L = (\partial I/\partial L)_{V,C_s(0)}\), and \(I^{C_s(0)} = (\partial I/\partial C_s(0))_{L,V}\). These differentials will be evaluated later from Equation (1.16).
We now return to Equation (1.14) and determine the response of $\delta L/\delta t$ to $\delta V$, $\delta L$, and $\delta C_i(0)$ by taking the total differential. Thus, for the relaxation in film thickness:
\[
d(\delta L)/dt = \Omega k_2^0 a_2 e^{a_i V} e^{-b_2 L} \delta V - \Omega k_3^0 b_3 e^{a_i V} e^{-b_3 L} \delta L - \Omega k_5^0 a_5 e^{a_i V} C_{H^*} \delta V.
\]
Considering that $d(\delta L)/dt = j \omega \Delta L e^{j\omega t}$, we obtain:
\[
j \omega \Delta L e^{j\omega t} = \Omega (k_2^0 a_2 e^{a_i V} e^{-b_2 L} - k_3^0 a_5 e^{a_i V} C_{H^*}) \delta V e^{j\omega t} - \Omega k_5^0 b_3 e^{a_i V} e^{-b_3 L} \Delta L e^{j\omega t}
\]
which upon rearrangement yields:
\[
\frac{\Delta L}{\Delta V} = \frac{\Omega (k_2^0 a_2 e^{a_i V} e^{-b_2 L} - k_3^0 a_5 e^{a_i V} C_{H^*})}{\Omega k_2^0 b_3 e^{a_i V} e^{-b_2 L} + j \omega} \quad \text{or} \quad \frac{\Delta L}{\Delta V} = \frac{\Phi}{1 + j \omega \tau_2}
\]
where:
\[
\Phi = \left( \frac{a_2}{b_2} \right) - \left( \frac{k_2^0}{k_3^0} \right) \left( \frac{a_5}{b_3} \right) e^{(a_i a_5 - a_2) V} e^{b_2 L} C_{H^*}
\]
and
\[
\tau_2 = \frac{1}{\Omega k_2^0 b_3 e^{a_i V} e^{-b_2 L}}
\]
For chromium interstitials, the relaxation for $C_i(0)$ is determined through the mass balance at the film/solution interface $dC_i(0)/dt = -k_3^0 C_i(0) = -k_3^0 e^{a_i V} C_i(0)$ (units of $k_3^0$ are s$^{-1}$). The total differential is $d(\delta C_i(0))/dt = -k_3^0 [a_3 e^{a_i V} C_i(0) \delta V + e^{a_i V} \delta C_i(0)]$.
Inserting the sinusoidal variations for $\delta V$ and $\delta C_i(0)$ therefore yields:
\[
j \omega \Delta C_i(0) e^{j\omega t} = -k_3^0 a_3 e^{a_i V} C_i(0) \delta V e^{j\omega t} - k_3^0 e^{a_i V} \Delta C_i(0) e^{j\omega t}
\]
\[ \Delta C_i(0)(j\omega + k'^0 e^{a_s\nu}) = -k'^0 a_s e^{a_s\nu} C_i(0)\Delta V. \quad (1.23) \]

Therefore,

\[ \frac{\Delta C_i(0)}{\Delta V} = \frac{-k'^0 a_s e^{a_s\nu} C_i(0)}{j\omega + k'^0 e^{a_s\nu}} = -\frac{a_s C_i(0)}{1 + j\omega \tau_3} \quad (1.24) \]

in which:

\[ \tau_3 = \frac{1}{k'^0 e^{a_s\nu}} \quad (1.25) \]

The expression for the faradic admittance is finally derived from Equation (1.26) as:

\[ Y_f = I^V + I^L \frac{\Phi_2}{1 + j\omega \tau_2} - I^{C_i(0)} \frac{a_s C_i(0)}{1 + j\omega \tau_3} + j\omega C \quad (1.26) \]

in which the parallel geometric capacitance \( C = \epsilon \epsilon_0 / \ell \) (dielectric constant \( \epsilon = 25 \) for a passive \( \text{Cr}_2\text{O}_3 \) barrier layer and vacuum permittivity \( \epsilon_0 = 8.85 \times 10^{-14} \text{F/cm} \)) is taken into consideration, and

\[ I^V = \left( \frac{\partial I}{\partial V} \right)_{V,C_i(0)} \quad (1.27) \]

\[ I^V = F[a_1 \chi k^0_1 e^{a_s\nu} e^{-b_2L} + a_2 \chi k^0_2 e^{a_s\nu} e^{-b_2L} + a_3 (\Gamma - \chi) k^0_3 e^{a_s\nu} C_i(0) + a_5 (\Gamma - \chi) k^0_5 e^{a_s\nu} C_{H^+}] \]

\[ I^L = \left( \frac{\partial I}{\partial L} \right)_{V,C_i(0)} \quad (1.28) \]

\[ I^L = F[-b_1 \chi k^0_1 e^{a_s\nu} e^{-b_2L} - b_2 \chi k^0_2 e^{a_s\nu} e^{-b_2L}] = -\chi F[b_1 k^0_1 e^{a_s\nu} e^{-b_2L} + b_2 k^0_2 e^{a_s\nu} e^{-b_2L}] \]

\[ I^{C_i(0)} = \left( \frac{\partial I}{\partial C_i(0)} \right)_{V,L} = (\Gamma - \chi) F k^0_3 e^{a_s\nu} \quad (1.29) \]
In the above expressions, the parameters that appear on the right side ($L$ and $C_i(0)$) are identified with the steady-state quantities. At steady state, Equation (1.12) and (1.13) become

$$\frac{\partial^2 C_i}{\partial x^2} + \chi K \frac{\partial C_i}{\partial x} = 0$$

(1.30)

$$\frac{\partial^2 C_o}{\partial x^2} + 2K \frac{\partial C_o}{\partial x} = 0$$

(1.31)

the solutions for which are:

$$C_i(x) = A_i e^{-\chi K x} + B_i$$

(1.32)

$$C_o(x) = A_o e^{-2K x} + B_o$$

(1.33)

The expressions for the fluxes therefore become:

$$J_i = -\chi KD_i B_i$$

(1.34)

$$J_o = -2KD_o B_o$$

(1.35)

From the boundary conditions, the coefficients are obtained as:

$$B_i = \frac{k_i^0 e^{\alpha_i} e^{-\beta_i L}}{\chi KD_i}$$

(1.36)

and

$$B_o = \frac{\left(\chi / 2\right) k_o^0 e^{\alpha_o} e^{-\beta_o L}}{2KD_o}$$

(1.37)

Because the fluxes for a given species at two interfaces are equal at steady state:
- $k_3^0 e^{\alpha_5^*} C_i(0) = -k_1^0 e^{\alpha_2^*} e^{-h_L}$ and $-(\chi / 2) k_4^0 e^{\alpha_5^*} C_o(0) = -(\chi / 2) k_2^0 e^{\alpha_2^*} e^{-h_L}$, the steady-state concentrations for chromium interstitials and oxygen vacancies at the film/solution interface are:

$$C_i(0) = \left( \frac{k_1^0}{k_3^0} \right) e^{(\alpha_1 - \alpha_2)*} e^{-b_L}$$  \hspace{1cm} (1.38)

$$C_o(0) = \left( \frac{k_2^0}{k_4^0} \right) e^{(\alpha_1 - \alpha_2)*} e^{-b_L}$$  \hspace{1cm} (1.39)

In the case of steady state, Equation (1.10) becomes:

$$J_o(L) = -(\chi / 2) k_3 C_i^*$$  \hspace{1cm} (1.40)

and from Equations (1.35) and (1.37):

$$-(\chi / 2) k_3 C_i^* = -2KD_o \left( \frac{\chi / 2 k_3^0 e^{\alpha_5^*} e^{-b_L}}{2KD_o} \right)$$  \hspace{1cm} (1.41)

Therefore, the steady-state barrier layer thickness is:

$$L_{ss} = \left( \frac{a_2 - a_5}{b_2} \right) V - \frac{1}{b_2} \ln \left[ \frac{k_3^0}{k_2^0} C_i^* \right]$$  \hspace{1cm} (1.42)

