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AC impedance studies of hot corrosion of Ni at 1200 K

Wu, Yiing-Mei, Ph.D.
The Ohio State University, 1990
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AC IMPEDANCE STUDIES OF HOT CORROSION OF NI AT 1200K

DISSERTATION

Presented in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in the Graduate School of
The Ohio State University

By
Yiing Mei Wu, B.S., M.S.

The Ohio State University
1990

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Approved by
Robert A. Rapp
Advisor
Department of Materials Science and Engineering
To my husband, Shang Jih.
ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

The degradation of metals or alloys at elevated temperatures by a thin fused salt in the presence of an oxidizing gas is called hot corrosion. Engineering systems affected by this form of corrosion include gas turbines, steam generators, incinerators, and petrochemical process vessels, among others. One of the earliest hot corrosion problems was found in the stainless steel superheater supports in a marine boiler (1). A white sodium sulfate deposit was observed covering the corroded components. Its origin was attributed to the contamination of the fuel by seawater. Hot corrosion attack was also found on aircraft engine blades and vanes during coastal service. These systems all involve the contact of metallic or ceramic materials with combustion product gases or other oxidizing gases containing inorganic impurities. As the gases are cooled, a fused salt film may deposit onto the equipment to yield a highly corrosive condition. One of the important constituents of the corrosive deposit is fused sodium sulfate which is formed from the oxidation of sulfur in the fuel with sodium salts arriving at the material surface via condensation or impaction (2).
Several mechanisms of hot corrosion have been proposed (3-18). The most widely discussed one is the salt fluxing model (10, 11, 16). To understand the concept of salt fluxing, the nature of acidic or basic dissolution of metal oxides in molten salts must be discussed. Acidic dissolution, e.g. NiO → Ni^{2+} + O^{2-}, will generate O^{2-} ions, while basic dissolution, e.g. 2NiO + 1/2O_{2} + O^{2-} ↔ 2NiO_{2}^{2-} will consume O^{2-} ions. Thus the solubility and the type of dissolution (acidic or basic) will depend strongly on the basicity of the molten salt solvent. For molten sodium sulfate, its basicity is controlled by the equilibrium Na_{2}SO_{4} ↔ Na_{2}O + SO_{3}. In the fluxing model, the oxide scales which are normally protective in gaseous oxidation are dissolved into the molten salt. When the dissolution of the scale is combined with a negative gradient in the oxide solubility caused by the basicity gradient in the salt film, the dissolved species migrate away from the corrosion site and reprecipitate. Thus, a porous and non-protective oxide is precipitated, and the compact adherent barrier oxide scale is destroyed. At this stage, contact between the metal and the salt film will produce oxides and sulfides. Formation of the latter locally depletes the melt of sulfur, and thus increases the melt basicity and oxide solubility. To understand the processes involved in hot corrosion, which must include oxidation of the metal and an electrochemical reduction of the oxidant, transport of reactants and products through the salt film, scale formation,
scale dissolution, and oxide precipitation, one needs to consider both the corrosion phenomena of metals and the chemistry/electrochemistry of the metal-salt system.

The usual experimental approaches employed in hot corrosion studies involve a metallographic investigation of the characteristic scale morphology, a thermogravimetric (TGA) determination of the corrosion kinetics, along with chemical analyses of the corrosion deposits and products, and perhaps electrochemical measurements in the "deep" salt melt. But since hot corrosion actually results from the attack by a thin film of fused salt, the deep melt experiments (19-28) fail to establish the relevant transport condition which is vital in understanding the hot corrosion mechanism. Furthermore, a considerable influence of the surrounding gas atmosphere must be taken into account. Recently, Otsuka and Rapp (18) used thin film potentiometric measurements to study the in-situ hot corrosion behavior of preoxidized Ni. Although the local corrosion chemistry (oxidizing potential and acid/base condition) at the corroding surface was obtained by using high temperature reference electrodes, polarization experiments to retrieve more kinetic or mechanistic information were not made.

In this work, a similar thin film arrangement was used. But a platinum counter electrode was added to the system to enable polarization measurements using the three-electrode configuration. The mechanism of hot corrosion was
investigated using the AC impedance technique whose small amplitudes and vast frequency range provide less disturbance to the system but extract more mechanistic information from the system than conventional scanning electrochemical methods. A computer program based on complex numbers has been used for data fitting and analysis. The equivalent circuits obtained in this way were then used to interpret the reaction mechanism.
Corrosion problems related to the attack of metals or alloys by molten salts have long been an important engineering concern. Most laboratory studies of this phenomenon have been carried out with molten sodium sulfate, which is important in high-temperature corrosion in the combustion product gases of low-quality fuels with impurities of sodium, sulfur, etc.

Pure sodium sulfate has a melting point of 884 °C, and hot corrosion attack at a high temperature above its melting point, e.g., 900 to 1000 °C, is named Type I (or high-temperature) hot corrosion. In this temperature regime, the molten sulfate at least has two effects according to previous studies: (i) it fluxes originally protective oxide scales and renders them non-protective, (ii) it serves as a source and/or a transport medium for species involved in hot corrosion.

Although the exact mechanisms of hot corrosion for various different sets of conditions are not fully understood, several models have been presented.

A. Mechanisms of Hot Corrosion

Simons, Browning and Liebhafsky (3) proposed a
sulfidation model to explain the accelerated attack of metals in aircraft gas turbines resulting from thin fused sodium sulfate films formed from the reaction of sulfur in the fuel with NaCl from seawater ingested with the combustion air. That model involved the oxidation of a metal-metal sulfide eutectic formed in a preceding step. Seybolt (4) compared the microstructure of Ni-Cr-X (X= Al, Ti, Mo and W) alloys reacted by sulfidation in H₂-H₂S mixtures, with those resulting from Na₂SO₄-induced hot corrosion, and concluded that the accelerated hot corrosion attack was attributed to the preferential oxidation of the matrix which was depleted in Cr after forming Cr₇S₈. Seybolt (4) also observed no temperature effect on the hot corrosion resistance of the alloys studied, regardless of the sulfide forming temperatures. Spengler and Visnsanathan (5) used a presulfidized Ni-Cr alloy containing principally chromium sulfides, or a mixture of chromium sulfides and nickel sulfides in the absence of Na₂SO₄ at 1600 F, to show that the penetration of the alloy by sulfur continued to occur in advance of the oxidation front. The total amount of sulfur was conserved in the sample during the oxidation reactions, lending support to the self-regenerative mechanism of sulfide propagation. At this time, sulfidation/oxidation was accepted as the explanation for accelerated corrosion.

One important postulate made in the sulfidation model is that the sulfide phase is highly reactive to oxygen. This was
criticized by Bornstein and DeCrescente (6) who found the rate of oxidation of a Ni-Ni$_3$S$_2$ coated B-1900 alloy was comparable to that of Ni and not that of Na$_2$SO$_4$-coated B-1900. The role of sulfur in hot corrosion was examined by two experiments. First, a specimen was presulfidized and subsequently oxidized. Then a specimen was coated with previously prepared Ni-Ni$_3$S$_2$ eutectic and then oxidized. These experiments showed that the oxidation rate was not enhanced by the pretreatments. Thus the authors suggested that hot corrosion cannot be attributed to the presence of sulfur, but rather to Na$_2$O originating from sodium compounds such as Na$_2$SO$_4$, NaNO$_3$, and Na$_2$CO$_3$ (7). Goebel and Pettit (8) also studied the oxidation behavior of a presulfidized Ni-Cr alloy. Although they found an increased oxidation rate in the presence of a liquid sulfide, the oxidation rate was not attributed to the high reactivity of the sulfide, but rather to the specific scale morphology whereby the liquid nickel sulfide created a rapid diffusion path through the protective Cr$_2$O$_3$ scale.

Bornstein and DeCrescente (6, 7, 9) first proposed that acceleration oxidation associated with Na$_2$SO$_4$, then termed sulfidation, was the result of an interaction between oxide ions in the melt and the substrate. A more detailed description of this model was given by Goebel and Pettit (10) for the Na$_2$SO$_4$-induced accelerated oxidation of nickel. The initial oxidation of bare Ni coated with a Na$_2$SO$_4$ film proceeds by the reaction:
Ni + 1/2 O₂ → NiO \[1\]

which lowers the oxygen activity at the oxide/salt interface. At sufficiently low oxygen activities the formation of nickel sulfide is thermodynamically favored. This sulfidation reaction removes sulfur from the melt and increases the oxide ion reactivity in the melt. Oxide ions react with NiO to form nickelate ions according to the following reaction:

NiO + O^{2-} → NiO_2^{2-} \[2\]

The nickelate ions diffuse out through the salt film toward the salt/gas interface, where a lower oxide ion concentration exists, and decompose to precipitate NiO particles. Thus an originally protective NiO is destroyed and converted to porous non-protective oxide particles in a salt film matrix.

Rapp (11) pointed out that these experiments, like those of Bornstein and DeCrescente (6, 7, 9), were conducted in pure O₂ or in air, which cannot maintain the salt acidity. Therefore, the argument that the basic fluxing reaction of pure Ni in a fixed amount of salt is not self-sustaining is not valid, because in practice the sulfur can be supplied from the surrounding gas atmosphere which usually contains SO₂ and SO₃. In summation of their interpretation of basic fluxing, Goebel and Pettit (10) superimposed a schematic reaction path on a log pO₂ - log pSO₃ phase stability diagram for the Ni-Na-S-O system corresponding to the following reaction:

Na₂SO₄ + 4Ni ⇌ Na₂O + 3NiO + NiS \[3\]

which is still accepted today.
Goebel, Pettit and Goward (12) studied the hot corrosion behavior of Ni-base alloys which are marginal Al₂O₃ formers and found that they are also subject to basic fluxing since alumina can form a basic ionic solute according to the following reaction:

\[ \text{Al}_2\text{O}_3 + \text{O}^{2-} \rightarrow 2\text{AlO}_2^- \]  \[\text{[4]}\]

An increase in oxide ion concentration at the oxide/salt interface dissolves the protective alumina scale and reprecipitation occurs near the salt/gas interface. However, reaction [4] is not so effective as the reaction of Cr₂O₃ to form CrO₄²⁻ in limiting the local increase in salt basicity for the hot corrosion of Ni-Cr-Al alloys. Therefore, while most oxidation-resistant alloys or coatings develop either a chromia or alumina protective scale, for hot corrosion resistance, a predominant chromia scale is preferred. For most oxidizing conditions, a minimum chromium content of 15-20% in a Ni-base alloy (2, 13) is required to form a protective chromia scale. If the chromium alloy content is too low compared to the aluminum content, then the production of oxide ions from Al₂S₃ formation contributes to the dissolution of the Cr₂O₃ scale.

Goebel, et al. (12) also demonstrated that Al₂O₃-forming Ni-base alloys can suffer a Na₂SO₄-induced catastrophic oxidation upon the hot corrosion of alloys containing the refractory metal components Mo, W, or V, usually as carbides. During the initial oxidation stage, NiO and oxides of these
elements are formed before the continuous layer of $\text{Al}_2\text{O}_3$ is completed. The formation of stable complex anions involving oxide ions ($\text{MoO}_4^{2-}$, $\text{WO}_4^{2-}$, or $\text{VO}_3^{-}$ ions, respectively) by the strong acidic oxides ($\text{MoO}_3$, $\text{WO}_3$ and $\text{V}_2\text{O}_5$) reduces the activity of sodium oxide so that acidic fluxing of NiO and $\text{Al}_2\text{O}_3$ can occur locally.

$$\text{NiO} \rightarrow \text{Ni}^{2+} + \text{O}^{2-} \quad [5]$$

$$\text{Al}_2\text{O}_3 \rightarrow 2\text{Al}^{3+} + 3\text{O}^{2-} \quad [6]$$

When $\text{MoO}_3$ or $\text{WO}_3$ vapor is evolved from the salt at the salt/gas interface, the local melt acidity is reduced and so is the $\text{Al}_2\text{O}_3$ solubility. The resulting precipitation of $\text{Al}_2\text{O}_3$ near the salt/gas interface maintains the negative solute concentration gradient in the salt film. Since $\text{MoO}_3$, $\text{V}_2\text{O}_5$, etc. are continually added to the $\text{Na}_2\text{SO}_4$ by oxidation at the alloy surface, this type of corrosion is self-sustaining.

Fryburg, Kohl, Stearns, and Fiedler (14) investigated the early stage of hot corrosion of two Mo-containing $\text{Al}_2\text{O}_3$-forming alloys and found that the initiation of hot corrosion was the basic fluxing of the protective oxide scale. However, upon the formation of a $\text{MoO}_3/\text{Na}_2\text{MoO}_4$ molten phase, the protective oxide scale was dissolved by an acidic fluxing during the catastrophic stage. Because $\text{Na}_2\text{SO}_4$ was nearly completely consumed by forming sulfides before acidic fluxing became dominate, $\text{MoO}_3$ was the major corrosive constituent which complexes the oxide ions in this process.
A similar experiment was conducted by Fryburg et al. (15) using IN-738, which forms Cr$_2$O$_3$-TiO$_2$ as a protective scale. Again, after an initial basic fluxing of the protective oxide scale, the catastrophic attack of the alloy resulted from an acidic oxide fluxing which occurred in the MoO$_3$-WO$_3$/Na$_2$MoO$_4$ molten phase, which was formed from a reaction between MoO$_3$ and Na$_2$CrO$_4$. From these experiments, the deleterious effect of Mo and W was satisfactorily explained qualitatively using the acidic scale fluxing model.

Rapp and Goto (16) pointed out the importance of electrochemistry in hot corrosion and developed the salt fluxing model into an electrochemical dissolution-reprecipitation model. They suggested that as a criterion for continued hot corrosion of a pure metal, the gradient in the solubility of the protective oxide (as a basic or acidic solute) in the salt film is negative at the oxide/salt interface:

$$\left(\frac{d \text{oxide solubility}}{dx}\right)_{x=0} < 0$$

Then, as illustrated in Fig. 1, the oxide scale would dissolve to its saturation concentration at the scale/salt interface. The solute ions would diffuse down a concentration gradient in the salt film and then reprecipitate as porous oxide particles where the oxide solubility is lower.

Since the oxide solubility depends strongly on the local basicity of the salt melt, the authors (16) examined the
conditions that would lead to oxide precipitation following either acidic or basic fluxing. In Fig. 2, a NiO solubility plot of Gupta and Rapp (50) is presented. Four different sets of basicities at the salt/gas interface II and at the oxide/salt interface I were superimposed on the solubility curve. Case A is observed in the basic fluxing model. The solubility at I is higher than that at II, thus a negative gradient is established across the salt film and sustained hot corrosion is expected. For case C, acidic dissolution of the oxide scale at I and reprecipitation at II should take place because interface I is more acidic than II. For the dual case B, sustained hot corrosion would be expected whenever the local basicities at interfaces I and II straddle the minimum.

Rapp and Goto (16) also considered the effect of electrochemical reactions in the overall reaction mechanism of hot corrosion, which is shown schematically in Fig. 3. The electrochemical reaction can be divided into two half-cell reactions. The reduction reaction should generally be expected to create a condition of locally high basicity, because reduction reactions generate oxide ions as reaction products. If the salt film contains only a low concentration of transition metal ions, then the reduction of the oxidant species dissolved in the salt film must occur at the oxide/salt interface, where electrons are supplied directly from the metal oxidation reaction (Fig. 3a). In Fig. 3b, the site for reduction of the oxidant species has been shifted to
Figure 1. Basic fluxing model. Reprecipitation of dissolved oxide to form a porous scale. (16)
Basic Dissolution

$$2\text{NiO} + \text{Na}_2\text{O} + \frac{1}{2}\text{O}_2 = 2\text{NaNiO}_2$$

$$P_{O_2} = 1\text{ atm.}$$

Figure 2. NiO solubility in fused Na$_2$SO$_4$ at 900 C. (16,50)
Figure 3. Local Cell Model. (a) Reduction of oxidant at oxide/salt interface. (b) Reduction site salt/gas interface due to presence of transition metal cations. (16)
the salt/gas interface because the electronic charge is carried through the salt either by the counterdiffusion of two differently charged transition metal ions, or as electronic conduction in the salt film resulting from electron hopping between the transition metal species. Clearly, in this case the reduction reaction would be accelerated since the need for oxidant diffusion through the salt film is avoided.