The parameters, $k_1^0$, $k_2^0$, $k_3^0$, $k_4^0$, $k_5^0$, in the above equations and Table 1.4 are a function of solution pH and are not the standard rate constants for the interfacial reactions, since the PDM defines $k_1^0 = k_1^{00} e^{-\alpha_1 \beta_y pH} e^{-\alpha_2 \gamma H+}$, $k_2^0 = k_2^{00} e^{-\alpha_1 \beta_y pH} e^{-\alpha_2 \gamma H+}$, $k_3^0 = k_3^{00} e^{-\alpha_1 \beta_y pH} e^{-\alpha_1 \gamma H+}$, $k_4^0 = k_4^{00} e^{-\alpha_1 \beta_y pH} e^{-\alpha_1 \gamma H+}$, and $k_5^0 = k_5^{00} e^{-\alpha_1 \beta_y (1-y) pH} e^{-\alpha_1 (1-y) \gamma H+}$, in which $\alpha_1$, $\alpha_2$, $\alpha_3$, $\alpha_4$, $\alpha_5$ are the transfer coefficients,
and $k_1^{00}$, $k_2^{00}$, $k_3^{00}$, $k_4^{00}$, $k_5^{00}$ are the standard rate constants. The standard rate constants are summarized in Table 1.5. The potential drop across the film/solution (f/s) interface is $\phi_{f/s} = \phi_f - \phi_s = \alpha V + \beta pH + \phi_{f/s}^{0}$, and that across the metal/film (m/f) interface is $\phi_{m/f} = \phi_m - \phi_s = (1 - \alpha)V - \varepsilon L - \beta pH - \phi_{f/s}^{0}$, in which $\alpha = d\phi_{f/s} / dV$ is the dependence of the potential drop across the barrier layer/solution interface on the applied voltage, $V$, [i.e., $\alpha$ is the polarizability of the barrier layer/outer layer (solution) interface]; $\beta = d\phi_{f/s} / dpH$ is the dependence of the potential drop across the same interface on $pH$; $\phi_{f/s}^{0}$ is the value of $\phi_{f/s}$ in the standard state; $\gamma = F / RT$; and $K = \varepsilon \gamma = \varepsilon F / RT$. 
Table 1.4. Rate constants $k_i = k_i^0 e^{a_i V} e^{-b_i L}$ for five interfacial reactions in terms of the Point Defect Model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$a_i$</th>
<th>$b_i$</th>
<th>Units of $k_i^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $Cr \xrightarrow{k_1} Cr^{x+} + v_{cr} + \mathcal{X}e'$</td>
<td>$\alpha_1(1-\alpha)\gamma$</td>
<td>$\alpha_1 \mathcal{X}K$</td>
<td>$\text{mol} \text{cm}^{-2} \text{s}$</td>
</tr>
<tr>
<td>(2) $Cr \xrightarrow{k_2} Cr^{x+} + \frac{1}{2}V_{O} + \mathcal{X}e'$</td>
<td>$\alpha_2(1-\alpha)\gamma$</td>
<td>$\alpha_2 \mathcal{X}K$</td>
<td>$\text{mol} \text{cm}^{-2} \text{s}$</td>
</tr>
<tr>
<td>(3) $Cr^{x+} \xrightarrow{k_3} Cr^{\gamma+} + (\Gamma - \mathcal{X})e'$</td>
<td>$\alpha_3 \alpha \Gamma \gamma$</td>
<td>0</td>
<td>$\text{cm} \text{s}^{-1}$</td>
</tr>
<tr>
<td>(4) $V_{O} + H_2O \xrightarrow{k_4} O_2 + 2H^+$</td>
<td>$2\alpha_4 \alpha \gamma$</td>
<td>0</td>
<td>$\text{cm} \text{s}^{-1}$</td>
</tr>
<tr>
<td>(5) $\text{CrO}_{\frac{1}{2}} + \mathcal{X}H^+ \xrightarrow{k_5} \text{Cr}^{\gamma+} + \frac{1}{2}H_2O + (\Gamma - \mathcal{X})e'$</td>
<td>$\alpha_5 \alpha (\Gamma - \mathcal{X}) \gamma$</td>
<td>0</td>
<td>$\text{mol}^{0.4} \text{cm}^{-0.2} \text{s}$</td>
</tr>
</tbody>
</table>

Table 1.5 Definition of the standard rate constants for the interfacial defect generation and annihilation reactions employed in the Point Defect Model.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$k_i^0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) $Cr \xrightarrow{k_1} Cr^{x+} + v_{cr} + \mathcal{X}e'$</td>
<td>$k_1^{00} e^{-\alpha_1 \beta \Gamma \gamma} e^{-\alpha_1 \mathcal{X} \gamma}$</td>
</tr>
<tr>
<td>(2) $Cr \xrightarrow{k_2} Cr^{x+} + \frac{1}{2}V_{O} + \mathcal{X}e'$</td>
<td>$k_2^{00} e^{-\alpha_2 \beta \Gamma \gamma} e^{-\alpha_2 \mathcal{X} \gamma}$</td>
</tr>
<tr>
<td>(3) $Cr^{x+} \xrightarrow{k_3} Cr^{\gamma+} + (\Gamma - \mathcal{X})e'$</td>
<td>$k_3^{00} e^{-\alpha_3 \beta \Gamma \gamma} e^{-\alpha_3 \mathcal{X} \gamma}$</td>
</tr>
<tr>
<td>(4) $V_{O} + H_2O \xrightarrow{k_4} O_2 + 2H^+$</td>
<td>$k_4^{00} e^{-\alpha_4 \beta \Gamma \gamma} e^{-\alpha_4 \mathcal{X} \gamma}$</td>
</tr>
<tr>
<td>(5) $\text{CrO}_{\frac{1}{2}} + \mathcal{X}H^+ \xrightarrow{k_5} \text{Cr}^{\gamma+} + \frac{1}{2}H_2O + (\Gamma - \mathcal{X})e'$</td>
<td>$k_5^{00} e^{-\alpha_5 (\Gamma - \mathcal{X}) \beta \gamma} e^{-\alpha_5 (\Gamma - \mathcal{X}) \mathcal{X} \gamma}$</td>
</tr>
</tbody>
</table>
1.3.3.2 Model for Data Fit

The ultimate objective of this work is to develop deterministic model parameters from experimental data that can be used for predicting corrosion behavior thousands of years into the future. Using the constitutive equations of the impedance model derived from the physical processes and boundary conditions of the PDM, a method for determining model parameters using a nonlinear least squares curve fit has been developed. This method uses the commercial software package, DataFit 8.0, by Oakdale Engineering. DataFit allows up to nine conditions to be defined in a single model. Because impedance data are recorded as two components, real and imaginary, one model is required for each. The nine model conditions are designated 'F1' through 'F9'. The variable that is compared to the experimental data to calculate the optimized parameters is designated as 'Y', which is either the real or imaginary component of impedance as a function of frequency. The independent variable, base 10 logarithm of frequency in Hz, is designated 'x'. The definition for each condition and, assuming \( \Gamma = \chi \), the corresponding code written for DataFit are as follows:

**F1:** Potential vs. SHE (F)

**F2:** pH

**F3:** \( ((1-m)/(e))^*F1-1/(99.998*m2*e)*log(k500/(k200*exp(-m2*99.998*(p1*F2+p2)))*(10^(-F2-3))^n) \)

\[
L_{ss} = \left( \frac{a_2 - a_5}{b_2} \right) V - \frac{1}{b_2} \ln \left[ \left( \frac{k_2^0}{k_2^c} \right)^n \right]
\]
\[ (1-\alpha) V - \frac{1}{\chi \alpha \gamma e} \ln \left[ C_H^0 \left( \frac{k_2^{100}}{k_2^{100} \exp(-\chi \alpha \gamma F_3) \exp(-\chi \alpha \gamma \phi^0_{1/s})} \right) \right] \]  

(1.43)

**F4:** \( 96486.7 \times (99.998 \times m1 \times (1-m) \times 3 \times k100 \times \exp(-m1 \times 99.998 \times (p1 \times F2 + p2)) \times \exp(99.998 \times m1 \times (1-m) \times F1) \times \exp(-99.998 \times m1 \times e \times F3) + 99.998 \times m2 \times (1-m) \times 3 \times k200 \times \exp(-m2 \times 99.998 \times (p1 \times F2 + p2)) \times \exp(99.998 \times m2 \times (1-m) \times F1) \times \exp(-99.998 \times m2 \times e \times F3)) \)

\[ I^V = \left( \frac{\partial I}{\partial V} \right)_{L,C_i(0)} \]

\[ = F[a_1 \chi k_1 e^{a \nu} e^{-b L} + a_2 \chi k_2 e^{a \nu} e^{-b L} + a_3 (\Gamma - \chi) k_3 e^{a \nu} C_i(0) + a_5 (\Gamma - \chi) k_5 e^{a \nu} C_H^0] \]  

(1.44)

**F5:** \(-e(1-m) \times F4\)

\[ I^L = \left( \frac{\partial I}{\partial L} \right)_{V,C_i(0)} \]

\[ = F[-b_1 \chi k_1 e^{a \nu} e^{-b L} - b_2 \chi k_2 e^{a \nu} e^{-b L}] = -\chi F[b_1 k_1 e^{a \nu} e^{-b L} + b_2 k_2 e^{a \nu} e^{-b L}] \]  

(1.45)

**F6:** \((1-m)/e\)

\[ \Phi_2 = \left( \frac{a_2}{b_2} \right) - \left( \frac{k_2^{100}}{k_2^{100}} \right) e^{(a_2-a_1) \nu} e^{b_L C_H^0} \]  

(1.46)

**F7:** \(1/(w \times k200 \times \exp(-m2 \times 99.998 \times (p1 \times F2 + p2)) \times \exp(99.998 \times m2 \times (1-m) \times F1) \times \exp(-99.998 \times m2 \times e \times F3) \times 99.998 \times e \times m2)\)

\[ \tau_2 = \frac{1}{\Omega k_2^{100} b_2 e^{a \nu} e^{-b L}} \]

(1.47)
\[ F8: F4 + F5 \cdot F6 / (1 + (2 \cdot 3.1415926 \cdot (10^x) \cdot F7)^2) + 1 / Re \]

Real Admittance
\[ Y'_r = I' + I \cdot \frac{\phi_2}{1 + (\omega \tau_2)^2} + \frac{1}{R_e} \]  
\[ (1.48) \]

\[ F9: -F5 \cdot F6 \cdot 2 \cdot 3.1415926 \cdot (10^x) \cdot F7 / (1 + (2 \cdot 3.1415926 \cdot (10^x) \cdot F7)^2) + 2 \cdot 3.1415926 \cdot (10^x) \cdot e1 \cdot 0.000000000000088542 / F3 \]

Imaginary component of admittance
\[ Y''_r = (-I' - \frac{\phi_2 \omega \tau_2}{1 + (\omega \tau_2)^2} + \omega C_{sc}) \]  
\[ (1.49) \]

where space charge capacitance is from the parallel plate formula, \( C_{sc} = \frac{\varepsilon_0}{L_{ss}} \), and \( L_{ss} \) is calculated from the expression for \( F3 \).

\[ Y: F8 / (F8^2 + F9^2) + Rs \]

Real impedance

OR

\[ Y: -F9 / (F8^2 + F9^2) - 1 / (2 \cdot 3.1415926 \cdot (10^x) \cdot Cdl) \]

Imaginary impedance

where the model parameter designations in DataFit, their corresponding designation in the PDM derivation above, and physically realistic values are shown Table 1.6. The number 99.998 in the lines of code for \( F3 \), \( F4 \), and \( F7 \) is \( \chi Y = \frac{F}{RT} = 99.998 \) where \( \chi = \)
3 and $T = 80^\circ C$. When executing the DataFit model, the model must be edited to change the value of $x^y$ to the temperature of interest. The parallel leakage and corresponding resistance, $R_e$, in the description for F8 Real Impedance, must exist, otherwise corrosion would not occur because the cathodic reaction could not take place on the outer surface of the film. In F9, the imaginary component of admittance includes the space charge capacitance for the passive film. This capacitance is calculated from the parallel plate capacitor formula:

$$C = \frac{\varepsilon \varepsilon_0}{L_{ss}}$$

(1.50)

where $C$ is capacitance and $L_{ss}$ is calculated using the equation for condition F3. Here it is assumed that $C$ is dominated by the space charge capacitance, $C_{sc}$, neglecting geometric and double layer capacitances. Impedance due to double layer capacitance is added as a series capacitance in the expression for imaginary impedance, $Y$.

Figure 1.53 is a schematic of the potential drops through the system as envisioned by the PDM, where $\phi_m$ is the potential in the metal, $\phi_{mf}$ is the potential drop across the metal/film interface, $\phi_{fs}$ is the potential drop across the film/solution interface, and $\phi_s$ is the potential in the solution or outer layer of the passive film. The potential drop through the barrier layer is linear. This is because the PDM assumes constant electric field strength in the barrier layer. For anodic polarization the metal is always more positive than the solution and therefore $\phi_{fs}$ and $\phi_{fs}^0$ are always negative. Also, $\alpha = d\phi_{fs}/dV$ is always negative because $\phi_{fs}$ becomes more negative with
increasing total potential difference between metal and solution. $\beta = d\phi_{f/s} / dpH$ may be positive or negative depending upon solution pH and point of zero charge of the outer layer.

The transfer coefficients, $\alpha_1$ and $\alpha_2$, which are related to activated complex formation, are always between 0 and 1. For passive films on Alloy 22 the transfer coefficients are expected to be small, about 0.1. From the PDM it is seen that passive current density, $I_{ss}$, is exponentially dependent upon $\alpha_1$, $\alpha_2$, pH, $\phi^0_f$, V, and steady state thickness, $L_{ss}$ (Equation 1.15). Using the definitions for standard rate constants for Reactions 1 and 2, Figure 1.53, $k_1^0 = k_1^0 e^{-\alpha_1 \beta \phi_f} e^{-\alpha_2 \phi_f}$, and $k_2^0 = k_2^0 e^{-\alpha_1 \beta \phi_f} e^{-\alpha_2 \phi_f}$, and assuming $\Gamma = \chi$, Equation 1.15 becomes:

$$I_{ss} = \chi F[k_1^{00} e^{-\alpha_1 \beta \phi_f} e^{-\alpha_2 \phi_f} e^{(1-\alpha)V} e^{-\alpha \phi_f} + k_2^{00} e^{-\alpha_1 \beta \phi_f} e^{-\alpha_2 \phi_f} e^{(1-\alpha)V} e^{-\alpha \phi_f}]$$  

Equation 1.51 shows that as $\alpha_1$ and $\alpha_2$ increase, the dependence of $I_{ss}$ on pH and voltage drop increases exponentially. Because the experimental data show that $I_{ss}$ is not strongly dependent on pH or voltage, $\alpha_1$ and $\alpha_2$ must be small.
Figure 1.53. Potential drops across the passive film (anodic polarization) as envisioned by the Point Defect Model, where $\phi_m$ is the potential in the metal, $\phi_{m/f}$ is the potential drop across the metal/film interface, $\phi_{f/s}$ is the potential drop across the film/solution interface, and $\phi_s$ is the potential in the solution or outer layer of the passive film.
Table 1.6. Description of DataFit model variables for determining PDM parameters from experimental data.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>e = $\varepsilon$, $\hat{e}$</td>
<td>electric field strength, approximately $1 \times 10^6$ V/cm.</td>
</tr>
<tr>
<td>e1 = $\hat{\varepsilon}$</td>
<td>dielectric constant, approximately 25 for $Cr_2O_3$, dimensionless</td>
</tr>
<tr>
<td>Rs = solution resistance of cell, value of $Z'$ at high frequency, approx. 1 – 10 ohm.</td>
<td></td>
</tr>
<tr>
<td>Re = parallel resistance, corresponding to electronic leakage across the film, ohm</td>
<td></td>
</tr>
<tr>
<td>k100 = $k_1^{00}$</td>
<td>standard rate constant for Reaction 1, ( Figure ), ( mol/cm^2\cdot s )</td>
</tr>
<tr>
<td>k200 = $k_2^{00}$</td>
<td>standard rate constant for Reaction 2, ( Figure ), ( mol/cm^2\cdot s )</td>
</tr>
<tr>
<td>k500 = $k_5^{00}$</td>
<td>standard rate constant for Reaction 5, ( Figure ), ( mol^{0.5}/cm^{0.5}\cdot s )</td>
</tr>
<tr>
<td>$m = \alpha = d\phi_{f/s}/dV$, polarizability of the film/solution interface, ( 0 &lt; \alpha &lt; 1 ), dimensionless</td>
<td></td>
</tr>
<tr>
<td>m1 = $\alpha_1$, transfer coefficient for Reaction 1, ( Figure ), ( 0 &lt; \alpha_1 &lt; 1 ), dimensionless</td>
<td></td>
</tr>
<tr>
<td>m2 = $\alpha_2$, transfer coefficient for Reaction 2, ( Figure ), ( 0 &lt; \alpha_2 &lt; 1 ), dimensionless</td>
<td></td>
</tr>
<tr>
<td>n = kinetic order of the dissolution reaction with respect to $[H^+]$, ( 0 &lt; n &lt; 1 ), dimensionless</td>
<td></td>
</tr>
<tr>
<td>p1 = $\beta = d\phi_{f/s}/dpH$, negative or positive depending upon which side of the point of zero charge the pH is on, V</td>
<td></td>
</tr>
</tbody>
</table>
\[ p2 = \phi^0_{f/s}, \text{ the value of } \phi_{f/s} \text{ in the standard state, always negative for anodic polarization, } V \]

\[ \omega = \Omega, \text{ Mol volume per cation of the barrier layer, } 14.59 \text{ for } Cr_{2+x}O_{3-y} \text{ films, mol/cm}^3 \]

1.3.3.3 Modeling Procedure and Results

Only impedance data from potentials found by Mott-Schottky analysis to be within the passive potential range and showing \( n \)-type semiconductor behavior should be used for impedance modeling and parameter determination. This is because the impedance model is derived only for \( n \)-type semiconductors (cation intersititials and oxygen vacancies) and does not include cation vacancies (\( p \)-type semiconductor), which are important at pre-transpassive and transpassive potentials.

A set of "best guess" PDM parameters, shown in Table 1.7 has been developed by D.D. Macdonald using phase space analysis. These parameters were used to model the impedance data collected at 411 mV SHE and 75°C in pH 3, 0.1 M Cl\(^-\) electrolyte. DataFit was run using the "best guess" parameters. All of the "best guess" parameters were set as constant and \( \varepsilon = 25 \) was used for the dielectric constant. For the imaginary component a good fit was obtained using \( C_{dl} = 90 \mu \text{F} \) for double layer capacitance, and \( R_e = 384 \text{ ohms} \) for the parallel leakage resistance. For the real component, the solution resistance of 8 ohm·cm\(^2\) (the value of \( Z' \) at 10,000 Hz) was set as constant. Figure 1.54 shows the measured vs. calculated imaginary impedance, while Figure 1.55 shows the
measured vs. calculated real impedance. The model and parameters used to calculate real impedance are identical to those used to calculate imaginary impedance except that the imaginary component model includes the parallel leakage resistance, Re, and the real component model does not. The curve fit for the real component failed when the parallel resistance was included; no value for Re was found that would give a convergent solution of the linear least squares curve fit while leaving all the other parameters unchanged.

It was found that multiple parameter sets will give nearly identical calculated impedance spectra. Holding all other parameters constant, the rate constants, \( k_i^{00} \), can be varied over at least four orders of magnitude without affecting the calculated impedance so long as the relative magnitudes of the \( k_i^{00} \)'s remains the same. Figures 1.56 and 1.57 show calculated impedance using \( k_i^{00} \)'s that are all four orders of magnitude smaller than those in the “best guess” parameter set; only the exponents were changed. These curves are virtually indistinguishable from those in Figures 1.54 and 1.55.

The reasonableness of the parameter sets was checked by calculating thickness of the film, \( L_{ss} \), and passive current density, \( I_{ss} \), using Equation 1.43 and Equation 1.51. The calculated values were compared to measured data. The calculated thickness is 1.6 nm and the calculated current density is 8.6 nA/cm\(^2\) (Table 1.8). These numbers match very well with the known thickness of passive films and the measured current density of 25 nA/cm\(^2\).
To further investigate the behavior of the system, the contributions to passive current density by cation interstitials and oxygen vacancies were separated. Equation 1.52 was derived for current density assuming that cation interstitials (Reaction 1, Figure 1.51) dominate and that oxygen vacancies (Reaction 2, Figure 1.51) can be neglected:

\[ I_{ss} = \chi F [k_1^{00} e^{-\alpha x_0 \rho F} e^{-\alpha x_0 \rho F z} e^{(1-\alpha)\nu} e^{-\alpha L}] \]  

(1.52)

and Equation 1.53 assumes that cation interstitials can be neglected:

\[ I_{ss} = \chi F [k_2^{00} e^{-\alpha x_0 \rho F} e^{-\alpha x_0 \rho F z} e^{(1-\alpha)\nu} e^{-\alpha L}] \]  

(1.53)

The results in Table 1.8 show that, according to the PDM, cation interstitials dominate the passive current density by about 10 to 1 over oxygen vacancies.