Shores (17) examined the Rapp-Goto precipitation criterion for the hot corrosion of pure Ni in detail and concluded that only basic dissolution, not acidic dissolution, of NiO can satisfy the "negative solubility gradient" criterion. The author emphasized the importance of the film thickness in the gas turbine environment. A thick salt film in a dilute SO$_3$ gaseous environment will shift to basic conditions at the substrate/salt interface as the reduction reaction occurs. But a very thin salt film, which is more likely in reality, could be dominated by an acidic atmosphere and hence could not allow basic dissolution to occur (17).

Recently, Otsuka and Rapp (18) used solid electrolyte probes attached to preoxidized nickel coupons coated with a thin film of Na$_2$SO$_4$ in an O$_2$/SO$_2$/SO$_3$ gas at 1173K. The trace of the average local chemistry for the salt film could then be followed as a function of time. As shown in Fig. 4, after 15 minutes of exposure, the salt film had penetrated the preformed oxide to permit Ni sulfidation. The sulfidation of the Ni substrate greatly increased the basicity of the film so
Figure 4. Trace of basicity and oxygen activity measured for a 99% Ni preoxidized at 900°C for 4 hr. in O₂ covered with a Na₂SO₄ film at 900°C in 0.1%SO₂-O₂ gas. (18)
that the salt basicity shifted from acidic NiO dissolution to the basic NiO dissolution, as indicated by the solubility minimum shown in Fig. 4. Thus, a nickel coupon which suffered rapid, sustained hot corrosion in the acidic gaseous environment actually was attacked by a basic salt to form a basic solute for NiO. In a different experiment, in which a preoxidized nickel coupon was exposed to a quite basic salt, rapid hot corrosion also resulted, although substrate sulfidation was not observed. Otsuka and Rapp (18) were also able to avoid hot corrosion by the formation of more protective initial NiO scales, and in that case, the local melt chemistry always remained to the acidic side of the solubility minimum of Fig. 4. These studies provided experimental evidence for the "negative solubility gradient" criterion, and introduced the possibility to perform "thin film" electrochemical studies.

B. Electrochemistry of Hot Corrosion

Because of the importance of the electrochemical approach in aqueous corrosion and the similarity between hot corrosion and atmospheric aqueous corrosion, the electrochemical aspects of hot corrosion have been recognized. The electrochemical techniques employed are usually the traditional methods, such as scanning polarization, cyclic voltammetry, and chronopotentiometry. Compared to these, AC impedance spectroscopy is a newer technique which has proved effective
in investigating reaction mechanisms and kinetics. Since successful application of AC impedance requires a knowledge of suitable models for the impedance behavior and a fitting of programs for the data analysis, only a very limited number of investigations of hot corrosion studies, mostly preliminary work, was found. For example, Farrell, et al. (19) have employed electrochemical noise and impedance techniques to monitor the corrosion behavior of Nimonic 75 in bulk sodium sulfate and sodium sulfate/1% sodium chloride at 900 C and at 750 C, where the salts are semi-solid. By comparing the impedance at a fixed low frequency (50 mHz.) which was deliberately defined as an estimated polarization impedance \( Z_p \), the authors concluded that the corrosion rate \( \approx 1/Z_p \) was higher in 900 C and with the addition of sodium chloride. The shape of the impedance diagrams also indicated diffusion-controlled reaction conditions, as shown in Fig. 5, which was resulted from the separation of the specimen from the gaseous environment by a deep melt. Gao et al. (20) have also used electrochemical impedance and electrochemical noise techniques to monitor the hot corrosion process of Ni-1% Co and Alloy 800 in molten Na\(_2\)SO\(_4\) and Na\(_2\)SO\(_4\)/10% NaCl. In addition to the deep melt test, they conducted a simulated combustion test, where a thin film of molten salt of 1 mm thickness covered the surface of a laminar probe consisting of two identical Alloy 800 electrodes, which were separated by a Mica insulator. In the deep melt experiments, the authors were able to detect the
propagation of hot corrosion from the difference between the impedance plot of a "clean" sample and that of a preoxidized one, whereby the former showed a small resistance value instead of a diffusional behavior. But no explanation concerning the reaction mechanism was given. In the simulated combustion test, they attributed the decrease of charge-transfer resistance to the breakdown of the preformed oxide scale, which indicated the commencement of rapid corrosion. From the shape of the impedance curve, as shown in Fig. 6, the authors declared a mixed charge transfer and diffusion behavior as the oxide scale thickened, although the nature of the diffusion species and the detailed mechanism again were not discussed. Furthermore, both investigations (19, 20) just mentioned were conducted in air, where the salt acidity could not be maintained.

In the following sections, earlier studies concerning the electrochemistry of hot corrosion are introduced.

(1) Electrochemical Reduction Reaction

Shores and Fang (21) studied the transport of oxidant through thin films of molten Na₂SO₄ in O₂-SO₂-SO₃ environments. From the limiting cathodic current densities observed in polarization experiments, SO₃ (as S₂O₅²⁻ ions) was found to be the predominant oxidant species transported and reduced for nominally acidic salts, with only a small contribution by O₂ diffusion. Fang and Rapp (22) found that
Figure 5. Nyquist plot of N75 in Na₂SO₄ after 2h exposure (a) at 750°C. $R_e=19.8$ ohm-cm², $|Z_p|=10100$ ohm-cm². (b) at 900°C. $R_e=3.3$ ohm-cm², $|Z_p|=2090$ ohm-cm². (19)
Figure 6. Nyquist plot and Bode diagram for preoxidized probe in contact with 5g Na$_2$SO$_4$. (20)
the AC impedance of a Pt working electrode immersed in Na₂SO₄ showed a sharp change from a slow electron exchange reaction in pure O₂ to more rapid diffusion control as SO₃ was added to the system.

Fang and Rapp (22) also used cyclic voltammetry and chronopotentiometry measurements via a three-electrode arrangement under controlled SO₂-SO₃-O₂ gas mixtures to investigate the reduction reactions in pure Na₂SO₄. The following reaction sequence was proposed:

\[ \text{SO}_3^- + \text{SO}_4^{2-} \leftrightarrow \text{S}_2\text{O}_7^{2-} \quad \text{Chemical equilibrium} \quad [8] \]

\[ \text{S}_2\text{O}_7^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_3^- \quad \text{reduction step} \quad [9] \]

followed by the gain of a second electron:

\[ \text{SO}_3^- + e^- \rightarrow \text{SO}_2 + \text{O}_2^- \quad \text{EC reduction step} \quad [10] \]

In the cathodic polarization of nickel, Numata, Nishikata, and Haruyama (23) found that the limiting currents increased as the amount of pyrosulfate increased in a sulfate electrolyte. The authors also attributed the electrochemical reduction step in acidic sulfates to the reduction of SO₃ and ultimately SO₂.

Sequeira and Hocking (24) studied the electrochemical behavior of pure sodium sulfate and sodium sulfate/sodium chloride melts at 900°C. From the results of electrolysis of pure Na₂SO₄ at Pt electrodes, the limiting cathodic process was suggested to be the SO₃ reduction to S²⁻ and O²⁻:

\[ \text{SO}_3^- + 8e^- \leftrightarrow \text{S}^{2-} + 3\text{O}^{2-} \quad [11] \]

The SO₃ reduction to SO₂ was also shown to occur at more
anodic potentials;

$$\text{SO}_3 + 2e^- \rightarrow \text{SO}_2 + \text{O}_2^-$$ \[12\]

Since the above proposed reactions were deduced from the correlation of decomposition voltage and standard Gibbs energy of reaction, they can only be treated, at best, as overall reactions. Several intermediate reaction steps were undoubtedly involved in Eq. [11] to account for the transfer of eight electrons.

In the absence of SO$_3$, and upon addition of 5 mol% Na$_2$O$_2$ into Na$_3$SO$_4$ to stabilize a very basic melt, Fang and Rapp (22) concluded that superoxide reduction was the dominant cathodic reaction:

$$\text{O}_2^{2-} + \text{O}_2 \rightarrow \text{2O}_2^-$$ Chemical equilibrium \[13\]

followed by a reduction reaction involving three of four electrons according to

$$\text{O}_2^- + 3\text{e}^- \rightarrow \text{2O}_2^-$$ EC reduction step \[14\]

or

$$2\text{O}_2^- + 4\text{e}^- \rightarrow \text{2O}_2^- + \text{2O}_3^{2-}$$ EC reduction step \[15\]

Numata (25) studied the cathodic reduction reaction on a Pt and Fe working electrode (WE) at 973K in fused (Na,K,Li)$_3$SO$_4$ containing dissolved ferric sulfate. In the absence of Fe$_2$(SO$_4$)$_3$, SO$_3$ and O$_2$ were not cathodically reduced for the given experimental conditions (low temperature deep melts at relatively high oxidation potentials). However, for both Pt and Fe WE's, the anodic (corrosion) reaction is controlled by the diffusion-limited cathodic reduction of
ferric ion, the rate of which was proportional to the ferric ion concentration. Thus, the ferric to ferrous reaction was the dominant reduction step. The corrosion mechanism illustrated in Fig. 7, which was called "autocatalytic" by the authors, is consistent with that of Fig. 3b.

(2) Polarization Studies

To estimate the hot corrosion resistance of Ni- and Co-base superalloys in Na₃SO₄ at 906°C, Shores (26) employed potentiokinetic anodic polarization relative to a Pt, O₂-ZrO₂ reference electrode (RE). An empirical correlation was established between values of log i_

_\text{corr} from the electrochemical test and penetration rates from the burner rig test. The author also observed that both basic (by adding Na₂O) and acidic (by bubbling SO₂/O₂ mixtures) melts produced considerably higher corrosion rates than were found in neutral (reagent-grade) salt.

Numata, et al. (23) studied anodic polarization, polarization resistance, and corrosion potentials for Ni and Ni-base alloys in a (Na,K,Li)₃SO₄ melt at 973K using a Ag-Ag⁺ RE. Metal dissolution occurred through a surface oxide to provide rapid anodic kinetics. The polarization resistance measurements correlated well with the measured corrosion rates. The authors also confirmed that chromium contents exceeding ~20% decrease the electrochemical corrosion rate of Ni-base alloys, but no correlation existed for high Mo
Figure 7. Schematic representation for corrosion reaction consisting of anodic dissolution of metal and cathodic reduction of ferric ion, whose concentration distribution is shown. (25)
Rahmel, Schmidt, and Schorr (27) investigated the influence of the electrode potential on the corrosion behavior of Ni- and Co-base alloys in (Na₂,Ca,Mg)SO₄ and (Na,K)₂SO₄ melts at 1073 and 1173K. Using a three-electrode arrangement under an air atmosphere, where the RE was the Ag,Ag⁺-mullite or supermax glass electrode, the authors found that anodic polarization resulted in extensive corrosion damage and a high corrosion current after a certain breakthrough potential was exceeded. Only acidic fluxing was observed in the (Na₂,Ca,Mg)SO₄ melt at positive potentials, but a protective scale rich in MgO was formed at negative potentials. This scale prevented basic fluxing because MgO is insoluble in neutral and basic melts.

A similar experiment was conducted by Wu, Rahmel and Schorr (28) for Ni-base superalloys in a (Na,K)₂SO₄ melt at 1173K in air using a Ag,Ag⁺-mullite RE. Acidic fluxing occurred above a critical potential leading to severe external and internal corrosion. Basic fluxing started below a second critical potential which again led to severe corrosion. Alloys with high chromium contents exhibited a potential range of stable protective scale formation, within which the melt at the specimen surface was neutral or nearly neutral. Alumina-forming alloys containing lower Cr contents did not form a protective scale at any potential.
In interpreting the applied potentials to the acidity of the melt, the above authors (27, 28, 29) made an assumption of constant oxygen pressure in the melt during polarization. Therefore the applied potential was assumed to be directly proportional to \( \log P_{\text{O}_2} \), i.e. the acidity. However, using Ag,Ag\(^+\)-mullite RE and ZrO\(_2\) oxygen RE, Park and Rapp (30) found that upon cathodically polarizing a porous coated Pt WE in 0.1%SO\(_2\)-O\(_2\) gas at 900°C, the oxygen pressure of the Na\(_2\)SO\(_4\) melt decreased significantly with a small increase in basicity, as shown in Fig. 8. Thus only by using both mullite and ZrO\(_2\) REs, can the basicity and oxygen pressure of the salt be unambiguously determined. The detailed interpretation of measured potentials with respect to both REs will be discussed in next chapter.
Figure 8. Trace of basicity and oxygen activity measured for porous Pt working electrode. (30)
CHAPTER III
PHASE STABILITY DIAGRAMS AND REFERENCE ELECTRODES

A. Phase Stability Diagrams

Oxyanion melts of alkali nitrates, carbonates, hydroxides and sulfates are known to exhibit an acid-base character whereby the acidic components can be taken as NO₂(g), CO₂(g), H₂O(g), or SO₃(g), respectively (31). Furthermore, for a pure Na₂SO₄ melt, the following equilibrium is established:

\[
\text{Na}_2\text{SO}_4 \leftrightarrow \text{Na}_2\text{O} + \text{SO}_3 \tag{16}
\]

where Na₂O is the basic component and SO₃ is the acid component. According to Eq. [17], a specification of \(-\log a_{\text{Na}_2\text{O}}\) (basicity) or \(\log P_{\text{SO}_3}\) (acidity) is redundant for pure Na₂SO₄. The equilibrium \(P_{\text{SO}_3}\) of a 0.1% SO₂-O₂ gas mixture at 1200K is calculated to be \(2.04\times10^{-4}\) atm. The basicity of a Na₂SO₄ melt in equilibrium with this gas mixture is calculated to be 13.1.

Figure 9 is a phase stability diagram of the Na-S-O system at 1200 K. At the phase coexistence boundaries, the condensed phase on either side are at unit activity. Thermodynamic data used for construction of this diagram are
Figure 9. Na-S-O phase stability diagram for 1200 K.
The superimposed diagonal lines in Fig. 9 are lines of constant sodium activity for Na$_2$SO$_4$ measured with respect to the Ag/Ag$^+$ reference electrode. As will be discussed later, the use of a second reference electrode allows the measurements of P$_{O_2}$ and basicity. The broad stability field of Na$_2$SO$_4$ in Fig. 9 has been divided into regimes denoting the dominant minority ionic species, based on the assumption of ideal solutions. In interpreting experiments, the consumption of unstable species and the formation of stable products for the local environmental conditions should be involved in the reaction mechanism.

Since the dissolution reactions of most oxides in an alkali sulfate melt involve oxide ions, superposition of the solubility data of oxides onto the phase stability diagram using $-\log a_{Na_{2}O}$ description is more appropriate. So, unlike the familiar stability diagrams used in high temperature corrosion studies which adopt log-log plots of P$_{SO_2}$ - P$_{O_2}$, or P$_{O_2}$ - P$_{O_3}$ as two coordinates, P$_{O_2}$ - $a_{Na_{2}O}$ was chosen in this study in analogy to the Pourbaix plots of aqueous corrosion.