An additional check can be performed by calculating the potential drop across the passive film by multiplying the calculated thickness by the modeled electric field strength. The result should be close to, but a little smaller than, the applied potential because it does not include all the potential drops in the system. In this case, the applied potential is 0.411 V SHE and the calculated potential drop \( \varepsilon \times L_{ss} \) is 0.294 V SHE, which agrees with the expected behavior.

These calculations show that the "best guess" parameters give physically reasonable film thickness and current density when used with the PDM equations. They also show that the DataFit model will calculate matching impedance spectra from multiple parameter
sets in which the \( k_i^{00} \)'s may vary greatly. Even though the DataFit model calculates matching impedance spectra for sets of \( k_i^{00} \)'s that cover four orders of magnitude, the calculated current densities are not in agreement with experimental observation. It has also been found that parameter sets that give very good mathematical fits with all of the parameters having physically valid values can be derived that result in negative values for thickness and current densities in the microamp to milliamp range, which are clearly invalid. This shows that the unconstrained nonlinear least squares method is inadequate for parameter derivation by optimization of the PDM on experimental data. A method for parameter derivation that is constrained by measured values for current density and film thickness, and possibly other experimental observations, must be developed.

Table 1.7. “Best guess” values for Point Defect Model parameters developed using Phase Space Analysis.

<table>
<thead>
<tr>
<th>PDM Parameter</th>
<th>DataFit variable</th>
<th>“Best guess” value from phase space analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \alpha )</td>
<td>M</td>
<td>0.7</td>
</tr>
<tr>
<td>( \alpha_1 )</td>
<td>M1</td>
<td>0.112</td>
</tr>
<tr>
<td>( \alpha_2 )</td>
<td>M2</td>
<td>0.123</td>
</tr>
<tr>
<td>n</td>
<td>N</td>
<td>0.6</td>
</tr>
<tr>
<td>( k_1^{00} )</td>
<td>k100</td>
<td>( 5.0 \times 10^{-14} )</td>
</tr>
<tr>
<td>( k_2^{00} )</td>
<td>k200</td>
<td>( 5.57 \times 10^{-15} )</td>
</tr>
<tr>
<td>( k_5^{00} )</td>
<td>k500</td>
<td>( 1.12 \times 10^{-11} )</td>
</tr>
<tr>
<td>( \beta )</td>
<td>P1</td>
<td>-0.005</td>
</tr>
<tr>
<td>( \phi_{f/s}^0 )</td>
<td>P2</td>
<td>-0.1</td>
</tr>
<tr>
<td>( \Omega )</td>
<td>W</td>
<td>14.59</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>E</td>
<td>( 1.85 \times 10^6 )</td>
</tr>
</tbody>
</table>
Table 1.8. Thickness and current density calculated from phase space analysis "best guess" parameter set with rate constants covering four orders of magnitude.

<table>
<thead>
<tr>
<th></th>
<th>$L_{ss}$</th>
<th>$I_{ss}$</th>
<th>$I_{ss}$</th>
<th>$I_{ss}$</th>
<th>$\varepsilon \times L_{ss}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td>(nA/cm$^2$)</td>
<td>(nA/cm$^2$)</td>
<td>(nA/cm$^2$)</td>
<td>(V)</td>
</tr>
<tr>
<td>$k_1^{00}$</td>
<td>$5 \times 10^{-13}$</td>
<td>1.5883</td>
<td>85.8</td>
<td>77.7</td>
<td>8.14</td>
</tr>
<tr>
<td>$k_2^{00}$</td>
<td>$5.57 \times 10^{-14}$</td>
<td>1.5883</td>
<td>8.58</td>
<td>7.77</td>
<td>0.814</td>
</tr>
<tr>
<td>$k_3^{00}$</td>
<td>$1.12 \times 10^{-10}$</td>
<td>1.5883</td>
<td>0.858</td>
<td>0.777</td>
<td>0.0814</td>
</tr>
<tr>
<td>Rate constants from &quot;Best Guess&quot; parameter set. Measured $I_{ss} = 25$ nA/cm$^2$.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$k_1^{00}$</td>
<td>$5 \times 10^{-14}$</td>
<td>1.5883</td>
<td>0.0858</td>
<td>0.0777</td>
<td>0.00814</td>
</tr>
<tr>
<td>$k_2^{00}$</td>
<td>$5.57 \times 10^{-15}$</td>
<td>1.5883</td>
<td>0.0858</td>
<td>0.0777</td>
<td>0.00814</td>
</tr>
<tr>
<td>$k_3^{00}$</td>
<td>$1.12 \times 10^{-11}$</td>
<td>1.5883</td>
<td>0.0858</td>
<td>0.0777</td>
<td>0.00814</td>
</tr>
</tbody>
</table>

Eq'n 5.42

Eq'n 5.43

Eq'n 5.44

$k_1^{00}$ and $k_2^{00}$

$k_1^{00}$ only (interstitials)

$k_2^{00}$ only (vacancies)
Figure 1.54. Measured and calculated imaginary impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl⁻ electrolyte. The solid line is calculated using phase space analysis “best guess” parameters in Table 1.7. Dots are measured values.

Figure 1.55. Measured and calculated real impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl⁻ electrolyte. The solid line is calculated using phase space analysis “best guess” parameters in Table 1.7. Dots are measured values.
Figure 1.56. Measured and calculated imaginary impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl⁻ electrolyte using rate constants four orders of magnitude smaller than the phase space analysis “best guess” parameters. The solid line is calculated and dots are measured values.

Figure 1.57. Measured and calculated real impedance for Alloy 22 at 411 mV SHE in 75°, pH 3, 0.1 M Cl⁻ electrolyte using rate constants four orders of magnitude smaller than the phase space analysis “best guess” parameters. The solid line is calculated and dots are measured values.
1.3.3.4 Summary and Conclusions

The need for predicting corrosion behavior into the far future covering the lifetime of a High Level Nuclear Waste repository environment requires deterministic modeling, which relies on time-invariant natural laws. Such modeling requires very high accuracy electrochemical data from which model parameters describing time-invariant natural laws may be derived.

In response to this need a laboratory designed specifically to conduct highly stable, long-term electrochemical experiments has been designed, built, and proven to generate very high accuracy electrochemical impedance spectroscopy and passive current density data. By continuously flowing fresh electrolyte through the test cell, tests can run continuously for thousands of hours with no accumulation of corrosion products and without changes in temperature, pH, solution redox potential or dissolved oxygen. Dissolved oxygen concentration is believed to be less than one per billion.

Validity of the EIS data was confirmed by examining short-term hysteresis and by applying the Kramers-Kronig transforms. Sequential scans run in the high-frequency to low-frequency direction followed immediately by the low-frequency to high-frequency direction showed no hysteresis. The Kramers-Kronig integrals transformed EIS data correctly.

EIS spectra collected hundreds apart and after stepping potential ascendingly and descendingly over the passive range showed minimal hysteresis demonstrating that the
system is stable over long time periods. However, three EIS spectra collected on a specimen held potentiostatically for 352 hours at 30°C showed a small monotonic change with time indicating that a true steady state had not been reached; the time required for Alloy 22 to reach a true steady state was not determined.

EIS and current density data were measured in deaerated, pH 6, 4 molar sodium chloride electrolyte at 30° and 60°C, and in deaerated, pH 3, 0.1 molar sodium chloride electrolyte at 30°, 60°, 75°, and 90°C. These data have been found to be accurate and internally consistent. For any given test condition (temperature, pH, chloride concentration), impedance and current density are weak functions of applied potential. The general trend is increasing impedance with increasing potential for the lower potentials and decreasing impedance with increasing potential for higher potentials. (The potential where impedance begins to decrease with increasing potential and the semiconductor character changes to p-type is defined as the pre-transpassive potential.) The largest increase in low frequency impedance with potential over the passive range is a factor of 2 with an average of 1.5. Current density effects are about the same, i.e., current density is nearly independent of applied potential, as predicted by the Point Defect Model. Low frequency impedance increases with increasing pH/chloride concentration. Because pH and chloride were not varied independently, the cause for this behavior cannot be determined. Overall, however, the impedance and current density change little over the range of conditions tested with temperature having the largest effect.
Mott-Schottky analysis was performed to further verify the validity and accuracy of the data and to characterize the semiconductor properties of the passive film. The conventional method for Mott-Schottky analysis requires that impedance be collected for the entire potential range so quickly that the passive film dimensions do not change, i.e., the film thickness is the same at each potential step. It is shown that impedance data collected over a long-term test, where the passive film is allowed to come to a steady state at each potential, give results identical to the conventional method, even though the film thickness is different for each potential step. This author believes the requirement that passive film dimensions must not change is not issue of semiconductor behavior. Rather, if the system is allowed to begin changing dimensions it is no longer at steady state, a condition which violates linear systems theory and invalidates the impedance data.

The film is found to behave as an n-type semiconductor at potentials in the lower part of the passive potential range (cation intersitials and oxygen vacancies are the dominant carriers). Donor density, $N_D$, is found to be between $3 \times 10^{20} \text{ cm}^{-3}$ and $8 \times 10^{20} \text{ cm}^{-3}$, which correlates well with the work of other researchers. For two mill-annealed Alloy 22 specimens in 60°C pH 6, 4 M NaCl electrolyte displaying current densities of 14 nA/cm² and 62 nA/cm², $N_D$ is larger at the higher current density, as expected. For solution-annealed Alloy 22 in pH 3, 0.1 M Cl⁻ electrolyte, $N_D$ increases with increasing temperature, also as expected. Correlation coefficients for linear regression are 0.99 or better for all ascending voltage data, indicating high accuracy. The results for 60°C data show a pH/chloride concentration effect on $N_D$. $N_D$ for the 60°C, pH 3, 0.1 M Cl⁻
condition is more than twice that for 60°C, pH 6, 4 M NaCl; lower pH/chloride concentration appears to increase donor density and decrease low frequency impedance, which is correspondingly 3.2 times smaller for the 60°C, pH 3, 0.1 M Cl⁻ condition.