A phase stability diagram of the Na-Ni-O-S system superimposed on the Na-S-O diagram is shown in Fig. 10 using the thermodynamic data listed in Table 1. Over the entire range of Na$_2$SO$_4$ stability, there is only a minor region where Ni is stable. The stable region of NiO lies within the Na$_2$SO$_4$ stable field, so in general Na$_2$SO$_4$ is incompatible or reactive.
Table 1. Thermodynamic data at 1200K

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G^\circ$ (kJ/mole)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{SO}_3(g)$</td>
<td>-260.584</td>
<td>32</td>
</tr>
<tr>
<td>$\text{SO}_2(g)$</td>
<td>-274.102</td>
<td>32</td>
</tr>
<tr>
<td>Na$_2$O($)</td>
<td>-249.215</td>
<td>32</td>
</tr>
<tr>
<td>Na$_2$O$_2$(s)</td>
<td>-252.540</td>
<td>32</td>
</tr>
<tr>
<td>Na$_2$SO$_4$(s)</td>
<td>-893.538</td>
<td>32</td>
</tr>
<tr>
<td>NaO$_2$(s)</td>
<td>-99.137</td>
<td>32</td>
</tr>
<tr>
<td>Na$_2$S($)</td>
<td>-275.864</td>
<td>32</td>
</tr>
<tr>
<td>Na$_2$SO$_3$(s)</td>
<td>-1120.234</td>
<td>33</td>
</tr>
<tr>
<td>Na$_2$SO$_4$(s)</td>
<td>-709.477</td>
<td>34</td>
</tr>
<tr>
<td>NiO($)</td>
<td>-132.072</td>
<td>35</td>
</tr>
<tr>
<td>NiSO$_4$(s)</td>
<td>-401.998</td>
<td>38</td>
</tr>
<tr>
<td>NiS($)</td>
<td>-52.547</td>
<td>32</td>
</tr>
<tr>
<td>Ni$_2$S$_2$(s)</td>
<td>-44.755</td>
<td>32</td>
</tr>
<tr>
<td>Ni$_3$S$_2$(s)</td>
<td>-161.493</td>
<td>32</td>
</tr>
<tr>
<td>Na$_2$NiO$_2$(s)</td>
<td>-374.342</td>
<td>37</td>
</tr>
<tr>
<td>Na$_2$NiO$_3$(s)</td>
<td>-299.742</td>
<td>37</td>
</tr>
<tr>
<td>Ag$_2$SO$_4$(l)</td>
<td>-334.242</td>
<td>38</td>
</tr>
</tbody>
</table>
Figure 10. Na-Ni-S-O phase stability diagram for 1200K.
with Ni. The dashed lines (-2, -4, -6) in Fig. 10 are calculated loci for the logarithm of the activities for the ionized solute species in fused Na$_2$SO$_4$.

B. Reference Electrodes

Two specific ion reference electrodes (REs) are required to obtain measures of both Na$_2$O activity and the oxidizing potential in molten sodium sulfate. One electrode is a Na$^{+}$-ion-conducting electrode and the other is an O$_2$-ion-conducting electrode.

The following cell constitutes the sodium activity sensor.

\[
\begin{array}{c}
\text{reference electrode} \quad \text{working electrode} \\
\text{(--) RE 1} \quad \text{WE (+)} \\
Ag(Pt), 10\% \text{Ag$_2$SO$_4$-Na$_2$SO}_4 \mid \text{fused-silica} \mid \text{Na$_2$SO$_4$, O}_2, \text{SO}_2, \text{Ni}
\end{array}
\]

The fused-silica membrane provides the exclusive transport of the impurity sodium ion at high temperatures (39). The preference of silica over the mullite membrane resulted from the work of Hwang and Rapp (40). The Ag/Ag$^{+}$/mullite RE was found to be degraded after use in an acidic Na$_2$SO$_4$ melt for an extended period of time; this resulted in a drift with time in the measured potentials. The degradation was caused by the penetration of silver, sulfur and sodium species into the mullite from the Ag$_2$SO$_4$-Na$_2$SO$_4$ reference melt. The Ag/Ag$^{+}$/fused-silica electrode provides better long term
stability along with additional simplicity of construction; therefore it was chosen for use in the following experiments.

The relation between the Gibbs energy change for reaction and an electromotive force (EMF) of the cell can be written as (30)

\[
E_T = \frac{1}{F}(\mu_{\text{RE}}(\text{RE} 1) - \mu_{\text{RE}}(\text{NB}))
\]

\[= E'_0 - \frac{RT}{2F} \ln \frac{a_{\text{Na}_2\text{SO}_4}(\text{RE} 1)}{a_{\text{Na}_2\text{SO}_4}(\text{NB})} \tag{18}
\]

where

\[
E'_0 = \frac{1}{2F} \left( \Delta G_{\text{Na}_2\text{SO}_4}^0 - \Delta G_{\text{Na}_2\text{O}}^0 - \Delta G_{\text{Ag}_2\text{SO}_4}^0 + RT \ln \frac{a_{\text{Na}_2\text{SO}_4}(\text{RE} 1)}{a_{\text{Na}_2\text{SO}_4}(\text{NB})} \right) \tag{19}
\]

the overall reaction is written as

\[
\text{Ag}_2\text{SO}_4(l) + \text{Na}_2\text{O} = \text{Na}_2\text{SO}_4(l) + 1/2\text{O}_2(g) + 2\text{Ag}(s) \tag{20}
\]

According to Shores and John (39), the Na$_2$SO$_4$-Ag$_2$SO$_4$ reference melt can be modeled by a regular solution with the activity coefficient of Na$_2$SO$_4$ in the RE given as

\[
\gamma = \exp \left( \frac{aN^2}{RT} \right) \tag{21}
\]

where \(a = -3441 \text{ cal/mole}\) and \(N\) is the molar fraction of Ag$_2$SO$_4$ in the RE. Thus, the electromotive force can be calculated from the basicity and oxygen pressure of the melt as follows:
This RE is made of a pure silver wire dipped into a 10m/o Ag$_2$SO$_4$-Na$_2$SO$_4$ solution contained in a one-end-closed fused-silica tube. The silver wire was spot-welded to a platinum lead wire and the silica tube was sealed with a high-temperature ceramic cement (Aremco Ceramabond 552).

The second specific ion reference electrode is a yttria-partially stabilized zirconia tube which conducts O$_{2}^{2-}$ ions. The use of the zirconia-Pt cell is unlike the procedure for room temperature aqueous systems where a common electrolyte solution exists between the RE and WE. Oxide ions carry the charge in the zirconia membrane while Na$^+$ ions carry the charge in the melt.

\[ E_1 = -1.427 - 0.119 \log \frac{a_{Na_2O}(WE)}{P_{O_2}^{1/2}(WE)} \]

The proposed overall cell reaction is given as (30)

\[ \text{Na}_2\text{O(ZrO}_2/\text{melt}) + \frac{1}{2}O_2(\text{WE}) = \text{Na}_2\text{O(WE)} + \frac{1}{2}O_2(\text{air}) \]

The Nernst equation for this reaction can be written as

\[ E_{II} = -\frac{RT}{2F} \ln \frac{P_{O_2}^{1/2}(\text{air})a_{Na_2O}(\text{WE})}{P_{O_2}^{1/2}(\text{WE})a_{Na_2O}(\text{ZrO}_2/\text{melt})} \]
If the distance between the WE and zirconia surface is small, i.e., if there is no difference in Na activity between the surface of the WE and the Na₂SO₄/ZrO₂ interface, Eq. [24] can be further reduced to

\[ E_{II} = 0.0403 + 0.0595 \log P_{O_2(WE)} \]  

[25]

This oxygen probe was made of a Y₂O₃-doped commercial one-end-closed zirconia tube (Zirconia Product 1372), the inside bottom of which was painted with Pt ink (Engelhard A-4338) and sintered for 48 hours at 1373 K in air. A Pt lead wire contacted this internal sintered Pt electrode and the tube was left open to air during the measurement. To eliminate any gradient in Na activity, the WE was attached directly to the zirconia tube in this experiment.

The basicity at the WE can be obtained by subtracting Eq. [25] from [22]

\[ E_{III} = E_I - E_{II} = -1.4673 - 0.119 \log a_{NaO(WE)} \]  

[26]
CHAPTER IV
AC IMPEDANCE TECHNIQUES

A. Introduction

Electrode reactions are heterogeneous chemical reactions, the rate of which can be measured as a current density upon applying Faraday's law. However, trying to understand why some reaction step in the process is slow and another is fast is not an easy task. Many different techniques have been developed for the measurement of kinetic parameters in the past decades. Among them, electrochemical impedance spectroscopy (EIS) seems to be the most valuable because of its ability, in a single experiment, to investigate reaction kinetics of vastly different nature at an interface for a wide range of relaxation times. With improving instrumentation, frequencies down to the $10^{-3} - 10^{-4}$ Hz range are now available, where relaxations involving adsorbed intermediates and diffusing species appear (41).

From an experimental point of view, EIS involves a relatively simple electrical measurement that can readily be automated. The most common and standard technique in EIS is to apply a single-frequency voltage to the interface and measure the phase shift and amplitude, or the real and...
imaginary parts, of the resulting current at that frequency. The advantages of this approach are the availability of the instruments and the ease of their use. But since the data can only be collected for one frequency at a time, experiments covering a wide range of frequencies, especially at low frequencies, can be very time-consuming. Thus, a second technique in EIS has been developed to apply a signal $V(t)$ composed of waveforms of varying frequencies to the interface and measure the resulting current as a function of time. This practice offers fast data collection and less disturbance to the system because only one signal is applied to the interface for a short time. But it also demands the generation of the complex waveforms and then the need to carry out a Fourier analysis of the response, which can be computationally difficult. Often a microcomputer is used for both purposes.

EIS is becoming a popular analytical tool in materials research and development because it can be used to investigate many complex materials properties: mass transport rates, chemical reaction kinetics, corrosion rates, and dielectric properties, as well as the influence of defects, microstructure, and composition on the conductance of solids. EIS is useful as an empirical quality control procedure; yet it can contribute to the interpretation of fundamental electrochemical and electronic processes. The disadvantages of EIS, however, are primarily associated with possible ambiguities in interpretation. Unless a theoretical model for
an EIS response is available, the most common method of data analysis is based on an equivalent electrical circuit where ordinary circuit elements are used to represent ideal electrochemical properties. Inevitably, most electrochemical cells are heterogeneous and distributed in space, and their microscopic properties may be also independently distributed. Under these conditions, simple circuit elements may be inadequate to describe the electrical response. Furthermore, a given equivalent circuit involving three or more circuit elements can often be described in different ways and still yield exactly the same electrical response. To overcome these difficulties, some basic understanding of the system and some physical intuition must be employed. Carrying out several EIS measurements for different conditions is also encouraged.

B. Physical and Electrochemical Models

A purely sinusoidal voltage can be expressed as

$$\Delta E = E \cdot \sin(\omega t)$$  \[27\]

where $\omega$ is the angular frequency. If the system is linear, the current response must also be sinusoidal:

$$\Delta I = I \cdot \sin(\omega t - \phi)$$  \[28\]

The relation between $\Delta I$ and $\Delta E$ is completely determined by $E/I=|Z|$ and the phase angle $\phi$. Thus the voltage is linked to the current through a vector $Z=|Z|\cos(\phi) - j|Z|\sin(\phi)$, called the impedance. $Z$ can also be defined as the quotient of the Laplace transforms of $\Delta E$ and $\Delta I$, with the imaginary Laplace
parameter \( j \omega \), \( j = (-1)^{1/2} \).

\[
\mathbf{z} = \frac{\mathbf{L}(\mathbf{E}(t))}{\mathbf{I}(\mathbf{A}(t))} - \frac{\Delta \mathbf{E}(j \omega)}{\Delta \mathbf{I}(j \omega)} = z' - jz''
\]

In a galvanic cell, the electric charge is transported by electrons in the electrodes and in the leads connecting the electrodes to the measuring circuit, but in a liquid electrolyte the current is carried by ions. The transition between the electronic to ionic charge transport necessarily takes place at the electrode-electrolyte interface. Two interfacial processes must be considered. First, the supply or removal of electrons generates a charge on the electrode side of the interface, which induces buildup of ions with opposite charge and a depletion of like-charged ions in the electrolyte at the interface. In this way, an electrical "Helmholtz" double layer is built up, closely resembling a capacitance. Second, electrons may be transferred across the interface by means of a faradaic process, i.e., the electrode may serve as the donor or acceptor of the electrons involved in the reduction or oxidation of a redox species.

As in an electrical circuit, the electrical response of a galvanic cell is determined by the way in which the current-conducting elements are interconnected. Therefore the equivalent circuit of the cell can be considered, as shown in Fig. 11. The resistances of the two electrodes and their respective leads are represented by \( R_1 \) and \( R_2 \). The electrolyte solution behaves as a resistance \( R_{\infty} \), which is a
function of the specific conductivity of the solution and the geometry of the cell. Usually the three resistances are taken together and represented by their sum \( R_n = R_1 + R_2 + R_{o1} \). The double layer charging and faradaic process are linked together as parallel components of a capacitance \( C_{a1} \) and impedance \( Z_f \).

To understand the impedance of an electrochemical cell, the following formulation is introduced. For a simple one-step electrode reaction

\[
\text{Red} \leftrightarrow \text{Ox} + n\text{e}^- \tag{30}
\]

Let us assume the rate is controlled solely by charge transfer and diffusional mass transfer. Any interaction between the electrode reaction and the double layer is ignored. Then the faradaic current can be expressed as

\[
i_F = nFk^0[C_m \exp\left(\frac{\alpha nF(E-E_0)}{RT}\right) - C_0 \exp\left(-\beta nF(E-E_0)\right)] \tag{31}
\]

where \( k^0 \) is the reaction rate constant, which is potential independent; \( \alpha \) is the transfer coefficient and \( \beta = 1 - \alpha \), and \( E-E_0 \) is the charge transfer overvoltage. \( F, R, \) and \( T \) have their usual meanings. The concentrations \( C_0 \) and \( C_m \) at the electrode surface are calculated by solving the equations describing the mass transport with the proper initial and boundary conditions. From Eq. [31], current \( i_F \) can be expressed as a function of \( E, C_m \) and \( C_0 \). Hence, when subjected to small voltage excitation,
\[ R_\Omega = R_1 + R_2 + R_{\text{sol}}. \]

(a)

(b)

Figure 11. (a) The total cell impedance. (b) The cell impedance in the case of a small electrode with a large counter electrode, DL, double layer impedance, F, faradaic impedance. (42)
from which $\Delta E$ can be solved:

$$\Delta E = \frac{1}{\Delta i_F} \left[ \left( \frac{\partial i_F}{\partial C_0} \right) \Delta C_0 + \left( \frac{\partial i_F}{\partial C_R} \right) \Delta C_R - \Delta i_F \right]$$

where all higher order terms have been neglected.

From the operational definition of the faradaic impedance following Eq. [29]

$$Z_F = \frac{1}{\Delta i_F} \left[ \left( \frac{\partial i_F}{\partial C_0} \right) \Delta C_0(j\omega) - \Delta i_F(j\omega) \right]$$

Combining Eq. [31] and [34],

$$Z_F = \frac{RT \left[ \exp((1-a)\Phi) + \frac{\Delta C_0(j\omega)}{\Delta i_F(j\omega)} - \frac{\Delta C_R(j\omega)}{\Delta i_F(j\omega)} \exp(\Phi) \right]}{nFk^0 nFk^0 aC_F\exp(\Phi) + (1-a)C_0^*}$$

where $C_R^*$ and $C_0^*$ are the mean concentrations imposed by d.c. polarization at the electrode surface. $\Phi = nF(E-E_0)/RT$.

Assuming semi-infinite linear diffusion with initial conditions $C_0(x,0)=C_0^*$ and $C_R(x,0)=C_R^*$, the solutions to the diffusion equations in the Laplace plane are:

$$C_x(0,s) = \frac{C_F^*}{s} - \frac{i_F(s)}{nF/D_k s}$$
\[ C_0(0, s) = \frac{C_0}{s} + \frac{i_p(s)}{nF/D_0 s} \]

where \( s \) is the Laplace plane variable.

Upon substituting Eq. [36a] and [36b] into Eq. [35], the faradaic impedance can be written as (42)

\[ Z_F = R_{ct} + (\sigma_0 + \sigma_R) \omega^{-1/2}(1-j) \]

where

\[ R_{ct} = \frac{RT}{n^2 F^2 k_0} \frac{\exp[(1-a)\phi]}{\alpha C'_k \exp(\phi) + (1-a)C'_0} \]

\[ \sigma_0 = \frac{RT}{n^2 F^2 \sqrt{2}} \frac{D_0^{-1/2}}{\alpha C'_k \exp(\phi) + (1-a)C'_0} \]

\[ \sigma_R = \frac{RT}{n^2 F^2 \sqrt{2}} \frac{D_R^{-1/2}}{\alpha C'_k \exp(\phi) + (1-a)C'_0} \]

With simple circuit elements representing the faradaic impedance, the equivalent circuit for this semi-infinite linear diffusion system is shown in Fig. 12, where \( R_{ct} \) is the charge transfer resistance and \((\sigma_0 + \sigma_R)\omega^{-1/2}(1-j)\) is the Warburg impedance.
From Eq. [37] to [39], a knowledge of the cell impedance should be useful in the study of electrode kinetics, provided that the measured impedances can be analyzed to yield the separate parameters $R_{ct}$ and $\sigma$. Since the faradaic impedance, the double layer capacitance, and the ohmic resistance combine in a rather complicated way, the properties of the total impedance can best be visualized in the so-called "complex plane," i.e., a plot of $Z''$ against $Z'$ as a function of some independent variables. Figure 13 shows such a plot, which is also called Nyquist plot. The total impedance $Z = Z' - jZ''$ represented in Fig. 13a can be expressed as

\[ Z' = R_0 + \frac{R_{ct} + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma \omega^{-1/2})^2} \]  \[ (40a) \]

\[ Z'' = \frac{\omega C_{dl} (R_{ct} + \sigma \omega^{-1/2})^2 + \sigma^2 C_{dl} + \sigma \omega^{-1/2}}{(\sigma \omega^{1/2} C_{dl} + 1)^2 + \omega^2 C_{dl}^2 (R_{ct} + \sigma \omega^{-1/2})^2} \]  \[ (40b) \]

where $\sigma = \sigma_m + \sigma_o$. Although these equations look complicated, some simplified cases are introduced to demonstrate the effect of frequency, $\sigma$ and $R_{ct}$. For example, at sufficiently high frequencies, provided that $\sigma \omega^{-1/2} C_{dl}$ is sufficiently small, and $R_{ct} >> \sigma \omega^{-1/2}$, Eq. [40a] and [40b] can be reduced, respectively, to

\[ Z' = R_0 + \frac{R_{ct}}{1 + \omega^2 C_{dl} R_{ct}^2} \]  \[ (41a) \]
After eliminating $a$, the components $Z'$ and $Z''$ have the following relation:

$$(Z' - R_o - R_{ct}/2)^2 + (Z'')^2 = R_{ct}^2/4$$

which is the equation of a circle with its center on the $Z'$ (real) axis at $Z' = R_o + R_{ct}/2$ and radius $R_{ct}/2$, as shown in Fig. 13b. Another extreme is when frequency is so low that the higher-order terms of $a^{1/2}$ and $a$ in Eq. [40] can be omitted, then

$$Z' = R_o + R_{ct} + a^{1/2}$$

$$Z'' = a^{1/2}$$

The complex plane plot for varying $w$ becomes a straight line with $45^\circ$ slope, which is shown in Fig. 13c.

Thus far, only semi-infinite boundary conditions have been considered in the diffusion impedance. For many problems, however, thin samples or unstirred electrolytes dictate the use of finite-length boundary conditions. Then using the same diffusion equation but with the new boundary condition

$$C(\delta, s) = C^*/s$$

the concentrations at the electrode surface are obtained as

$$C_0(0, s) = \frac{C_0^*}{s} + \frac{[\tanh(\delta\sqrt{D}/s)]}{\sqrt{D_0}} \frac{i_p(s)}{nF\sqrt{D_0}s}$$
Figure 12. Equivalent circuit for an electrochemical cell with semi-infinite linear diffusion.
Figure 13. Equivalent circuits and simulated data for (a) mixed- (b) charge transfer- (c) diffusion-controlled cell. $R_\alpha=10\ \Omega$, $R_{ct}=50\ \Omega$, $\sigma=1000\ \Omega/\text{s}^{1/2}$, $C_{dl}=20\ \mu\text{F}$. 
\[ C_x(0, s) = \frac{C_x^*}{s} - \left[ \tanh\left( \frac{\delta \sqrt{s}}{D_x} \right) \right] \frac{i_p(s)}{nF\sqrt{D_x s}} \]  

where \( \tanh(x) \) is the hyperbolic tangent function and \( \delta \) is the diffusion length.

Equation [31] can be rewritten as the following:

\[ i = i_0 \left[ \frac{C_x(0, t)}{C_x^*} \exp(\alpha \phi) - \frac{C_0(0, t)}{C_0^*} \exp(-\beta \phi) \right] \]  

where \( i_0 \) is the exchange current. For small overpotentials, a linearized form of Eq. [46] is employed (43):

\[ \frac{\Delta i}{i_0} = \frac{\Delta C_x}{C_x^*} - \frac{\Delta C_0}{C_0^*} + \frac{nF}{RT} \Delta \phi \]  

After applying Eq. [29] and [45], the total faradaic impedance for bounded diffusion can be expressed as

\[ Z = R_{ct} + Z_0 + Z_m \]  

with

\[ R_{ct} = \frac{RT}{nF i_0} \]  

\[ Z_0 = \frac{RT}{n^2 F^2} \]  

\[ D_0 C_0^* \]  

\[ \left\{ \begin{array}{l} \frac{j\omega \delta^2}{D_0} \\ \sqrt{\frac{j\omega \delta^2}{D_0}} \end{array} \right\} \]  

\[ \tanh\left( \frac{j\omega \delta^2}{D_0} \right) \]  

\[ \sqrt{\frac{j\omega \delta^2}{D_0}} \]
Since \( \tanh(x) \to 1 \) as \( x \to \infty \), at high frequencies or under semi-infinite diffusion conditions (\( \delta \to \infty \)), the transport impedance is given by the limits

\[
\lim_{\omega \to \infty} Z = \frac{RT}{n^2 F^2} \frac{\delta}{DC^*} \frac{1}{\sqrt{\frac{j \omega \delta^2}{D}}}
\]

corresponding to a normal Warburg impedance behavior with a 45° phase angle. The low frequency behavior of the transport impedance is given by

\[
\lim_{\omega \to 0} Z = \frac{RT}{n^2 F^2} \frac{\delta}{DC^*}
\]

which is a simple resistance. Figure 14 shows a typical complex plane plot for limited diffusion. Notice the high and low frequency limits which were described above.

The theory of impedance introduced in this section has focused on a fairly simple model of the electrode process (single electron transfer + diffusion and separate parallel double layer charging). More involved systems, such as multiple-step charge transfer (44), adsorption of reactants (44), and 3-D inhomogeneous electrode surface problems (45) are not discussed, but these have received treatment in the literature.
Figure 14. Complex plane plot for a limited-diffusion case. $R_n = 100$ ohm, $C_{dl} = 20$ $\mu$F, $Z = R \cdot \tanh(g \sqrt{T})/g \sqrt{T}$ where $R = 100$ ohm, $g = 0.283$ sec$^{-1/2}$. 
C. Measurement Methods and Data Analysis

Ideally, an electrochemical impedance measurement instrument should have the following advantages: (i) a wide range of excitation frequency to measure systems of diverse electrical parameters, (ii) high signal-to-noise ratios for the accurate measurement of low level responses which can result from low amplitude excitation, (iii) minimal data acquisition times to minimize the exposure of the test system to instrumental excitation, (iv) variable dc offset to enable investigations of a polarized electrode, (v) convenient parameter selection and simple, automatic operation.

Early experiments were done using an ac bridge circuit over a very limited frequency range. The most frequently used type was the Wien bridge, schematically represented in Fig. 15. The principle is classical (46): the unknown impedance is matched by a known one, constructed of a variable resistance and a variable capacitance of precision quality. The matching network may be either a series connection \( (R_s, C_s) \) or a parallel connection \( (R_p, C_p) \). Although these measurements were precise, they were extremely time-consuming and tedious. Data acquisition has been greatly enhanced by the use of direct measurements, i.e., the system is perturbed by a stabilized input (potentiostatic or galvanostatic) and the response is read on a phase-sensitive detector (lock-in amplifier).
Figure 15. Schematic for Wien bridge. $R_1, R_2$: ratio arm resistors; $C_m, R_m$: matching impedance. A: ac input; B: output to detector. Balance equation: $Z_u/Z_m = R_1/R_2$. (44)
Phase-sensitive detection may be accomplished by the sequential operation of multiplexing and time-averaging circuits (47). The perturbing signal $A = A_m \sin(\omega t)$ is used as a reference voltage which is multiplied by the response signal $B = B_m \sin(\omega t + \phi)$. The multiplexer output will be

$$e_{\text{out}} = A_m \sin(\omega t) \cdot B_m \sin(\omega t + \phi) - \frac{A_m B_m}{2} \left( \cos \phi - \cos(2\omega t + \phi) \right)$$  \[53\]

when $e_{\text{rms}}$ was applied to the time-average circuit, the result is

$$e_{\text{out}} = \frac{A_m B_m}{2} \cos \phi$$  \[54\]

This is obviously a phase-sensitive dc output voltage, which is maximum at $\phi = 0$.

However, bridge circuit and direct measurements still operate in the "frequency domain", e.g., data are taken and analyzed frequency-by-frequency. Since at least one full ac excitation cycle is required at each frequency, and at least several data points per decade of frequency are needed, excessively long data acquisition times are required for frequencies less than 0.01 Hz. When applied to unstable systems, such as actively corroding electrodes, these long measurement times are objectionable.

With the advent of digital computers and transfer function analysis instrumentation, an alternative approach of "time domain" techniques has become popular in recent years. From the definition given in Eq. [29], the impedance can be
calculated from the perturbation and response in the time domain, in which the excitation can be any arbitrary function of time (i.e., current step, current impulse, or potential step, etc.). But since the current-potential relation is relatively simple in the frequency domain, as compared with the corresponding relations in the time domain, several linear integral transforms are used to convert from the time domain into the frequency domain. The two most commonly used are the Laplace and Fourier transforms:

\[ F(s) = \int_0^\infty F(t) e^{-st} dt \]

where \( s \) is the Laplace frequency. Noting that \( s = j\omega \), Eq. [55] leads to

\[ F(j\omega) = \int_0^\infty F(t) e^{-j\omega t} dt \]

which is referred to as a single-sided Fourier transform.

As noted above, any arbitrary time domain excitation can be used to measure the system impedance provided that the excitation is applied and the response recorded over a sufficiently long time to complete the transforms over the desired frequency band. If a mixture of excitation waveforms of varying frequencies is applied to the test system simultaneously, the fast Fourier transform (FFT) technique must be employed. The principle of the FFT waveform is
illustrated in Fig. 16(a), which shows how three odd harmonics of a sine wave can be summed. Figure 16(b) shows an excitation waveform that contains twenty frequencies from 0.05 Hz. to 5 Hz. Once the complex excitation waveform has been applied to the system, an equally complex response is obtained. An inverse FFT operation is performed on this waveform to resolve it into discrete frequency data. In this way, low frequency data can be obtained faster than using conventional excitations; the polarization time is also minimized.

The next step in applying EIS to electrochemical studies is data analysis. Several methods will be introduced in the following section. Among them, equivalent circuit analysis is the most simple one. To illustrate this method, the electrochemical reactions are assumed to be of very simple nature, so that they can be represented by the equivalent circuit shown in Fig. 17(a). This circuit consists of the resistance, $R_n$, which includes the resistance of the electrolyte, surface films, circuit leads, etc. The polarization resistance, $R_p$, is in parallel with the double layer capacitance, C. The impedance $Z$ is given by:

$$Z = R_n + \frac{R_p}{\omega^2C^2R_p^2} - \frac{j\omega CR_p^2}{1 + \omega^2C^2R_p^2}$$

and the corresponding complex plane plot shown in Fig. 18(a) features a semicircle with a radius of $1/2R_p$, the center of
which lies on the \( Z' \)-axis at \( R_0 + 1/2R_p \). At the apex of the semicircle,

\[
\omega_{\text{max}} = \frac{1}{CR_p}
\]

It is possible, therefore, to obtain all three parameters (\( R_0 \), \( R_p \), and \( C \)) from a complex impedance plot as shown in Fig. 18(a) provided a sufficient frequency range is investigated.

Another method for evaluating the impedance data is the analysis of the frequency dependence of the absolute value \(|Z| = (Z' + Z''^2)^{1/2}\) and the phase angle \( \phi \), which is defined as

\[
\tan \phi = \frac{Z''}{Z'} = \frac{\omega CR_p^2}{R_0 + R_p + R_q(\omega CR_p)^2}
\]

From plot of \( \log|Z| \) and \( \phi \) as a function of \( \log(\omega) \), i.e., the Bode plot, the parameters of the circuit can be determined.

As an example, the data for the dummy cell in Fig. 17(a) are replotted in Fig. 18(b). From the horizontal segments of \(|Z|\), which are the high frequency and low frequency limits, the values of \( R_0 \) and \( R_p \) can be determined. For an intermediate frequency range, \(|Z|\) is inversely proportional to \( \omega \) and a straight line with a slope of \(-1\) is observed in a \( \log|Z| - \log(\omega) \) plot. From an extrapolation of this straight line to \( \omega = 1 \), the capacitance can be determined as \( C = 1/|Z| \). In the Bode-phase plot one can identify the maximum for the phase angle \( \phi_{\text{max}} \) and the corresponding frequency \( \omega_{\text{max}} \) where
with these equations, \( R_p, R_n, \) and \( C \) can be calculated for unknown systems.

For some electrode reactions, more than one reaction step might be involved and, consequently, more than one semi-circle will occur in the complex plane plots. Figure 17(b) shows the equivalent circuit for such a system. But if the rate of one reaction step is very different from that of the other, the occurrence of this reaction might not be detected in a complex plane plot, as shown in Fig. 19 which represents the data for the circuit in Fig. 17(b). With \( R_{p2} \gg R_{p1} \), only one semicircle can be observed in Fig. 19(a); the high frequency semicircle for the parallel combination of \( C_1=0.3 \mu F \) and \( R_{p1}=1000 \Omega \) can barely be seen in this plot. However, when the same data are plotted in a Bode plot (Fig. 19(b)), both circuit elements can be determined. The one maximum frequency in the lower frequency range is

\[
\omega_{\text{max},1} = \frac{1}{C_1 R_{p2}} \sqrt{1 + \frac{R_{p2}}{R_n + R_{p1}}}
\]

because when frequency is relatively low, the smaller
Figure 16. (a) Summation of three odd harmonics of a sine wave, (b) an FFT excitation waveform, from Princeton Applied Research Inc. operation manual.
Figure 17. Two equivalent circuits simulating simple electrochemical systems in ideal conditions. \( R_\Omega = 10 \ \Omega, \ R_p = R_{p1} = 1000 \ \Omega, \ R_{p2} = 1 \ \text{M}\Omega, \ C=C_1=0.3 \ \mu\text{F}, \ C_2=10 \ \mu\text{F}. \)
Figure 18. Simulated data for equivalent circuit shown in Fig. 17(a). (a) Nyquist plot, (b) Bode plot.
Figure 19. Simulated data for equivalent circuit shown in Fig. 17(b). (a) Nyquist plot, (b) Bode plot.
capacitance \( C_1 \) is inactive, the equivalent circuit in Fig. 17(b) can be reduced to one parallel \( C_2-R_p \) loop. The value for \( C_1 \) can be decided from the slope of the \( \log|Z| \) vs. \( \log(\omega) \) curve in the high frequency range.