There is a transition to $p$-type semiconductor at higher potentials (cation lattice vacancies dominate). An increase in current density accompanies the transition. These observations are explained as the result of cation vacancy formation through oxidative ejection of cations as described by the Point Defect Model.

A nonlinear least squares method to derive PDM parameters by optimizing the PDM on experimental data has been developed. This tool can also calculate impedance spectra and evaluate the behavior of the model from parameters sets developed by other means such as phase space analysis. Phase space analysis is shown to estimate PDM parameters that accurately predict the impedance, current density, and film thickness of passive Alloy 22.

To further investigate the behavior of the system using the PDM, the contributions to passive current density by cation intersitials and oxygen vacancies were separated. It was found that cation intersitials dominate the passive current density by about 10 to 1 over oxygen vacancies.

The nonlinear curve fit program will generate multiple parameter solution sets in which reaction rate constant may vary by many orders of magnitude while still providing a good match between calculated and measured impedance. Holding all other parameters
constant, the rate constants, $k_i^{00}$, can be varied over at least four orders of magnitude without affecting the calculated impedance so long as the relative magnitudes of the $k_i^{00}$'s remains the same. The measured impedance cannot be matched if the relative order of magnitude between $k_2^{00}$ and $k_3^{00}$ is changed. This invalidates the curve fitting method, but shows that the PDM is fundamentally correct; in order for the passive film to reach a steady state thickness and not increase or decrease without bound, the relationship between $k_2^{00}$ and $k_3^{00}$ must be balanced.

The Point Defect Model in its present state of development successfully accounts for observed behavior with few discrepancies. The PDM also provides insight into observed behavior that cannot be obtained by other methods. Numerical modeling using the PDM requires development of a constrained curve fitting method.

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Subtask 2: Scientific Investigation Plan: Corrosion under Dust Deposits Containing Hygroscopic Salts

2.1 Introduction

The waste package (WP) Materials Performance Peer Review Panel has identified three conditions under which the surfaces of Alloy-22 may be subject to corrosion at Yucca Mountain:

1) Accumulated dust and particulate on the metal,
2) deposits and scale on the metal, and
3) tight areas of contact (crevices) between metals.

The development of a strong technical basis for materials performance under these conditions was recommended by the panel. Alloy-22, proposed for use as the high-level nuclear waste package (WP) container material at YM, may experience corrosion under a hygroscopic dust deposit due to absorption of moisture from air, moisture diffusion through defects and porosity in the deposits, formation of a solution layer under the deposits, and dissolution of salts in the deposits. Hydration of chloride-containing deposits, including calcium chloride, produces entrapped solutions of reduced pH, which causes crevice type corrosion in many stainless alloys. The diffusion of O\textsubscript{2} into the entrapped solution from ambient air through the mouth at deposit fissures and/or through the porous deposit is expected to accelerate the corrosion by providing local oxygen concentration cells. The transport of O\textsubscript{2} and the hydration of chloride-containing deposits both favor the localized crevice corrosion of Alloy-22. This crevice type corrosion may result in failure of the WP containers much earlier than their projected lifetimes.
2.2 Experimental:

2.2.1 Material:

Alloy 22 which heat treated at 800°C for 100 hrs was used with a surface finish obtained by 0.3µm Al₂O₃ powder.

2.2.2 Test solutions:

The chemical composition of the solution used are shown in the Table 2.1.

Table 2.1 Chemical composition of solution used for the drip testing

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<th>New Solution (5x Dilution of SCW in SIP 36)</th>
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<td>Mw (g/mol)</td>
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<td>18.0194</td>
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<td>5.41E-08</td>
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</table>
2.2.3 The drip test set up:

The sample Alloy 22 was used as a disk (Figure 2.1)

Figure 2.1 Alloy 22 before dripping test
The solution was made to drip on to this disk (about an inch height on the hot surface) with different dripping intervals ranging from 3, 5, 10, and 20 minutes for simulating the possible time-delay dripping pattern in the YM tunnel. The total time tested was for 40 days. Alloy 22 was maintained at a temperature of 90°C and the salt solution drops were made to drip on to it intermittently at a predetermined rate. As soon as the drop touched the surface of Alloy 22, the temperature was found to be dropped slightly (about 2 to 3°C). The variation in these temperatures with respect to time with different dripping intervals are recorded and shown in Figure 2.2. Because of evaporation of water with time, the surface of Alloy 22 was found to become dry. Then the dripping was resumed. This process continued for 40 days.
Figure 2.2 Temperature variations during the dripping test with different dripping intervals
2.3 Results and Discussion:

Alloy 22 is shown along with salt deposit after the dripping test in Figures 2.3.
Figure 2.3 b

Figure 2.3  Alloy 22 - Salt deposits on the hot surface

a) at the beginning of the dripping test

b) at the end of the dripping test (top view)
Figure 2.4  Alloy 22 at the end of the dripping test (side views)
Schematic view of salt deposited on Alloy 22 at the end of dripping test is shown in Figure 2.5.

Figures 2.3-2.5 show the accumulation of the salt deposits on the hot surface of Alloy 22. A cavity was found to be formed under the dripping tube at the beginning of the test. As the dripping proceeded, the accumulated salts around the cavity disappeared. This could be attributed to the dripping force and evaporation. At the end of the test, a dome-like salt deposit was found to be formed on the metal surface (See schematic in Figure 2.5). It is fair to assume that during the dripping test with drip-wet-dry-drip cycles, the environment inside of the dome-like deposit consisted a cyclic humidity variation. At the same time, in regions other than this dome-like structure, the interface between salt deposit and Alloy 22, crevices were found to be formed. This is because of the formation...
of a mechanical contact between salt deposit and Alloy 22. The morphology of the corrosion products formed in this test was similar to the one observed in a filiform corrosion that often found beneath a paint film.

The interface region between Alloy 22 and the salt deposit were found to be attacked by intergranular corrosion (Figures 2.6 and 2.7). It is interesting to note that no pitting attack was noticed on these samples.

Figure 2.6 Optical micrograph of Alloy 22 indicating intergranular corrosion by salt deposits
The surface of Alloy 22 was cleaned after the dripping test and observed for detailed examination. Figure 2.7 shows optical micrographs of different regions on the disk surface. As mentioned earlier, there was a central portion (dripping site) with cavity and rest of it with salt deposit mechanically bonded to Alloy 22 with crevices. There was an interface region between the two. Generally, the surface appearance was found to be mixed with dark colors (brown or brown on blue) at the dripping site as well as at the mechanically bonded salt deposit region. The interface between dripping site and mechanically bonded salt region, was found to be bright.

As shown in Figure 2.7 a and b, the dark areas is covered with worm-like or bead-like corrosion products (38 to 57% as measured by image analysis software). In contrast, the area of corrosion products on the bright area was relatively small (6%) (Figure 2.9 c). For comparison sake, micrograph of interface between dripping site and mechanically bonded salt region is shown in Figure 2.9d. It shows the relatively more attacked region at mechanically bonded salt region than dripping site.
(a) Area Fraction 38%

(b) Area Fraction 57%
d) Interface between dripping site and mechanically bonded salt region

Figure 2.7  corrosion products and the area fraction on the surface of Alloy 22

(Area fraction was calculated by the image processing software ImageJ ver. 1.37)
Discussion: In the current design of the potential Yucca Mountain repository US Department of Energy\textsuperscript{1} crevice corrosion could be initiated if accumulations of rock rubble cause drip shield buckling and contacting the waste package\textsuperscript{2}. Corrosion on a surface of an alloy will be more localized in the presence of crevices than flat surfaces. This is because the concentration of corrosion species will increase with respect to time. Further, because of lack of accessibility, these areas under crevices will be depleted of oxygen. These differential aeration conditions under aqueous environment will result in dissolution in a lower oxygen region of the alloy leading to localized attack.

Apart from accessibility of oxygen, the effect of corrosive species present in the environment and chemical inhomogeneity in Alloy22 are also to be considered. In view of considerable amounts of chloride ions in the test solution, one can expect the concentration of these ions decreasing pH. These factors aided by relatively high temperatures in the range of 88-90 °C, may affect the passive behavior of Alloy22.

Potential degradation processes causing the loss of persistence of passive film on Alloy 22 can be categorized into three areas: (1) enhanced dissolution by anodic sulfur segregation; (2) alteration of passive oxide film (e.g. chromium oxide); and (3) other degradation processes\textsuperscript{3}. The SEM X-ray mapping studies showed S concentration at the grain boundary which may enhance selective attack by anodic sulfur segregation\textsuperscript{3}.

Marcus\textsuperscript{4} postulated that sulfur enrichment at the interface of passive film and base alloy (i.e. metal–film interface) may cause passivity breakdown or alteration of passive current
density in nickel-based and related alloys. Numerous studies \(^5\text{-}^9\) show the detrimental effects of sulfur on persistence of passive film on nickel-based alloys, through relatively short-term (e.g. hours to days) laboratory tests, by accelerating corrosion processes.

Additionally, the induction time for passive film break-down by anodic sulfur segregation could be very long, compared with laboratory test times. Assuming that the sulfur content in Alloy 22 is 5 parts per million (ppm) by weight and the passive current density is \(1 \text{nA/cm}^2 \ (= 10^{-8} \text{cm/year} \approx 3.9 \times 10^{-7} \text{inch/year})\), Marcus \(^10\) estimated the induction time of about 900 years for passivity breakdown, if 100% of the sulfur atoms are retained at the metal-film interface.

\textbf{2.4 Conclusions:}

In order to create hygroscopic dust deposit on Alloy 22, dripping solution method was adopted. After the 40 day drip test, the specimen surface was assessed for corrosion attack, if any. Under hot and dry and wet conditions with a salt deposits creating crevice type of corrosion conditions, Alloy 22 did not exhibit any pitting attack.
2.5 References


Subtask 3: Heated Electrode Approach for the Study of Corrosion Under Aggressive Conditions

3.1 Introduction

Following three conditions under which the surfaces of Alloy-22 may be subject to corrosion at Yucca Mountain were identified:

1) Accumulated dust and particulate on the metal,
2) deposits and scale on the metal, and
3) tight areas of contact (crevices) between metals.

The ground water seeping through the faults of volcanic rocks could contain varying levels of anions such as chloride, nitrate, sulfate and bicarbonate and cations of sodium, potassium, calcium and magnesium. Since the nuclear decay process heats the waste packages, they are always hotter than the surrounding drift walls.

In view of heat generated, ground water with high ionic strength contacting the surface of the WP would evaporate and form concentrated brines. Continued evaporation would result in the formation of a dry-salt deposit on the surface of the WP (or drip shield). Evaporation of water increases the ionic strength and decreases the thickness of the aqueous layer of the brine solution (in contact with the WP or drip shield) with time.

Further, the waste package surface temperature is predicted to decrease from 160 °C to 55 °C in the high-temperature operating mode and from 85 °C to 50 °C in the low-
temperature mode during the regulatory lifetime of the repository\textsuperscript{2}. Temperature is one of the critical environmental parameters in corrosion studies because

1. it affects physicochemical and electrochemical reaction rates and

2. it affects passive film stability and solubility and

3. decreases pitting and crevice corrosion resistance

Therefore, changes in humidity or the dripping of ground water with high ionic strength onto the waste package surface may induce repeatable wet-dry conditions that occur with fluctuating temperature.

While corrosion studies being carried out on Alloy-22 and Ti-Grade 7 (drip shield material) pertain to aqueous conditions, there isn't a significant amount of work addressing wet-dry environments in detail. Increased corrosion rates and stress corrosion crack growth rates of low alloy steels have been reported in alternate exposure to wet and dry environments as compared to that in continuous exposure to aqueous environments\textsuperscript{3}.

The passive oxide of the low alloy steel was observed to lose its corrosion resistance due to de-hydration of the outer layer of the passive film during exposure to dry conditions\textsuperscript{4}. It is not known how the properties of the passive film of Alloy-22 and Ti-Grade 7 would change with a change in water content in the outer re-precipitated layer of the passive film.
Therefore, this subtask proposes to investigate the corrosion behavior of Alloy-22 during alternate wet-dry environmental conditions that simulate the repository evaporation-saturation events using a heated electrode approach.

### 3.2 Experimental details

A schematic of the electrochemical test set up is shown in Figure 3.1. An electrochemical cell was built on a support vessel. The heater and working electrode were insulated from the support vessel, and a PTFE holder with an O-ring exposed a limited surface area of the Alloy 22 working electrode to the test solution. The potentiostat was integrated with testing and analytical software on Windows XP (Gamry PC4/750). A programmable, proportional-integral-derivative (PID) temperature controller (Omega CN9300) was connected to the RS-232C port of the potentiostat computer and the temperature was remotely controlled. A J-type thermocouple was located 2 mm under the test surface, where the temperature is considered to be the same as that on reaction surface. The measured temperature was sent to the temperature controller as feedback for the PID control and was continuously recorded during the tests. The test material was mill annealed Alloy 22 with nominal composition (wt%) of 56Ni, max. 2.5Co, 22Cr, 13Mo, 3W, 3Fe, max. 0.08Si, max. 0.5Mn, max. 0.01C, and max. 0.35V. The surface was wet-polished up to 0.3 μm using Al₂O₃ particles, and was thoroughly cleaned with ethanol and distilled water. A surface area of 3.14 cm² was then exposed to the test solution.
The electrolytes, which simulate Yucca Mountain ground waters\(^2\) were prepared using analytical-grade chemicals: KCl, NaCl, Na\(_2\)SiO\(_3\) \(\cdot\) 9H\(_2\)O, Na\(_2\)SO\(_4\), Na\(_2\)NO\(_3\), MgCl\(_2\) \(\cdot\) 6H\(_2\)O, CaCl\(_2\) \(\cdot\) 2H\(_2\)O, and 18.2 M\(\Omega\)/cm deionized water. The molarities of anion and cation were 0.3558Na\(^+\), 0.0002Si (aq.), 0.005Ca\(^{2+}\), 0.0174K\(^+\), 0.0082Mg\(^{2+}\), 0.1368Cl\(^-\), 0.0742NO\(_3^-\), and 0.0804SO\(_4^{2-}\). The solution alkalinity was about pH 9.8. In some tests, the pH values were adjusted with hydrochloric acid. The temperature of the solution was measured with a calibrated mercury thermometer at a position 3 cm above the reaction surface.

The electrochemical cell consisted of an Alloy 22 sample as the working electrode, a coiled platinum wire as the counter electrode, and a miniature silver/silver chloride reference electrode (Ag/AgCl, 3.5 M KCl, 205 mV vs. SHE at 25 °C) which was placed
in a 2 mm diameter PTFE tube with a fine porous fritted end. The distance between the porous tip and specimen surface was kept at about 2 mm; no salt bridge was used.

All of the electrochemical tests were performed under ambient air conditions, and were started after 1 h of immersion in order to attain a stable temperature. Cyclic polarization was conducted potentiodynamically with a potential scan rate of 10 mV/min, as recommended in ASTM-G 61-86 (Reapproved 1998). The potential scan started at −50 mV below the corrosion potential, and the reverse scan was started when the current density reached 1.6 mA/cm². The test was terminated when the anodic current fell below 0.2 μA. Additionally, in the potentiostatic test, the current decay transient observed upon application of a constant potential from the corrosion potential was investigated. Temperature triangle wave control was started when the current reached a quasi-steady state. After each test, the surface of the test specimen was examined under an optical microscope.

3.3 Results and Discussion

Figure 3.2 shows an oscillating result from the cyclic polarization test, which was carried out in the simulated Yucca Mountain ground water with a temperature that fluctuated between 78 °C and 94 °C. The upper and lower temperature points are marked on the figure.
The test was able to distinguish effects on current due to temperature variations within temperature ranges of approximately 10 °C or greater. The results show that passive current density at approximately 90 °C was 1–2 μA/cm², which is about twice that which was observed at approximately 80 °C. It is clear that temperature oscillation affected polarization behavior, and that the TOHET approach was able to overcome the difficulty of studying temperature effects over a narrow temperature range. Because temperature-oscillating heated electrode technique allows data to be taken on a single sample during a single test it is an improvement over existing methods. Temperature-oscillating heated electrode technique eliminates the test-to-test variability of existing methods, which
require multiple specimens and multiple tests to collect data at different temperatures. The variability witnessed by other researchers when using existing methods may be the result of imprecise control of temperature, electrolyte chemistry, and other test parameters, particularly inconsistency in surface finish which subsequently affects surface reaction rates. The advantage of the temperature oscillating method is to be able to continuously evaluate the temperature effect on the corrosion rate even over a narrow temperature range, as little as 10 °C.

Moreover, cyclic polarization tests were conducted with different temperature oscillation amplitudes. The resulting polarization curves are shown in Figure 3.3

Figure 3.3 Polarization curves with different temperature variation mode.
In the case of the polarization test with a ±2 °C temperature amplitude, a small oscillation is seen in the current. However, a smooth polarization curve (i.e., without current oscillation) was obtained when the temperature oscillation was within ±0.5 °C. The passive current density in the pH 1.5 solution was about 1.75 μA/cm², which is higher than in pH 2.8 and pH 5.3 solutions at 80 °C. It was noticed that the passive current density in the pH 9.8 solution at about 90 °C was almost as same as in the 80 °C pH 1.5 solution. This implies that a 10 °C higher temperature has an influence on the rising passive current, which is almost the same as lowering the pH value to pH 1.5. Hayes et al. found that chromium plays a strong role in maintaining the passivity of the alloy, while molybdenum acts to stabilize the passive film after a localized breakdown event. Sunil et al. showed that the aging of a passive film was different in HECT in comparison to a conventional heated solution test. Accordingly, it might be possible that the stability and solubility of Cr-rich passive film was changed when the sample surface temperature was increased from 80 °C to 90 °C. The temperature-oscillating heated electrode technique was able to observe changes in the properties of the passive film when exposed to heat.

According to the results described above, the heated electrode method combined with temperature oscillation is suitable for accurate and continuous controlling of sample surface temperatures. Temperature-oscillating heated electrode technique provides an accurate method of studying corrosion properties that correspond to continuous temperature fluctuations.
The effect of temperature fluctuation on corrosion potential was investigated in the same pH 9.8 solution and the results are shown in Figure 3.4.

Figure 3.4 The effect of temperature oscillation on corrosion potential.

As shown in the small inside figure, corrosion potential was continuously recorded during the test in which the temperature oscillated over a range of about 30 °C. The temperature oscillation range was supposed to be as close as possible to the boiling temperature of the solution. As shown in Figure 3.4, under an oscillating temperature profile, corrosion potential becomes more negative with an increase in temperature and
more positive with decrease in temperature, and displays an increasing trend superimposed upon the oscillation. Corrosion potential increased from −293 mV to −256 mV when temperature decreased from 102 °C to 72 °C. It shows an obvious linear relationship. As described in experimental setting up, the recorded temperatures were hot surface temperatures. The thermometer indication of solution temperature was 53 ± 2 °C during the test with an approximate 30 °C oscillation in surface temperature. This implies that the temperature of the reference electrode Ag/AgCl element was not significantly changed while the Alloy 22 surface temperature was oscillating. Therefore, over the temperature ranges studied here, the effect of temperature on the reference electrode potential is considered to be negligible.