Another useful method of analysis is called deconvolution. Its operating principle is very similar to that of equivalent circuit analysis, except that it is applied in the reverse sense. Instead of adding up circuit elements to simulate an impedance response, values of circuit elements are vectorially subtracted from the original data to make a complicated EIS easier to be analyzed. To explain this method, the EIS plot shown in Fig. 20 is used. The first step is to eliminate the contribution of \( R_o \) and \( C_1 \). The value of \( R_o \) can be determined from the high frequency intercept in the real axis in the complex plane plot. After subtracting \( R_o \), an admittance plot is used to determine the value of \( C_1 \), which is equal to the low frequency intercept of the semicircle at the imaginary axis \( Y''/\omega \), as shown in Fig. 21. Then \( R_1 \) and \( C_2 \) can be eliminated using the same procedure. The resulting impedance is a straight line with 45° slope shown in Fig. 20, clearly a Warburg behavior.

When the test system deviates from the simple behavior described by the equivalent circuit, applying the equivalent circuit analysis or the deconvolution method is not appropriate. Mansfeld (48) found that EIS for pure iron in aerated 1N \( H_2SO_4 \) and 1N HCl showed a depressed semicircle with
the center lying below the $Z'$-axis. A computer program called CIRFIT was developed (49) using the minimization method to fit the data.

According to Fig. 22, the sum of radial residual over $N$ data points ($Z_{1\prime}, Z_{1\prime\prime}$) can be calculated as

$$S = \sum_{i=1}^{N} (x_i^2 + y_i^2)$$

where

$$x_i = Z_{1\prime} - x_0 - R_0 \cos \theta_i$$  \hspace{1cm} [64a]

$$y_i = Z_{1\prime\prime} - y_0 - R_0 \sin \theta_i$$  \hspace{1cm} [64b]

$$\theta_i = \tan^{-1} \frac{Z_{1\prime\prime} - y_0}{Z_{1\prime} - x_0}$$  \hspace{1cm} [65]

Minimization of $S$ with respect to $x_0, y_0,$ and $R_0$ can produce a theoretical EIS from which the values of solution resistance and polarization resistance can be extracted.

This method is applicable when the low frequency data approach or intersect the real axis, i.e., the imaginary parts converge to zero. But in some cases, a diffusional step is involved in the mechanism so that the low frequency data have non-negligible imaginary components. Thus a theoretical semicircle, even depressed, cannot be established to obtain the value of polarization resistance. To overcome this
problem, some researchers (19, 20) designated rather arbitrarily a low frequency as the limiting frequency and used the impedance at that frequency as the polarization resistance. Although their purpose was to obtain a "relative" polarization resistance for comparison between the performance of different materials, from the coupled charge-transfer and diffusion behavior introduced in the last section, this practice bears no physical significance. To obtain a true value of the polarization resistance, an appropriate impedance model or equivalent circuit must be established, as described previously.

Finally, as EIS has become very popular and has been applied to many corrosion problems, care must be taken in using and interpreting the data, otherwise enormous errors could be made.
Figure 20. Complex plane plot for equivalent circuit before and after deconvolution. $R_0 = 10\Omega$, $R_1 = 1000\Omega$, $R_2 = 5000\Omega$, $\sigma = 10^4 \text{ ohm/sec}^{1/2}$, $C_1 = C_2 = 20\mu\text{F}$.
Figure 21. Admittance plot for data in Fig. 20 curve (1).
Figure 22. Schematic for a complex plane impedance plot used in minimization. (49)
The experimental apparatus used in this study is shown in Fig. 23. The reaction chamber is a one-end-closed mullite tube which was closed by a gas tight, water-cooled brass flange joined by epoxy. The $\text{Na}_2\text{SO}_4$ melt was held by a silica crucible within an alumina crucible supported by an alumina tube. All solid state electrodes and gas conduit tubes were inserted into the reaction chamber through brass adapters (Cajon Ultra-Torr) soldered into the top stainless steel flange. A teflon O-ring which is resistant to $\text{SO}_2$-$\text{SO}_3$ was placed between the top and the bottom flanges to ensure a gas tight system.

Reagent-grade $\text{Na}_2\text{SO}_4$ was used without further purification. All gases were dried by passing them through drierite ($\text{CaSO}_4$). A quartz tube filled with platinum catalyst served as a gas inlet, which insured the establishment of the $\text{SO}_2$/$\text{SO}_3$ equilibrium. The flow rates of the gases were maintained at 60 ml/min by a flow meter (Matheson 610). The gas outlet from the reaction chamber was closed to the atmosphere by bubbling through a reservoir of dibutyl phthalate.
Preoxidized nickel wires of different purity and preoxidation condition were used to observe the mechanism of the hot corrosion reaction. The nickel wire was wound around the outer surface of a yttria-stabilized zirconia reference electrode (RE) to serve as the working electrode (WE), as shown in Fig. 24a. For 99.9975% pure nickel wire of diameter = 1 mm., another WE configuration was also used, in which one piece of nickel wire was attached to the outer surface of zirconia RE by a high-temperature ceramic cement (Ceramabond 552), as shown in Fig. 24b. The WE was spot-welded to a Pt lead wire. The Pt lead wire was embedded in a high-purity alumina tube and sealed with ceramic cement so that the it did not directly contact the fused salt. A platinum foil counter electrode (CE) encircled the zirconia electrode without touching the nickel WE. The space between the CE and WE was made small (about 2 mm.) so that a thin layer of fused salt could be held there during an experiment. A fused silica electrode also contacted the nickel WE to act as the second RE. The combination of the zirconia and silica electrodes provided measures for both the basicity and oxygen pressure at the WE according to Eqs. [25] and [26].

The system was heated by an electric tube furnace and the temperature was controlled to 1200±2 K by a solid-state temperature controller (Omega CN-2010) using a Type-S (Pt-Pt/10%Rh) thermocouple. A separate thermocouple inserted into the supporting tube of the crucible measured the temperature
of the salt which was maintained at 897 °C (1170 K) so that salt vapor did not deposit on the hotter WE. The WE was within a uniform temperature zone of about 4 cm length.

For each experiment, 36 grams of pure Na₂SO₄ powder (J. T. Baker Anhydrous) was placed inside the quartz crucible and the cell assembly was dried at 500 °C for 1 hour in air. Then the cell was heated to 1200 K in 3 hr in air. When the temperature had been reached, air or pure oxygen gas (Union Carbide, extra-dry grade) was used to preoxidize nickel. The preoxidizing time ranged from 5 min to 2 hr.

After the preoxidation, the electrode arrangement shown in Fig. 24 was immersed briefly into the fused sodium sulfate contained in the silica crucible and the gas atmosphere was changed to a catalyzed 0.1% SO₂-O₂ gas mixture. Upon withdrawal of the sample from the melt, a thin fused salt film of volume \( \approx 0.294 \text{ cm}^3 \) covered the electrodes. The thickness of the salt covering the space between the WE and CE was about 2 mm.

AC impedance measurements were performed with a Princeton Applied Research (PAR) 5208 two-phase lock-in analyzer and a PAR 273 potentiostat interfaced through an IEEE-488 bus to an IBM PS-2 computer (Fig. 25). This system generated a sinusoidal voltage which was applied to the WE with a maximum amplitude less than 10mV and frequencies ranging from \( 10^{-3} \) to \( 10^9 \) Hz. A Fast Fourier Transform (FFT) technique was employed for frequencies from \( 10^{-3} \) to 10 Hz to increase measurement
speed and lower the degree of perturbation to the cell. Through the potentiostat, polarization of the WE with respect to either of the two REs was performed and impedance measurements were made after the polarization potential was stabilized (change of less than 10%). The potentials between the WE and the two REs were recorded before and after the impedance measurement to avoid interference. Impedance data were stored and plotted by the computer.
Figure 23. Schematic assembly of the experimental set-up.
Figure 24. Two configurations of the WE.
Figure 25. Impedance measurement system.
CHAPTER VI
RESULTS AND DISCUSSION

Because of different metal purity and preoxidation conditions, three distinctive reaction states were observed during the hot corrosion process. A. Passive State. In this state, no appreciable reaction occurred, and the final product was only slightly corroded. B. Pseudo-Passive State. At first, the condition was similar to case A, but once the system was forced to some unstable condition, passivity ended and a corrosion reaction occurred so that finally the WE was heavily corroded. C. Active State. In this state, hot corrosion occurred almost immediately with a little or no incubation time and the WE was heavily corroded. The experimental observations and interpretations for these different types of behavior are given in the following sections.

A. Passive State

Pure Ni (99.9975%) was preoxidized in \( O_2 \) at 1200 K for 2 hr before brief immersion into fused \( Na_2SO_4 \). The average scale thickness was calculated to be 4.3 \( \mu m \) from a separate weight-gain experiment. After the surface of the preoxidized
Ni was coated with a salt film of about 2 mm thickness, the basicity and oxygen pressure at the Ni WE were continuously recorded from the potentiometric measurements between the silica RE, the zirconia RE and the WE, and the results are plotted in Fig. 26. Both basicity and oxygen pressure remained almost unchanged for 6 hrs. Note that the basicity value corresponds to an equilibrium with the gaseous atmosphere, but the indicated oxygen pressure ($\approx 10^{-9}$ atm.) assumed a value much lower than that for the ambient gaseous atmosphere ($P_{O_2} = 1$ atm.). The dashed line shown in Fig. 26 represents the location of the solubility minimum for NiO using the data reported by Gupta and Rapp (50) for NiO in pure Na$_2$SO$_4$ at 1200K in $P_{O_2} = 1$ atm (Fig. 27). This line of minimum solubility can be interpreted as a boundary between two different regimes, such that basic dissolution of NiO occurs to the left of the boundary whereas dominant acidic dissolution occurs to the right of the line.

According to the dissolution-reprecipitation model proposed by Rapp and Goto (16), a negative gradient in the solubility of the protective oxide in the salt film is necessary for self-sustained hot corrosion of a pure metal. For the experimental condition of the present research, this requirement can only be met when the salt film chemistry is located in the basic dissolution regime, because the gas/salt interface is always more acidic than the salt/oxide interface (17). This criterion was confirmed recently by Otsuka and
Rapp (18), who used a thin film potentiometric method to study the hot corrosion of preoxidized Ni by a thin fused Na₂SO₄ film at 900°C.

The salt film chemistry remained unchanged in the acidic dissolution regime during the observation period of 6 hrs. When the WE was taken out after this period, the nickel wire was covered by compact oxide scale and no corrosion products were observed in the clear, solidified salt film.

To understand the nature of this seemingly passive state, impedance measurements were conducted. Typical impedance spectroscopy data for this period are plotted in the complex plane as shown in Fig. 28 for the two WE configurations described in Fig. 24. In Fig. 28a, the dominant part is a straight line of 45° slope which indicates a diffusion process. However, in the high frequency end, where \( \text{Z''} \to 0 \), a deviation appears. In Fig. 28b, three different time constants can be clearly resolved. In the low frequency range, linear Warburg behavior with a slope of 45° indicates that this process is diffusion-controlled. In the high frequency range, two semicircles emerged as the process became reaction-controlled (or charge-transfer-controlled). Figures 28a and 28b were plotted using impedance values before normalization with respect to surface area. The surface area of the WE for the spiral configuration was about 8.5 times greater than that for the straight wire configuration. The normalized impedance data are replotted in Fig. 29 for both
Figure 26. The melt basicity for a 99.9975% Ni remained unchanged in first 6 hours (preoxidized in O₂ at 1200K for 2 hours).
Figure 7. Solubility of NiO in fused Na₂S₀₄ at 1200°K.
Figure 28. Nyquist plot for 99.9975% pure Ni preoxidized in $O_2$ at 1200K for 2 hr. The melt chemistry is: $\log a_{Ni^{2+}} = -12.725$, $\log P_{O_2} = -7.736$ (a) WE configuration as in Fig. 24a, (b) WE configuration as in Fig. 24b.
Figure 29. Impedance data in Fig. 28 after normalization with respect to surface area. (Δ): spiral configuration, (□): straight wire configuration.
Figure 30. Bode plot of the data of Fig. 28b.
configurations. The similarity between the two configurations is obvious. Since configuration b gives better resolution of impedance spectroscopy, it was adapted for the following experiments for 99.9975% pure nickel. Figure 30 is the Bode plot of the data shown in Fig. 28b. The approach of the phase angle to 45° in the low frequency range again confirms the diffusion behavior. Two phase-angle peaks at intermediate to high frequencies indicate the two reaction-controlled processes.

The type of impedance response shown in Figs. 28b and 30 for metals in a passive region has been reported in aqueous corrosion for pure Ni in Na₂HPO₄/Na₃PO₄ buffer solutions of different pH values at ambient temperature by several researchers (51, 52). In the following discussion, appropriate impedance models are introduced to explain the passive behavior (51, 53, 54). Some necessary modifications and corrections are introduced and discussed to correspond with hot corrosion.

As drawn schematically in Fig. 31, for the system of the metal/metal oxide/electrolyte, assuming that the oxide film is continuous, i.e. not porous, the total series impedance can be written as:

$$Z_T = Z_{M/O} + Z_{Ox} + Z_{O/S}$$  \[66\]

where $Z_{M/O}$, $Z_{Ox}$ and $Z_{O/S}$ are the impedance contributions of the metal/oxide interface, the oxide film, and the oxide/salt.
Figure 31. Equivalent circuit for the total impedance of metal/oxide/salt system in passive state.
interface, respectively. In NiO, doubly ionized cation vacancies and holes have been reported as the predominant ionic defects (55-58). Therefore, in the following model only these two defects are considered.

At the metal/oxide (M/O) interface, the metal is oxidized according to the following reaction expressed in point defect notation,

\[ \text{Ni}^0 + \text{V}_{\text{M}^+} + 2\text{h}^- \rightarrow \text{Ni}_{\text{M}^+} \]

where Ni\(^0\) is Ni in the atomic state, V\(_{\text{M}^+}\) is a nickel cation vacancy whose relative charge is 2\(^-\), h\(^-\) is an electron hole of charge +1, and Ni\(_{\text{M}^+}\) is a Ni cation on a normal Ni site in NiO with zero relative charge. Both holes and cation vacancies are exchanging at the interface between the metal and the oxide. This leads to an impedance of two charge transfer resistances in parallel with a capacitance of the metal/oxide interface, C\(_{\text{M/O}}\),

\[ Z_{\text{M/O}} = \left( j\omega C_{\text{M/O}} + \frac{1}{R_h} + \frac{1}{R_M} \right)^{-1} \]

where \(R_h\) and \(R_M\) are the resistances for the transfer of holes and cation vacancies, respectively, from the metal to the oxide.

In general, because both phases are electronic conductors, the resistance to the movement of holes across the interface is small compared with the resistance to the
movement of cation vacancies, i.e.,

\[ R_h \ll R_M \] \[69\]

Then Eq. [68] can be rewritten as

\[ Z_{WO} = \left[ j\omega C_{WO} + \frac{1}{R_h} \right]^{-1} = \frac{R_b}{1 + j\omega C_{WO} R_h} \] \[70\]

If \( 1/(C_{WO} R_h) \gg \omega \) over the frequency range of our experimental conditions (5 \times 10^{-3} to 10^5), one can safely conclude that

\[ Z_{WO} = R_h \] \[71\]

Chao, et al. (51) proposed a transport model to explain the oxide film impedance during passive anodic oxidation in aqueous solutions using a point defect concept. Before introducing their theory, it must be mentioned that the origin of the passive film in the present case is quite different. While Chao, et al. (51) used an externally applied potential to form their passive film via anodic oxidation, there was no applied external potential here for the preoxidation of the Ni WE. Nevertheless, the formulation suggested by those authors can serve in understanding the impedance response of a passive oxide film.

The impedance of the oxide film can be expressed, considering only the majority ionic and electronic defects, in the following equation,
where $Z_h'$ and $Z_m'$ are the impedances of the holes and cation vacancies in the oxide, respectively, and $C_{0x}$ is the capacitance of the oxide. The impedances caused by those two defects are assumed to be independent in writing Eq. [72].