Furthermore, a potentiostatic test was carried out at +150 mV vs. Ag/AgCl with temperatures ranging between 65 °C and 95 °C in the same pH 9.8 solution with temperature-oscillating heated electrode technique. The programmed temperature oscillation and the current density transients during the test are shown in Figure 3.5.
Figure 3.5  The effect of temperature oscillation on passive current at 150 mV vs.
Ag/AgCl

Current decay started from 200 μA/cm² after applying +150 mV potentiostatically from the corrosion potential of ~253 mV. Temperature was cyclically controlled between 65 °C and 95 °C at a rate of 0.5 °C/min, and the sample was cooled down after three cycles. Alloy 22 is susceptible to crevice corrosion under O-rings under certain conditions during potentiostatic polarization. It should be noted that precautions for minimizing the risk of crevice corrosion, such as the use of electroplating stop-off lacquer under O-rings or other similar mounting techniques, should be taken. Repassivating metastable pitting observed in the work presented here was evidenced by the small
current spikes as seen in Figure 3.5. The presence of inhibiting oxyanions in the electrolyte may have facilitated the repassivation of crevice corrosion. The data of the three cycles in Figure 3.5 are shown as the relationship between current density and temperature in Figure 3.6.

Figure 3.6 The relationship between passive current density and temperature.

The arrows in the figure show the direction of the current and temperature cycles, and current decay features at 65 °C and at 95 °C. It is clear that current density is logarithmically proportional to temperature. In addition, current decay occurred
simultaneously with the current fluctuation. Current decayed at nearly the same rate at both the minimum temperature of 65 °C and the maximum temperature of 95 °C.

Summarizing the results of above electrochemical tests, it was found that temperature oscillation influenced polarization behavior, had a linear relationship with corrosion potential, and was proportional to logarithmic passive current density. Figure 3.6 shows a relationship between current density and temperature, which can be expressed by Eq. (3.1)

\[ T = T_0 + k \log \frac{i}{i_0} \]  

(3.1)

in which \( i \) and \( i_0 \) are currents at temperatures \( T \) and \( T_0 \), respectively. \( k \) is the slope as shown in Figure 3.6. The average \( k \) of the three temperature cycles was about 38.4 in this test. In this way, the dependency of passive corrosion rate on temperature is assessable. Theoretical analysis of the observed behavior will be presented in subsequent communications.

Burstein and Moloney\(^8\) developed Cyclic Thermammetry for studying temperature effect on pitting, and described repassivation temperature. Temperature-oscillating heated electrode technique provides an additional unique approach for accurately and continuously studying temperature dependence of corrosion behavior. It is extremely efficient for assessing temperature fluctuation effects on the corrosion rates of CRMs, such as Alloy 22. Moreover, periodic wet-dry conditions include the process of thermal absorption and dissipation, and subsequent temperature variation. The test results by
applying temperature-oscillating heated electrode technique may be valuable for understanding the mechanism of corrosion under wet–dry conditions, such as the presumed environment in the Yucca Mountain nuclear waste repository.

3.4 Conclusions

Temperature fluctuation effects on cyclic polarization, corrosion potential, and passive current density of Alloy 22 under simulated Yucca Mountain waters open to ambient air were investigated using a newly developed temperature-oscillating heated electrode technique (TOHET).

Fluctuating cyclic polarization curves were obtained which show that current is sensitive to temperature variation when the temperature amplitude was greater than 2 °C.

Corrosion potential and logarithmic-scale passive current density were found to be linearly proportional to temperature. Accordingly, combining typical electrochemical tests with the application of temperature-oscillating heated electrode technique provides a method to assess the temperature effect on corrosion rates within a temperature range as small as 10 °C.

In addition, temperature-oscillating heated electrode technique is expected to be a useful approach for studying the effects of temperature variation on corrosion behavior of passive alloys under cyclic wet/dry conditions.
3.5 References:


Subtask 4: Effect of Hydrogen Permeation on the Stability of the Passive Film of Alloy-22

4.1 Introduction

The Department of Energy has selected Yucca Mountain as the sole high level waste repository for the United States. Yucca Mountain was selected for its geographic location, chemical and geological properties. However, despite the geological barrier that the mountain provides, an engineered barrier is required for the waste deposited therein. The engineered barrier consists of a titanium drip-shield under which rest metallic packages loaded with high level nuclear waste.

The objective of the engineered barrier is to physically support the nuclear waste and to mechanically separate it from the environment. In the event that the drip shield is compromised (for instance through rock-falls), the waste package will be exposed to dripping water containing dissolved ionic solids, creating an excellent environment for corrosion. In addition, it has been suggested that deliquescent salts in Yucca Mountain dust can create similar corrosion environments by extracting water from the ambient atmosphere without the need of a liquid water source. However, the effectiveness of such deliquescent dust is disputed. The most likely failure-mode for such cyclic point-sources of corrosion is localized corrosion.
The alloy selected by the Department of Energy for this purpose is Alloy-22. In addition to corrosion resistance through chromium oxide, the Alloy 22 contains molybdenum which provides additional corrosion protection in reducing environments. The general corrosion rate of alloy-22 is very low. Over 10,000 years at 60°C, alloy-22 is expected to corrode only 6.08 mm in pH 6, 4M NaCl solution. Because the corrosion-resistant layer is 20 mm thick, the primary concern from a corrosion standpoint for alloy-22 is that of localized corrosion.

Evolution of hydrogen occurs during corrosion processes, which could result in ingress of hydrogen into the metal. Welding with coated electrodes, cathodic protection, acid pickling, and electroplating also could result in diffusion of hydrogen into metals. Hydrogen reducing bacteria is reported to be present in the YM repository site. At higher hydrogen fugacity, atomic hydrogen could diffuse into the Alloy-22 WP container wall. It is widely documented that ingestion of hydrogen could change the passive film properties of austenitic stainless steels and enhance susceptibility to pitting. Therefore, it is imperative to investigate the effect of hydrogen ingestion on the stability of passive film of Alloy-22. In this subtask pitting potentials of Alloy-22 will be evaluated under different hydrogen charged conditions in a chloride-containing environment.

It has been reported that the presence of hydrogen enhances the anodic dissolution of austenitic stainless steels and decreases the critical chloride content required for breakdown of the passive film. The diffusivity of hydrogen in passivated iron is reported to be around 12 orders less than that in the metallic iron. Both n-type passive film (on
iron) and p-type film (on nickel) were found to be affected by hydrogen in an chloride-containing environment. Most investigations studying the effect of hydrogen were carried out in strong hydrogen charged conditions, such that hydrogen transport occurred due to both a potential and a concentration gradient. Hydrogen generating bacteria present in the soil/ground water could cause ingress of hydrogen in the WP or drip shield. In this condition the hydrogen entry occurs mainly by the concentration gradient. However, the electronic structure of the passive film could be affected by the presence of hydrogen and the electric field within the passive film may be altered to facilitate further transport of the hydrogen. There has not been a significant amount of work done to understand the effect of hydrogen on the electronic structure and the degradation mechanism(s) of the passive film in the presence of hydrogen. Moreover a quantitative analysis of the effect of hydrogen on the degradation of passive films is required in order to estimate the life prediction of nuclear waste containers. As the pH inside the pits is usually low (acidic); there could be a correlation between pH of the electrolyte inside a growing pit and the critical concentration of hydrogen required inside the passive film to nucleate a pit in a neutral chloride environment.

Apart from localized corrosion, hydrogen is known to cause serious corrosion damage in the form of hydrogen induced cracking (HIC), hydrogen embrittlement, and under stress, hydrogen stress cracking. In the case of HIC, atomic hydrogen diffuses into the material until it reaches an impurity or void where it forms diatomic hydrogen gas. The gas builds in pressure until it deforms the material in response to the buildup in pressure, resulting in
an internal crack in the metal. This effect is seen in steels, especially in the petroleum industry.

4.2 Experimental

4.2.1 Apparatus

Standard ASTM G 149-97 [32] was chosen as the initial template for the hydrogen permeation experimentation. A custom Devanathan-Stachurski cell was fabricated with the expert assistance of William Cobb (UNR, Berkley). The design was improved over previous attempts in several ways (Figure 4.1).

![Devanathan Cell](image-url)

Figure 4.1: Drawing of a modified Devanathan Cell
The specific improvements over previous designs are threefold. First, electrolyte temperature is carefully moderated in this cell, with a water-jacket of constantly circulating, temperature-controlled water. Because diffusion and reaction rates are highly dependant on temperature, the data collected are more precise. Secondly, the luggin probes have been modified to prevent contamination of the reference electrodes by the test solution while keeping the potassium chloride in the bulb of the luggin probe from contaminating the solution in the "bridge" portion of the devanathan cell. A fiberglass thread is fitted through the stopcock to provide an ion-channel from the stem to the bulb. Test solution was injected into the luggin capillary with the stopcock open, up to the stopcock level. The stopcock was then closed, and the bulb portion was filled with saturated potassium chloride solution. A standard calomel electrode (SCE) sits in the bulb portion of each luggin probe. Hydrogen gas generation is discouraged through the use of Arsenic Trioxide (As2O3).

4.2.2 Materials

Foil samples of UNS N06022 ASTM B 575 Annealed, Non-Welded alloy-22 (Table 4.1) were obtained from the department of energy. They have a nominal thickness of 0.002" (55 µm) and possess equiaxed grains of size less than 5 µm. Samples were from heat # 2277-4-31459.
Table 4.1: Chemical Analysis of foil samples

<table>
<thead>
<tr>
<th>Element</th>
<th>wt %</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>0.018-0.017</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Chromium</td>
<td>21.78</td>
<td>20</td>
<td>22.5</td>
</tr>
<tr>
<td>Iron</td>
<td>4.05</td>
<td>2</td>
<td>6</td>
</tr>
<tr>
<td>Manganese</td>
<td>0.33</td>
<td>-</td>
<td>0.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>13.26</td>
<td>12.5</td>
<td>14.5</td>
</tr>
<tr>
<td>Nickel</td>
<td>Remainder</td>
<td>Remainder</td>
<td>Remainder</td>
</tr>
<tr>
<td>Phosphorous</td>
<td>0.008</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.02</td>
<td>-</td>
<td>0.08</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.002</td>
<td>-</td>
<td>0.02</td>
</tr>
<tr>
<td>Tungsten</td>
<td>3.05</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td>Vanadium</td>
<td>0.16</td>
<td>-</td>
<td>0.35</td>
</tr>
</tbody>
</table>

Chemicals used are cataloged and subject to the Department of Energy Quality Assurance Program.