Since no net electrochemical reaction occurs in the oxide, both $Z_h'$ and $Z_m'$ can be treated as diffusion impedances. Because electron hole transport across the film is fast, provided that a limiting electron exchange process does not occur at the oxide/salt interface, we can write $Z_h' = R_h'$.

The diffusion impedance of cation vacancies can then be written as

$$Z_m' = \sigma_m \omega^{-1/2} (1-j)$$

where $\sigma_m$ is given by

$$\sigma_m = \frac{RT}{4F^2} \left( \frac{1}{\sqrt{2D_m C_{vm} (M/O)}} \right)$$

In Eq. [73], $D_m$ is the self-diffusion coefficient of cation vacancies, $C_{vm}$ is the concentration of cation vacancies at metal/oxide interface, and $R$, $T$ and $F$ have their usual meanings.
The impedance of the oxide film can then be written as

\[ Z_{\text{ox}} = \left( \frac{1}{R_h} + \frac{1}{\sigma \omega^{-1/2}(1-j)} + j\omega C_{\text{ox}} \right)^{-1} \]  

with \( Z_n' \approx R_n' \).

At the oxide/salt interface, the arriving oxidant, \( S_2O_7^{2-} \), is formed according to the following step,

\[ SO_3(g) + SO_4^{2-}(G/S) \rightarrow S_2O_7^{2-}(O/S) \]  

The \( S_2O_7^{2-} \) ion is reduced at the oxide/salt interface to yield NiO and evolve \( SO_2 \).

\[ Ni^{2+} + S_2O_7^{2-} \rightarrow SO_2 + SO_4^{2-} + NiO + V^{2+} + 2e^- \]  

The reduction reaction [77] at the oxide/salt interface involves (i) the transport of \( S_2O_7^{2-} \) ions from the gas/salt interface to the oxide/salt interface, and (ii) charge exchange of cation vacancies and holes at the oxide/salt interface. Since the transport of \( S_2O_7^{2-} \) is a preceding step for the charge transfer of Eq. [77], these two processes are considered to be in series. The electron exchange at the oxide/salt interface is again a process in parallel. Thus the impedance of the oxide/salt interface can be expressed as

\[ Z_{\text{ox}} = \left( \frac{1}{R_h'} + \frac{1}{R_m'/\sigma \omega^{-1/2}(1-j)} + j\omega C_{\text{ox}} \right)^{-1} \]  

where \( R_n'' \) and \( R_m'' \) are the charge transfer resistances of
holes and cation vacancies at the oxide/salt interface, respectively, \( \sigma_0 \) is the Warburg coefficient for the diffusion impedance of \( S_2O_7^{2-} \), and \( C_{0/e} \) is the capacitance of the oxide/salt interface. By assuming semi-infinite diffusion, \( \sigma_0 \) is given by

\[
\sigma_0 = \left( \frac{RT}{4F^2} \right) \left( \frac{1}{\sqrt{2D_0C_0(S/G)}} \right)
\]

where \( D_0 \) is the diffusion coefficient of \( S_2O_7^{2-} \) ions in the salt, \( C_0 \) is the concentration of \( S_2O_7^{2-} \) near the gas/salt interface.

Finally, the total impedance of the metal/oxide/salt system is the sum of the individual impedances (Eqs. [71], [75] and [78]) described above. The equivalent circuit of the total impedance is shown schematically in Fig. 31.

From the total impedance shown in Fig. 31 and the experimental data shown in Fig. 28b, the low-frequency diffusional impedance could be attributed to the diffusion of cation vacancies in the oxide film or the transport of \( S_2O_7^{2-} \) in the salt. For the first case, the Warburg coefficient \( \sigma_m \) in Eqs. [73] and [74] can be calculated and should match known experimental values. From the work by Volpe and Reddy (58) for high-purity nickel oxide single crystals at 1200 K, the diffusivity of nickel vacancies at 1200 K was found to be \( 4.876 \times 10^{-16} \text{ cm}^2/\text{s} \) at \( \log P_{O_2} = -11.5 \) (for equilibration with Ni). The nickel vacancy concentration for Ni/NiO equilibrium
reported by Sockel and Ilschner (59) was calculated to be 7.4×10⁻⁸ mole/cm³. Substitution of these values with R= 8.314 joule/mole-K and F= 96487 coul/mole into Eq. [74] gives \( \sigma_M = 3.67 \times 10^7 \) ohm-cm²/s¹/².

To establish an experimental value of \( \sigma_M \), a Randles plot was constructed after first vectorially subtracting the solution resistance and the double layer capacitance from the original impedance data. The slope of the Randles plot, as shown in Fig. 32, corresponds to the Warburg coefficient \( \sigma_M \) according to Eq. [74], which was found to be 62.07 ohm/s¹/² or 13.65 ohm-cm²/s¹/² after multiplying the area of the WE. Upon comparing the theoretical (3.67×10⁷) and experimental (13.66) values for \( \sigma_M \), the huge discrepancy means that cation vacancy diffusion is not the important impedance. The large value of diffusion impedance of cation vacancies also suggests that, in the available frequency range, no ac current can pass through it, i.e., only \( R_n' \) in the oxide impedance can be observed.

For the diffusion of \( S_2O_7^{2-} \) in the salt, the diffusion coefficient \( D_0 \) at 1200 K was estimated to be 2.09×10⁻⁴ cm²/sec (21). The concentration of \( S_2O_7^{2-} \) is taken to be the solubility of \( Na_2S_2O_7 \) which can be calculated from thermodynamic stability data assuming an ideal solution behavior. At 1200K in a pure \( Na_2SO_4 \) melt, this value was found to be 2×10⁻⁴ mole/cm³. Substitution of \( D_0 \) and \( C_0 \) into Eq. [79] gives \( \sigma_0 = 6.6 \) ohm-cm²/s¹/², which is reasonably
Figure 32. Randles plot of data shown in Fig. 29 after vectorially subtracting solution resistance and double layer capacitance. Slope of the curve = 62.069 ohm/s^{1/2}. 
close to the experimental value (13.66). Therefore, the observed low-frequency diffusion impedance was attributed to the diffusion of $S_2O_7^{2-}$ in the salt.

Since the diffusion of cation vacancies in the oxide has been excluded from the total impedance, some simplification of the equivalent circuit shown in Fig. 31 can be made. First, the impedance of the oxide can be replaced by a resistor $R_m\prime$. Then the two resistors $R_m\prime\prime$ and $R_h\prime\prime$ in the O/S interfacial impedance are combined into one resistor $R_{O/S}$. After these simplifications, the resulting equivalent circuit was shown in Fig. 33a. Using the deconvolution method introduced in previous chapter, suitable values can be obtained from the experimental data for the elements in the model equivalent circuit, as shown in Fig. 33b, in which $R_m$ and the solution resistance $R_{soln}$ were combined into $R_s$. The computer simulation using the equivalent circuit shown in Fig. 33b is plotted in Fig. 34. Both Bode and Nyquist plots agree very well with the experimental data shown in Figs. 28b and 30. The two semi-circles at high frequencies could be attributed to the charge transfer resistances at the metal/oxide and oxide/salt interfaces. Since $R_{O/S}$ (diameter of the semicircle at lower frequency of the two) is the charge transfer resistance for the reduction reaction at the oxide/salt interface, it can be eliminated from the resistance caused solely by NiO. From the work by Meier and Rapp (60), the electrical conductivity of an NiO single crystal at 1200 K
Figure 33. Simplification of the equivalent circuit shown in Fig. 31.
Figure 34. Computer simulation for the metal/oxide/salt system in passive state using the equivalent circuit shown in Fig. 33b.
under oxygen pressure $10^{-8} - 10^{-10}$ atm is found to be $3 \times 10^{-3}$ ohm$^{-1}$ cm$^{-1}$. The resistance can then be calculated using the following equation,

$$R = \frac{1}{\sigma_{\text{cond}}} \left( \frac{L}{A} \right)$$

For an oxide thickness of $L = 4.3$ µm, and area $A = 0.22$ cm$^2$, $R$ is calculated to be 0.7 ohm, which is close to the diameter of the semicircle at highest frequencies $R_m'$ (1 ohm). These calculations prove that the experimental data are consistent with the actual physical properties of the system. Note that only the electrical resistances of the more conductive parallel resistors are identified in the above calculations, but these do not evaluate the rate of attack (scale growth) for passive state, which is limited by the diffusion of cation vacancies in NiO.

For 6 hours, the impedance response remained unchanged and the melt chemistry stayed in the acidic dissolution regime. At that time, cathodic polarization (with respect to the Ag/Ag$_2$SO$_4$ RE) for about 25 minutes each for several given potentials was applied in an attempt to initiate active hot corrosion at the WE. The changes in $P_{O_2}$ and basicity during the cathodic polarization are recorded in Fig. 35 as points A, B, and C. According to Otsuka and Rapp (18), in an unpolarized state, an induction period of slow attack precedes active hot corrosion, at which time the metal undergoes a sulfidation reaction. The chemistry of the salt film is
thereby shifted from the acidic dissolution regime to the basic dissolution regime for NiO. However, in this experiment, although the local melt chemistry (at the salt/oxide interface) fell into the sulfide stable region, no significant change in basicity was observed. The obvious explanation is that the thickness and the perfection of the oxide layer maintained the sample so protective (for the short polarization time) that the metal never contacted the salt electrolyte. Plate I shows the scanning electron microscopy (SEM) of a cross section and surface morphology of the preoxidized Ni WE before coating with a thin Na$_2$SO$_4$ film. From the micrograph of the cross section, the protective oxide layer is found to be compact.

Figures 36, 37, and 38 are the impedance spectroscopies for the different polarization stages A, B, and C. Note that although the basic features are similar to the open-circuit case, the diameters of the two semicircles decreased as the polarization increased. Since cathodic polarization drives the reduction reaction at the oxide/salt interface, as well as increases the supply of cation vacancies and holes (see Eq. [77]), $R_H$ and $R_0$ are expected to decrease in magnitude, which was the experimental observation.

When the sample was taken out of the furnace after the experiment, it appeared to be slightly corroded. The solidified salt film covering the Ni sample was clear, i.e., without obvious corrosion products. This observation again is
Figure 35. Trace of melt chemistry during the cathodic polarization in the passive state. A: $E - E_{\text{open}} = \Delta E = -65$ mv vs. Ag/Ag$_2$O RE. B: $\Delta E = -165$ mv. C: $\Delta E = -265$ mv.
Plate I. SEM examination of a 99.9975% pure Ni preoxidized in O₂ at 1200K for 2 hr. (a) cross section; (b) surface morphology.
Figure 36. Impedance data of 99.9975% pure Ni preoxidized in O₂ for 2 hr. in polarized state A.
Figure 37. Impedance data of 99.9975% pure Ni preoxidized in O₂ for 2 hr. in polarized state B.
Figure 38. Impedance data of 99.9975% pure Ni preoxidized in O₂ for 2 hr. in polarized state C.
consistent with the negative solubility gradient criterion proposed by Rapp and Goto (16) for sustaining hot corrosion. It also confirmed that high-purity Ni after a sufficiently long preoxidation would remain in the passive state for at least 12 hours of total experimental time for this given corrosive environment.

B. Pseudo-Passive State

To initiate the active hot corrosion reaction, 99+% pure Ni wires of 0.5 mm dia. were used in the following experiments instead of the higher purity Ni. 99+% pure Ni was preoxidized in air at 1200 K for 1 hour and the thickness of the oxide scale was measured to be 2.7 μm, about one half of the oxide thickness of the previous experiment. When the preoxidized Ni was coated with a thin film of fused sodium sulfate of 2 mm thickness, the trace of the salt chemistry shown in Fig. 39 resulted. The WE remained in the acidic dissolution regime for 2 hours with some changes in oxygen pressure at constant basicity. The corresponding impedance data are shown in Fig. 40. Only one time constant is observed in the Nyquist plot where the data approach the real axis in the low frequency region.

After 2 hrs., since the system remained passive, anodic and cathodic polarization were applied. The polarizations changed the oxygen activity (increasing it for the anodic polarization, decreasing it for the cathodic polarization),
but caused little variation in basicity (see Fig. 39). The melt chemistry remained in the acidic dissolution regime. The resulting impedance spectroscopies for anodic and cathodic polarization are shown as Figs. 41 and 42, respectively, which are quite similar except the anodic impedance has a higher value at the low frequency region than the cathodic impedance. One notable feature in Figs. 41 and 42 is that the high frequency limit in the complex plane approaches a straight line with a slope approximating 45°. This behavior is characteristic for a diffusion-controlled process. But as the frequency was decreased, the impedance data did not follow the 45° straight line, especially for the cathodic polarization case. To account for this behavior, the simplest interpretation would be to assume that the diffusion process occurred over a finite length, not over an infinite length. A computer-simulated model was built by using the finite diffusion impedance

\[ Z_w = \frac{RT}{(nF)^2} \left[ \frac{\delta}{DC} \right] \left[ \frac{\tanh \left( \frac{j\omega \delta^2}{D} \right)}{\sqrt{\frac{j\omega \delta^2}{D}}} \right] \]

where \( D \) is the diffusion coefficient, \( C \) is the bulk concentration and \( \delta \) is the diffusion length. The resulting impedance for the anodic or cathodic reaction is

\[ Z_1 = R_s + \left[ Z_{m1}^{-1} + j\omega C_s \right]^{-1} \]
Figure 39. Trace of melt chemistry for a 99+% Ni preoxidized in air at 1200K for 1 hr. After 2 hr. of free corrosion observation, the sample was anodically polarized to A and then cathodically polarized to B and C. Details see text.
Figure 40. Impedance data of 99+\% Ni preoxidized in air at 1200K for 1 hr. after 1 min. of immersion in fused Na\textsubscript{2}SO\textsubscript{4}. log \textit{a}_{\text{Ni}} = -12.08, log P\textsubscript{O\textsubscript{2}} = -8.476.
Figure 41. Impedance data of 99+% Ni preoxidized in air at 1200K for 1 hr. at polarized state A. $\Delta E = -0.1$ v vs. ZrO$_2$ RE. log $a_{Na^{2+}} = -12.08$, log $Po_2 = -2.358$. 
Figure 42. Impedance data of 99+2% Ni preoxidized in air at 1200K for 1 hr. at polarized state B. $\Delta E=-0.53$ vs. ZrO$_2$ RE. log $a_{\text{Ni}}=12.09$, log $P_O=9.585$. 
where \( i \) indicates the anodic or cathodic reaction, \( C \) is the capacitance and \( R_a \) is the solution resistance.