NaOH

NaCl

4.2.3 Procedure

4.2.3.1 Sample Preparation

Due to the dimension of the samples (55 μm), grinding and polishing may not take place without destruction of the sample. Instead, the sample is ultrasonically cleaned in methanol for at least 30 minutes and then rinsed in de-ionized water just prior to insertion in the test apparatus.
4.2.3.2 Solution Preparation

Solutions were prepared in class-A volumetric flasks. All weights of dry salts were taken on an analytical balance. Three solutions were required for the experiments:

- 0.1M NaOH solution
- 0.1M NaOH + 0.1M NaCl solution
- Saturated KCl (for luggin probe and reference electrode storage)

4.2.3.3 Potentiodynamic Scans

The sample is allowed to go to open circuit potential, and then anodically scanned into the transpassive region to observe the critical pitting potential. These scans generally were performed from -300 mV to around +1V.

4.2.3.4 Hydrogen Permeation

-1mA/cm2 current density is galvanostatically controlled on the charging surface of the alloy-22 sample to generate hydrogen. At the same time, oxygen will form on the platinum counter electrode. The opposite, oxidation side of the sample is maintained potentiostatically at a potential in the passive region (+400 mV vs. SCE) while the current is measured.

In early experiments, Hydrogen permeation was periodically interrupted to procure EIS samples.

4.2.3.5 Electrochemical Impedance Spectroscopy

The oxidation side of the sample is perturbed with 10 mV amplitude over a frequency spectrum from 0.1Hz to 1.0 Mhz. Upon completion of an EIS measurement, the
potentiostatic and galvanostatic control is replaced and the experiment continues normally.

4.2.3.6 Conditions

All tests were carried out at 60°C. The nominal pH of all solutions was about 12.5. Sample thickness was 0.02" (53 μm).

005 – 0.1M NaOH
006 – 0.1M NaOH, repeated for comparison with 005
007 – 0.1M Cl, 0.1M NaOH
008 – 0.1M NaOH - critical pitting potential test
009 – 0.1M Cl, 0.1M NaOH – critical pitting potential test

4.3 Results and discussion

4.3.1 Hydrogen Transients

005 – 0.1M NaOH
Figure 4.2: Current density timeline for hydrogen permeation of alloy-22. Numbers indicate collection of impedance spectra.

006 – 0.1M NaOH

Figure 4.3 Current density timeline for hydrogen permeation of alloy-22. Numbers indicate collection of impedance spectra.
007 – 0.1M Cl, 0.1M NaOH

Figure 4.4 Current density timeline for hydrogen permeation of alloy-22 in 60°C 0.1 M NaOH solution. Numbered spikes indicate collection of impedance data.
Critical Pitting Potential Investigation by Potentiodynamic Scan

Figure 4.5 Alloy-22 anodic polarization curves showing transpassive initiation potentials in pH 12.5, 0.1M NaOH solutions (A) No hydrogen permeation at 60°C (B) With hydrogen permeation at 60°C (C) With hydrogen permeation at 40°C
Critical Pitting Potential was unaffected by the addition of hydrogen, and Chloride. A linear fit of the transpassive slope yields 104.5 mV/decade for cases without chloride and 93.12 mV/decade for cases with 0.1M Chloride. This indicates a slight increase in the derivative of corrosion rate with respect to voltage in the transpassive region when chloride is present.
4.3.2 Hydrogen bubble measurements

Figure 4.7 Galvanostatic voltage reacting to reduction in active surface area due to a growing bubble of hydrogen on alloy-22 sample surface.

4.3.3 Microscopy

Deposition of a dark black arsenic compound was observed on the charging face of all samples. The deposition appeared more heavily when the luggin capillary was surrounded by a large hydrogen bubble.

EDX indicates the bright-colored compound is 55% Arsenic and 25% Oxygen, while the darker base metal indicates some arsenic (11 atomic%) presence. (Figure 4.8)
Figure 4.8 Electron microscopy and EDX of the deposited arsenic compound on alloy-22

To the naked eye, the compound appears a dark black color, which is most likely “black arsenic”¹⁰. All other known Arsenic compounds include Se.

### 4.3.4 Passive Layer Thickness Calculations

The passive layer may be treated as the dielectric in a parallel plate capacitor for purposes of determining the thickness.

\[
C = \frac{1}{j\omega \varepsilon'} = \frac{1}{2\pi f \varepsilon'}
\]

\[
L = \frac{\varepsilon_0}{C}
\]

\[
\varepsilon = 8.85418782 \times 10^{-12} \frac{A^2 s^4}{m^3 kg} = 8.85418782 \times 10^{-14} \frac{F}{cm}
\]

Normalized thickness \( L_e = \frac{L}{\varepsilon} = \frac{\varepsilon_0}{C} = 2\pi f \varepsilon' \varepsilon_0 \)

\( L = L_e \varepsilon \)
From capacitance theory, the relationship between the distance between the conducting capacitor plates (in this case, metal and electrolyte), is mathematically coupled by the permittivity of free space times the dielectric constant of the dielectric in question.

The CRC handbook lists dielectric constant values of Cr2O3 single crystal at 25°C at 11 and 13, while others have chosen a dielectric constant between 20 and 30 as a better fit to the hydrated chrome-oxide passive layer. It can be shown that the thickness of the passive film is directly proportional to the imaginary impedance.

We can therefore compare film thicknesses between experiments, assuming the dielectric constant remains constant, without knowing the precise film thickness.

Taking the value of imaginary impedance at 3136.66 Hz, it can be seen that the film thickness in the absence of chloride, for all cases of hydrogen saturation is relatively constant. The frequency 3136.66 Hz was chosen because it is higher than 3 khz and was measured in every EIS spectrum for this work.

At high frequency (3 kHz and above), the impedance behavior is no longer dependant on diffusion processes, but the semiconductor nature of the film. Thus, the film thickness measurements described are independent on the saturation of hydrogen in the film. Treating every 3 khz data point in this manner, it can be shown graphically that there is no strong correlation between hydrogen presence and film thickness over the time scales examined.
Figure 4.9: Alloy-22 passive film thickness estimation from the parallel plate capacitor method.

In fact, the general trend is time dependant, indicating that the film actually grows over the course of the experiment.

4.3.5 Measurement of Hydrogen Reaction

Initially, the corrosion rate of alloy-22 with hydrogen present was expected to be measured during the experiment through EIS. However, it has become apparent that the change in the Nyquist plot is due to the measurement of a hydrogen reaction which does not interfere with the passive film in a measurable way.
ASTM diffusivity calculations

Fitting diffusivity observations to a model:

A proprietary model was provided by Frank Dean of Ion Science.

The ASTM standard g149-97 was found to have a difficult time in fitting to the measured data.

\[
\frac{J_l}{J_{l,\infty}} = 1 + \sum_{n=1}^{\infty} \left( \frac{c_2}{c_1} - 1 \right) \cdot \left( -D \cdot n^2 \cdot \pi^2 \cdot t \right) \cdot e^{-\frac{-D \cdot n^2 \cdot \pi^2 \cdot t}{l^2}}
\]

Figure 4.10: Standard Fick's laws flux function regression showing inability to converge.
4.4 Conclusions

4.4.1 Pitting Potential

For the conditions tested (pH 12.5, 60° C, 0.1M NaCl, -1mA/cm² hydrogen charging), the critical pitting potential is unaffected. This has important implications for long term nuclear waste storage in containers clad in Alloy-22. Localized corrosion, such as pitting is expected to be the corrosion failure mode for the waste package, and hydrogen does not appear to influence the possibility of localized corrosion.

The quantity of hydrogen in the experiments conducted far exceeds the expected hydrogen content of the waste packages in use.

Of special importance is the fact that these tests were carried out in basic conditions, which are more similar to the in-use conditions than other critical pitting work, which was carried out in acidic environments.
4.4.2 Hydrogen Permeation Kinetics

Estimates for the diffusivity of hydrogen in alloy-22 have been made based on the ASTM standard. However, the further investigation with either an established geometry or an advanced diffusion model considering the passive layer are required to extract a highly accurate value.

4.4.2.1 Electrochemical Impedance Spectroscopy

It has been shown that increases in Hydrogen content of the passive film result in reduction of the impedance spectra of the system. However, this does not indicate an increase in corrosion rate as previously thought. Instead, the reaction expressed in the spectra is attributed to hydrogen absorption, adsorption and redox processes. It should be noted, however, that the impedance for these reactions is quite high, indicating that alloy-22 and its passive film would make a decent barrier for hydrogen premeation to begin with. A patent filed in 1985 describes a plasma deposition and oxidation method where Cr, Al, Si, or NiCr may be deposited on an intermediate layer of Vanadium on the surface of a metal substrate with the hope of attenuating the susceptibility of hydrogen ingress[37]. This same effect may be seen in alloy-22 naturally, with the exception of Vanadium

4.4.3 Film thickness Measurements

Alloy-22 passive film normalized thickness has been verified to remain statistically constant, regardless of the content of hydrogen in the film. Therefore, hydrogen permeation is not a concern in regards to film thickness
4.5 References


9. ANAMET, F., Laboratory Certificate. 2001, FTI ANAMET: Hayward, CA. p. 4


4.6 Datasets

Data presented in this report have been submitted to the Nevada System of Higher Education Technical Data Archive and may be accessed in electronic format using the following information:

Subtask 1: 014MM.001, “Impedance of solution annealed and mill annealed Alloy 22.”

Subtask 3: 014MM.002, “Cyclic polarization test results.”

Subtask 4: 014MM.003, Current density and polarization curves for hydrogen permeation of alloy 22

END OF REPORT