To sum up, the impedance behavior of the WE at the open-circuit potential can be represented by the equivalent circuit of Fig. 43. Because of the mixed nature of the open-circuit potential, the equivalent circuit is considered to be composed of the cathodic and anodic impedances in parallel. To illustrate this point, a simplified corrosion system is considered in Fig. 44 where both anodic and cathodic reactions are charge transfer controlled. When the system is at its corrosion potential, the anodic current must equal the cathodic current, i.e., no net current can result. If a small, positive perturbation \( \Delta E \) is applied to this system at the corrosion potential, the resulting current response can be written as

\[
\Delta i = i_{corr} \left( e^{\frac{\Delta E}{\Delta E_c}} - e^{\frac{-\Delta E}{\Delta E_c}} \right)
\]

where \( i_{corr} \) is the corrosion current, \( \Delta E \) are Tafel constants for the anodic and cathodic reactions, respectively. In Eq. [83], the only significant anodic and cathodic reactions are assumed to be the metal oxidation and the \( O \) reduction. Since \( \Delta E \) is small, equation [83] reduces to

\[
\Delta i = i_{corr} \frac{\Delta E}{\beta_a} + \frac{\Delta E}{\beta_c}
\]

From that, the impedance can be expressed as

\[
Z = \frac{\Delta E}{\Delta i} = \frac{1}{i_{corr}} \left( \frac{1}{\beta_a} + \frac{1}{\beta_c} \right)^{-1}
\]
Figure 43. Equivalent circuit of the Ni WE at open-circuit potential.
Figure 44. Relationship between potential and current for a corroding system consisting of two coexisting electrochemical reactions.
Now if an anodic polarization $E$ is applied to the system in addition to the perturbation $\Delta E$, the resulting anodic current is

$$i_a = i'_a + \Delta i_a = i_{0,a} \frac{(E + \Delta E - E_{corr})}{\beta_a}$$

$$= i_{0,a} \frac{E - E_{corr}}{\beta_a} (1 + \frac{\Delta E}{\beta_a})$$

where $i_a'$ is d.c. anodic current at potential $E$ and $i_{0,a}$ is the exchange current for metal oxidation. The variation in anodic current caused by $\Delta E$ can be expressed as

$$\Delta i_a = \frac{\Delta E}{\beta_a} i_{0,a} \frac{E - E_{corr}}{\beta_a} - i'_a \frac{\Delta E}{\beta_a}$$

From Eq. [87], the impedance for this anodic reaction is defined as

$$Z_a = \frac{\Delta E}{\Delta i_a} = \frac{\beta_a}{i'_a}$$

Following the same procedures, impedance for the cathodic reaction can be written as

$$Z_c = \frac{\beta_c}{i'_c}$$

If $E$ approaches $E_{corr}$, then both $i'_a$ and $i'_c$ approach $i_{corr}$. Substitution of $\beta_a$ and $\beta_c$ into Eq. [85] leads to
which indicates that the total impedance at $E_{corr}$ can be represented by a parallel circuit of $Z_a$ and $Z_o$. In the present case, both cathodic and anodic impedances are bounded diffusion processes represented by Eq. [81]. Then the total impedance at the open-circuit potential can be written as

$$Z_T = R_s + [Z_{wa}^{-1} + Z_{wc}^{-1} + j\omega C_{dl}]^{-1}$$

The simulated impedance data for the WE at the open-circuit potential, upon anodic polarization, and upon cathodic polarization are shown in Figs. 45, 46, and 47, respectively. The fitting parameters are listed in Table 2.

Until now, the nature of the diffusing species in the proposed equivalent circuit has not been discussed. From Table 2, the values of the Warburg coefficient $\sigma$ are of the same magnitude as the value in the passive case, i.e. when the diffusing species is $S_2O_7^{2-}$ in the molten salt. So at least the diffusing species responsible for the cathodic polarization impedance must be $S_2O_7^{2-}$. Furthermore, the oxide formed on the 99+% pure Ni was not as compact as the oxide in the previous case. This can be seen from plate II. The oxide layer of the preoxidized Ni WE before coating with Na$_2$SO$_4$ had cracks and pores, as compared with the compact oxide shown in
Figure 45. Computer simulation of data shown in Fig. 40, \( R_m = 1.41 \, \Omega \), \( C_{d1} = 3000 \, \mu F \). For other fitting parameters, see Table 2.
Figure 46. Computer simulation of data shown in Fig. 41, $R_e = 1.106$ ohm, $C_e = 1350$ μF. For other fitting parameters, see Table 2.
Figure 47. Computer simulation of data shown in Fig. 42. $R_s = 1.156$ ohm, $C_e = 722$ µF. For other fitting parameters, see Table 2.
Table 2. Fitting parameters of the equivalent circuit shown in Figs. 45, 46, and 47.  

a: anodic reaction, b: cathodic reaction.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Fig. 45</th>
<th>Fig. 46</th>
<th>Fig. 47</th>
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</tr>
<tr>
<td>$\delta_{c}/(2D)^{1/2}$ (sec$^{1/2}$)</td>
<td>1.65</td>
<td></td>
<td>0.75</td>
</tr>
</tbody>
</table>
Plate II. SEM examination of a 99+\% pure Ni preoxidized in air at 1200K for 1 hr. (a) cross section; (b) surface morphology.
Figure 48. Schematic of the transport model of Ni/NiO/salt in the pseudo-passive state.
plate I. Thus, as shown schematically in Fig. 48, the protective scale can be modeled as an inhomogeneous layer with some active sites (pores) surrounded by less active sites. A similar model for 3-D inhomogeneous surfaces has been proposed by Jüttner, Lorenz, Kendig and Mansfeld (45) and was experimentally tested for the aqueous system Fe (rotating disc electrode)/0.5M Na₂SO₄, aerated, \(6 \leq \text{pH} \leq 8\), \(T = 298\) K, with and without an inhibitor. The authors suggested that the diffusion-controlled cathodic oxygen reduction takes place predominantly at the bottom of the oxide pores, i.e., at the uncovered areas of the metal substrate. In the present case, since bare Ni cannot coexist with an acidic Na₂SO₄, it is assumed that a thin oxide layer covers the metal at the bottom of the pores. \(\text{SO}_4^{2-}\) diffusing through the pore is reduced at the surface of the thinnest oxide sites where the small oxide thickness provides less resistance to the transfer of cation vacancies and holes. Since the pore dimensions are small compared with the salt film, the diffusion of \(\text{SO}_4^{2-}\) in the pores can be treated as bounded and it is the rate limiting step in the cathodic polarization.

As for rate control during anodic polarization, two possibilities exist. First, the diffusion process could result from the diffusion of Ni cation vacancies in the oxide film. Although this process was excluded for the passive case, the morphology of the thinner oxide film for 99+\% Ni must provide an easier path for Ni vacancy diffusion,
especially in the thin oxide at the base of a pore. Second, if the nickel ion concentration in the molten salt were high enough, diffusion of nickel ions could account for the observed anodic diffusion impedance. For both possibilities, the importance of diffusion for the anodic polarization is obvious. This is a characteristic property of corrosion in molten salts, unlike the active corrosion of metals in aqueous solutions at room temperature, where the process is often controlled by a charge transfer reaction (61).

When the nickel electrode was further polarized to log $P_{O_2} = -11.602$, active reaction occurred. The melt basicity changed drastically from $-\log a_{Na_2O} = 12.12$ to $8.019$ (from point C to point D in Fig. 39) during polarization, and the impedance spectroscopies also revealed different features as shown in Fig. 49. The magnitudes of the resistances decreased, indicating that active corrosion was in progress. In this case, active corrosion is thought to involve direct contact of the fused salt with nickel sulfide or nickel. The shape on the complex plane suggests at least two time constants were involved in the process. From the Bode plot in Fig. 49, some abrupt change at intermediate frequencies can be observed. This was possibly caused by the unstable condition of the system when the transition from passive to active state occurred. Once the active reaction started, the melt basicity remained in the basic dissolution regime even after the polarization was removed whereas the oxygen activity did
increase as the reaction continued. A typical impedance response during this active corrosion period is shown in Fig. 50. Although the magnitudes of resistances increase as compared to the data shown in Fig. 49 when active hot corrosion just started, the high frequency part of Fig. 50 is different from those of Figs. 40-42. The behavior is quite similar to the one shown in Fig. 49, with two clearly resolved time constants.

This stage is called pseudo-passive because active hot corrosion did not occur initially when the preoxidized sample was left undisturbed. But cathodic polarization caused a reduction in oxygen activity (at essentially fixed basicity) which then produced a shift in melt chemistry to the basic side of the NiO solubility minimum such that active hot corrosion started.

After the experiment which lasted about 200 minutes in the basic regime, a severely corroded WE resulted. The Ni wire was almost completely converted to NiO, which was porous and fragile. The solidified salt film was no longer clear but contaminated with greenish NiO and other corrosion products.

A detailed mechanism for the hot corrosion reaction and an explanation of the impedance response for active corrosion are given in the next section.
Figure 49. Impedance data for 99+7% Ni preoxidized in air at 1200K for 1 hr at polarized state C. $\Delta E = -0.65$ v vs ZrO$_2$ RE. log $P_{O_2} = -11.602$. During the measurement, the basicity changed from C to D in Fig. 39.
Figure 50. Impedance data of 99+% Ni preoxidized in air at 1200K for 1 hr in active reaction state E in Fig. 39, \( \log a_{N_{2}O}= -7.557, \log P_{O_{2}}= -7.854. \)
C. Active State

To induce an immediate hot corrosion reaction upon exposure to the fused salt film, the time of preoxidation was shortened so that the oxide layer could not prevent the fused salt penetration. The 99+7% pure nickel WE in these experiments was preoxidized in air at 1200 K for only 5 min, resulting in an oxide of average thickness 0.8 μm, which was about one-half of that for the pseudo-passive Ni WE. After preoxidation, the electrode arrangement was coated with a layer of fused Na₃SO₄ of about 2 mm depth. Then the corrosion potential of the WE was recorded using the REs. The oxygen activity and melt basicity calculated from these potentials are plotted in Fig. 51.

When the sample was coated with the thin fused salt, the salt chemistry dropped into the stability region of Ni₃S₂ at a very low Pₒ₂ value. But after a relatively short time (less than 10 min.), the melt chemistry shifted to the basic dissolution regime, where it remained throughout 420 min. Finally, at 670 min., the melt basicity approached the equilibrium ambient value, but Pₒ₂ equalled 10⁻⁷ atm.

Figures 52-56 are the corresponding impedance responses. When the hot corrosion reaction first started, there was some scatter in the data because of the instability of system as shown in Fig. 52. The shape of the data in the complex plane resembled a severely depressed semicircle. After 30 min. of reaction, two time constants could be clearly resolved from
Fig. 53, which is very similar to Fig. 50 for the pseudo-passive state when the hot corrosion reaction was induced for the originally passive nickel sample. The influence of diffusion became more important as the reaction proceeded, as depicted in Figs. 54 and 55. Finally, after 670 min, the salt chemistry crossed the minimum NiO solubility line into the acidic dissolution regime, and the impedance data revealed pure diffusion behavior (see Fig. 56).

After the experiment, the Ni WE was found to be severely corroded. Not only the sample surface but also the surrounding salt film was filled with the porous NiO. Once again, sustained hot corrosion reaction only happened when the salt chemistry was in the basic dissolution regime, corresponding to a negative solubility gradient for NiO.

Because of the complicated nature of the reaction mechanism involved in active hot corrosion (11, 22), to propose a theoretical model to explain the full features of impedance spectroscopy during the whole reaction time is difficult. However, in the following, a simplified model is introduced which gives a good description to some stages of hot corrosion reaction. It is based on the theoretical work done by Sluyters-Rehbach and Sluyters (44) in which the effects of homogeneous chemical reactions coupled with electrochemical reaction were considered. The authors assumed the following scheme for a hypothetical system,
Figure 51. Trace of salt chemistry when 99% pure Ni in active state (preoxidation time of 5 min. at 1200K in air). Numbers in the figure designate the free corrosion time in minutes.
Figure 52. Impedance data of 99+\% pure Ni preoxidized in air at 1200K for 5 min. Reaction time = 10' min.
\[ \log \Delta N_{20} = -7, \log P_{O_2} = -7.15. \]
Figure 53. Impedance data of 99+% pure Ni preoxidized in air at 1200K for 5 min. Reaction time = 30 min. 
$log a_{\text{Ni}^{2+}} = -6.8$, $log P_{O_2} = -6.24$. 
Figure 54. Impedance data for 99+\% pure Ni preoxidized in air at 1200K for 5 min. Reaction time = 90 min.

$log a_{\text{Ni}_2O}_3 = -7.1, log P_{O_2} = -6.73.
Figure 55. Impedance data for 99+% pure Ni preoxidized in air at 1200K for 5 min. Reaction time = 260 min.
\( \log a_{\text{Ni}_2\text{O}_3} = -7.3 \), \( \log P_{\text{O}_2} = -4.64 \).
Figure 56. Impedance data for 99+% pure Ni preoxidized in air at 1200K for 5 min. Reaction time = 670 min. 
$\log a_{N_2O_5} = -11.4$, $\log P_{O_2} = -7.85$. 

[Graph showing impedance data with log frequency on the x-axis and log modulus on the y-axis, with a scatter plot of real and imaginary components of impedance.]
where the electroactive species $O$ are generated by a reaction that precedes the electron transfer at the electrode. The product of that electrode reaction, $R$, reacts to produce a species that is not electroactive. Using diffusion equations and a chemical/electrochemical kinetics mechanism, they developed a theoretical impedance model to demonstrate the implications of the reactions $A \rightarrow O$ and $R \rightarrow B$ accompanying the diffusion process.

In the present system for active hot corrosion, the anodic reactions involved are quite complicated. Besides metal oxidation and a diffusion process, formation/dissolution of the oxide, which are chemical reactions, should also be included in the total reaction scheme. Therefore, the mathematical development of Sluyters et al. (44) is used with some minor modifications to adapt it to the present system.

Assuming that nickel is oxidized according to the reactions listed below

\[ \begin{align*}
    Ni &\rightarrow Ni^{2+} + 2e^- \quad [93] \\
    Ni^{2+} + O^2- &\rightarrow NiO \quad [94]
\end{align*} \]

then basic dissolution would occur by
One usually considers that dissolved SO$_3$ forms ionic S$_2$O$_7^{2-}$

\[ \text{SO}_3 + \text{SO}_4^{2-} \rightarrow \text{S}_2\text{O}_7^{2-} \]  \[[96]\]

Then the reduction reaction could be

\[ \text{S}_2\text{O}_7^{2-} + 2e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{O}_2 \]  \[[97]\]

Figure 57 summarizes these reactions which are supposed to take place during the self-sustaining hot corrosion of Ni by a thin pure fused Na$_2$SO$_4$ salt film in a SO$_2$-O$_2$ gas atmosphere. As stated in previous sections, sulfidation of Ni induced active hot corrosion at the metal/oxide interface. At the beginning of hot corrosion, the sulfides formed would exist mainly along the grain boundaries and/or cracks of the oxide, i.e., where the salt can penetrate and come into direct contact with the base metal. Since these sulfide-wetted areas are small compared to the oxide covered areas, at least in the beginning of active hot corrosion, the oxidation of Ni is assumed to occur mostly at the metal/oxide interface. The mechanism of later stages, when nickel sulfide almost completely covers the base metal, is discussed later.

In the reduction sequence, sulfur trioxide gas is dissolved into the salt, or reacted with the salt, at the salt/gas interface according to Eq. [96]. That reaction is assumed to be at chemical equilibrium at the salt/gas
A. \( \text{Ni} \rightarrow \text{Ni}^{2+} + 2e^- \)
\[
4\text{Ni} + \text{SO}_4^{2-} \rightarrow 3\text{NiO} + \text{NiS} + \text{O}_2^{2-}
\]

B. \( \text{Ni}^{2+} + \text{O}_2^{2-} \rightarrow \text{NiO} \)
\[
2\text{NiO} + \text{O}_2^{2-} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{NiO}_2^{-}
\]
\[
\text{S}_2\text{O}_7^{2-} + 2e^- \rightarrow \text{SO}_4^{2-} + \text{SO}_2 + \text{O}_2^{2-}
\]

C. \( \text{NiO}_2^{-} \rightarrow 2\text{NiO} + \text{O}_2^{2-} + \frac{1}{2}\text{O}_2 \)

Figure 57. Possible reaction for the active hot corrosion of Ni coated with a thin Na\(_2\)SO\(_4\) film.
interface (22). The pyrosulfate ions then diffuse through the thin salt film to the sample surface. The electrochemical reduction reaction takes place at the oxide/salt interface and the product oxide ions participate in the formation of oxide. Overall, because the electron exchange reaction (Eq. [97]) proceeds at a fast rate, the resulting charge transfer resistance would be very small. Only the diffusional steps involved in these reduction reactions need to be considered in the analysis of impedance data.

As can been seen in Fig. 57, the nickel oxidation reactions are far more complicated than the reduction reactions. First, nickel metal is oxidized to nickel ions by inward migration of cation vacancies and electron holes. This oxidation reaction, which occurs at the metal/oxide interface, requires the supply of cation vacancies which is accomplished by a diffusion process. After nickel is oxidized, nickel ions react with \( \text{O}^{2-} \) to form nickel oxide at the oxide/melt interface according to Eq. [94]. Although the oxidation reactions occur when the melt chemistry is in the basic dissolution regime, Eq. [94] is still applicable especially at the beginning of the hot corrosion reaction where the local salt melt is not saturated with NiO. Once a certain amount of oxide is formed, it dissolves and reprecipitates according to Eq. [95]. In the reaction sequence of Eqs. [93], [94] and [95], the most notable feature is that two chemical reactions are associated with one electrochemical reaction. That
sequence can be rewritten as

\[ \text{Ni} = \text{Ni}^{2+} + 2e^- \quad [98a] \]
\[ \text{Ni}^{2+} + \text{O}^{2-} = \text{NiO} \]
\[ \text{NiO} + \frac{1}{2} \text{O}^{2-} + \frac{1}{4} \text{O}_2 = \text{NiO}_2^- \]

or

\[ \text{Ni} = \text{Ni}^{2+} + 2e^- \quad [98b] \]
\[ \text{Ni}^{2+} + \frac{3}{2} \text{O}^{2-} + \frac{1}{4} \text{O}_2 = \text{NiO}_2^- \]

or to represent it in a simplified form

\[ R = \text{O} + 2e^- \quad [99] \]
\[ O \xrightarrow{k_A} A \]

where \( R \) is the nickel cation vacancy, \( O \) is \( \text{Ni}^{2+} \), and \( A \) is \( \text{NiO}_2^- \). From Eq. [99], the mass transfer or diffusion of the oxidized species \( O \) is affected by the following chemical reaction which produces \( A \), i.e., \( \text{NiO}_2^- \). In writing Eq. [99] and in the following derivations, the effect of another reactant, \( \text{O}^{2-} \), in the chemical reaction is neglected for mathematical simplicity. This can also be justified from the trace of chemistry during hot corrosion shown in Fig. 51. The basicity of the melt remained more or less constant once the hot corrosion reaction started, as compared to the change in oxygen pressure.

Using the scheme shown in Eq. [99], Sluyters-Rehbach and Sluyters (44) derived the theoretical impedance response for coupled chemical reactions in the following way.

The differential equations to be solved for the
concentration of O; \( C_0 \), are

\[
\frac{\partial C_A}{\partial t} = D_A \frac{\partial^2 C_A}{\partial x^2} + k_A C_0 - k_A C_A
\]

\[\text{[100a]}\]

\[
\frac{\partial C_0}{\partial t} = D_0 \frac{\partial^2 C_0}{\partial x^2} - k_A C_0 + k_A C_A
\]

\[\text{[100b]}\]

where \( k_A \) and \( k_A \) are the rate constants of the forward and backward chemical reaction, respectively.

If one defines the following auxiliary functions:

\[
C_p = \left( \frac{D_A}{D_m} \right) C_A + \left( \frac{D_0}{D_m} \right) C_0
\]

\[\text{[101a]}\]

and

\[
C_q = C_A - K_A C_0
\]

\[\text{[101b]}\]

with

\[
D_m = \frac{(K_A D_A + D_0)}{(K_A + 1)}
\]

\[\text{[102]}\]

where \( K_A = \frac{k_A}{k_A} \). Equation \([100]\) can be approximated as

\[
\frac{\partial C_p}{\partial t} = D_m \frac{\partial^2 C_p}{\partial x^2}
\]

\[\text{[103a]}\]

\[
\frac{\partial C_2}{\partial t} = D_m \frac{\partial^2 C_2}{\partial x^2} - k_A \frac{D_2}{D_0 D_A} C_0
\]

\[\text{[103b]}\]
with the omitted terms: \[
\frac{(D_A - D_0)}{(K_A + 1)D_0} \frac{\partial C_p}{\partial t}
\]
in Eq. [103a]

and

\[
\frac{K_A D_0 (D_0^{-1} - D_A^{-1})}{(K_A + 1)} \frac{\partial C_p}{\partial t}
\]
in Eq. [103b].

which can be justified if \(D_A \approx D_0\). Note that \(k_A = \hat{k}_A + \hat{k}_A\) in Eq. [103b].

The Laplace transform solutions of Eqs. [103a] and [103b] are

\[
C_p(x, s) = \frac{C_p^0}{s} + P(s) \exp \left[ -\frac{x\sqrt{s}}{\sqrt{D_A}} \right]
\]

[104a]

\[
C_q(x, s) = Q(s) \exp \left[ -\frac{x\sqrt{s + k_A}}{\sqrt{D_A}} \right]
\]

[104b]

where \(P(s)\) and \(Q(s)\) are transform functions to be determined by using the proper boundary conditions. For the following boundary conditions,

\[
2FD_M \left( \frac{\partial C_p}{\partial x} \right)_{x=0} = -j_p(s)
\]

[105a]

\[
2FD_M \left( \frac{\partial C_q}{\partial x} \right)_{x=0} = +j_p(s) \left( \frac{D_M}{D_0} \right) K_A
\]

[105b]
where \( j_F \) is the faradaic current, \( P(s) \) and \( Q(s) \) can be solved as

\[
P(s) = \frac{j_F(s)}{2F \sqrt{BD_M}} 
\]

\[
\frac{1}{K_A} \frac{D_0}{D_M} Q(s) = -\frac{j_F(s)}{2F \sqrt{(S+K_A)D_M}} 
\]

From the definitions of the auxiliary functions in Eqs. [101a] and [101b],

\[
C_0(0,s) = \frac{1}{K_A+1} \left[ C_F(0,s) - \frac{D_A}{D_M} C_0(0,s) \right] 
\]

After substituting \( P(s) \) and \( Q(s) \) into Eq. [107], the solution for \( C_0 \) in the Laplace domain is

\[
C_0(0,s) = \frac{C_0^*}{s} \left[ -\frac{1}{K_A+1} + \frac{1}{\sqrt{S}} + \frac{K_A}{K_A+1} \frac{D_A}{D_0} \frac{1}{\sqrt{S+K_A}} \right] \frac{j_F(s)}{2F \sqrt{D_M}} 
\]

Following the same procedure, \( C_M \) can be written as

\[
C_M(0,s) = \frac{C_M^*}{s} - \frac{1}{\sqrt{S}} \frac{j_F(s)}{2F \sqrt{D_M}} 
\]

Assuming that \( K_A \gg 1 \) and \( D_A \approx D_0 \) then \( D_M \approx D_0 \), Equations [108] and [109] can be rewritten as
\[ L(\Delta C_0) = \frac{L(\Delta j_F)}{2R_\text{ct}D_0} \left[ \frac{1}{K_A+1} \frac{1}{\sqrt{S}} + \frac{K_A}{K_A+1} \frac{1}{\sqrt{S+K_A}} \right] \]

\[ L(\Delta C_R) = -\frac{L(\Delta j_F)}{2R_\text{ct}D_2} \left[ \frac{1}{\sqrt{S}} \right] \]

where \( L(f) \) is the Laplace transform for function \( f \).

The first-order Taylor expansion for \( j_F \) is

\[ L(\Delta j_F) = \frac{L(\Delta E)}{R_\text{ct}} + \sum_i \left( \frac{\partial j_F}{\partial C_i} \right) L(\Delta C_i) v_i \]

where \( R_\text{ct} \) is the charge transfer resistance and \( v_i \) is the stoichiometric number with \( i = 0, R \).

Using Eq. \([111]\) with \( s = j\omega \), the complex faradaic impedance \( Z_F = L(\Delta E)/L(\Delta j_F) \) for coupled chemical reaction Eq. \([99]\) can be rewritten as

\[ Z_F = R_\text{ct} + \frac{K_A\sigma_0 \omega^{-\frac{1}{2}}}{K_A+1} \left[ \frac{(g^2+1)^{\frac{1}{2}} - j[(g^2+1)^{\frac{1}{2}} - g]^{\frac{1}{2}}}{(g^2+1)^{\frac{1}{2}}} \right] \]

\[ + \sigma_0 \left[ \frac{1}{K_A+1} \right] \omega^{-\frac{1}{2}} (1-j) + \sigma_0 \omega^{-\frac{1}{2}} (1-j) \]

where

\[ \sigma_0 = \frac{R_\text{ct}}{2\sqrt{2} R_\text{ct} D_0} \left| \frac{\partial j_F}{\partial C_0} \right| \]
The faradaic impedance $Z_F$ expressed as Eq. [112] consists of one charge transfer resistance, which is a small value since the reaction rate in molten salt is fast, and three Warburg diffusion terms. The first two Warburg terms describe the diffusion behavior of nickel ions in the salt which is a coupled effect of chemical reaction. The last Warburg term is the diffusion impedance of nickel cation vacancies in the oxide film. A computer program has been developed based on Eq. [112] to fit the experimental data of this research. Figure 58 is the result of that simulation. Upon varying the values of $K_a$, $k_A$, $n$ and $d$, the shape of the impedance data on the complex plane can be changed. When $K_a$ is increased and the other parameters remained unchanged, the impedance becomes more charge transfer controlled because then the total reaction of Eq. [99] can be treated as $R \leftrightarrow A$. If $K_a$ is decreased, the mass transfer part of the impedance would be more significant. No matter what value for $K_a$ is assumed, the high frequency part of the impedance spectroscopy is always dominated by a diffusion effect because $g \to 0$ as $\omega \to \infty$ in Eq. [112], therefore eliminating the coupling reaction effect.

In Eq. [112], the diffusion terms are all based on the semi-infinite length condition. But as for previous
simulations, bounded linear diffusion (i.e., Eq. [81]) is more suitable in our case. So the term \( \sigma_i \omega^{-1/2} (1-j) \) in Eq. [112] was substituted by Eq. [81] for this modification.

In the process of using the mentioned computer program to simulate the experimental data, the largely depressed impedance plots (toward the x-axis in the complex plane) have caused some difficulties in curve fitting. One of the possible reasons for this depression is the inhomogeneity of the electrode surface (49). The original nickel oxide formed from preoxidation did not yield a homogeneous surface (see Plate III). After the active hot corrosion reaction started, the formation and dissolution of new nickel oxide further aggravated the surface inhomogeneity. Therefore the data reported in Fig. 50, which correspond to the active hot corrosion in the pseudo-passive state, were used to show the result of computer fitting.

The equivalent circuit for active corrosion is shown in Fig. 59. The anodic reaction (oxidation) is described by Eq. [112]. The cathodic step in parallel with the anodic reaction is the diffusion process of \( \text{S}_2\text{O}_8^{2-} \) in the salt. The resulting total impedance calculated by the computer is plotted in Fig. 60. Upon comparing Figs. 50 and 60, the agreement between the two is quite good. The values of the fitting parameters are listed under the graph.

With the help of Eqs. [98] and [112], we can get a clearer idea of the reaction mechanism of hot corrosion. For
Figure 58. Computer simulation of Eq. [112]. Curve D: pure diffusion controlled. Curve R: pure reaction controlled. $k_A = 500 \text{ sec}^{-1}$, $c_t = 1$, $c_0 = 101$. Varying $K_A$ values are indicated in the figure.
Plate III. SEM examination of a 99+% pure Ni preoxidized in air at 1200K for 5 min. (a) cross section; (b) surface morphology.
Figure 59. Equivalent circuit for active hot corrosion of Ni coated with a thin Na$_2$SO$_4$ film.
Figure 60. Computer simulation of data shown in Fig. 50 using Eq. (112) as anodic reaction where $a_o=166.7$, $a_R=400$, $K_A=1.25$, and $k_A=1540$. The cathodic reaction:

\[ \sigma = 38000, \text{L/(2D)}^{1/2} = 0.01. \]
a hot corrosion reaction, the metal ions must diffuse through the oxide layer via vacancy diffusion to the metal/oxide interface. Therefore the thickness and the structure of the oxide film are important. If the oxide is too thick, then diffusion through the oxide layer become rate-limiting, as demonstrated by the Warburg term $Z_m'$ in Eqs. [72] and [73]; this reduces the rate of passive hot corrosion. When the oxide layer is too thin, the diffusion of metal cation vacancies can no longer constitute a high impedance. The rate-controlling step then shifts to the diffusion of the metal ion in the solution, or to the chemical reaction process (formation/dissolution of the basic oxide). Since the two effects are coupled, to separate them is difficult. But from the impedance data observed throughout the hot corrosion process, the reaction term dominates in the early stage (see Figs. 52 and 53). After that short period, hot corrosion is dominated by the diffusion process of $\text{Ni}^{2+}$.

As the process parameters involved in Eq. [112] are all complicated functions of other variables, it is difficult to extract any actual values of physical significance from them. But the mechanistic information obtained from the impedance data is very useful.

In the latter stages of active hot corrosion, a substantial amount of nickel sulfide has been formed along the metal/oxide interface (see Fig. 61). If the sulfide is in the liquid state, the diffusional resistance in Ni oxidation would
at metal/sulfide interface
Ni → Ni^{2+} + 2e^{-}
4Ni + Na_{2}SO_{4} → 3NiO + NiS + Na_{2}O

at oxide/salt interface
Ni^{2+} + O^{2-} → NiO
2NiO + 1/2O_{2} + O^{2-} → 2NiO_{2}^{-}

Figure 61. Possible reaction for active hot corrosion at a later stage.
no longer exist because of the fast transport of Ni\(^{2+}\) in liquid sulfide. Then the active hot corrosion would be controlled solely by the formation/dissolution of the oxide, which involves the diffusion NiO\(_{2-}\) in the salt film. Since the diffusion length for this process gradually expands throughout the whole salt film as corrosion proceeds, the diffusion process is thought to be unbounded, as shown in Figs. 55 and 56 for the latter stages of active hot corrosion.

D. Hot Corrosion Mechanisms

In this section, the mechanism of hot corrosion of preoxidized Ni is discussed, using the available thermodynamic information, phase stability diagrams and the experimental results of this research. From the trace of oxygen activity and basicity shown in Fig. 39 in the pseudo-passive state, active hot corrosion did not occur until the chemistry of the melt reached the sulfide stability region, where the oxygen activity is about 4 orders of magnitude smaller than its initial value. This decrease in oxygen activity at nearly constant basicity during cathodic polarization was also observed by Park and Rapp (30) using a porous Pt WE. As suggested by Park and Rapp (30), the major reduction reaction should be

\[ \text{S}_2\text{O}_3^{2-} + 2\text{e}^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \]  

[114]

followed by a chemical reaction
$SO_3^{2-} + 2O_2 \rightarrow SO_4^{2-} + 2O_2^-$

$SO_3 + SO_4^{2-} \rightarrow S_2O_7^{2-}$

Thus the cathodic polarization causes the consumption of dissolved oxygen (or oxidized oxygen ions) at the oxide/salt (O/S) interface, while the basicity remains almost unchanged. As the cathodic polarization continues, another reduction reaction occurs at a lower (more cathodic) potential;

$\frac{1}{2} O_2 + 2e^- \rightarrow O^{2-}$

That reaction should contribute a minor increase in basicity.

But a significant change in basicity occurs when the salt directly contacts a bare metal surface; then the following reaction as suggested by Goebel and Pettit (10) takes place.

$4Ni + Na_2SO_4 \rightarrow NiS + 3NiO + Na_2O$

$Na_2O$ produced by that reaction shifts the melt chemistry from the acidic dissolution regime to the basic dissolution regime for NiO. Since Eq. [118] forms NiS, the local melt chemistry has to reach the stability region of nickel sulfide via cathodic polarization. If the protective nickel oxide is thick and compact, no direct contact between the salt and the base metal can be made, so that reaction in Eq. [118] will not
occur regardless of the melt chemistry. But if the thickness of oxide is marginal, or if flaws exist, dissolution of locally thin oxides could permit direct contact eventually between the metal and the salt.

From the microstructure observation of the NiO scale done by Rapp (62) and this research (see Plates I, II, and III), the oxide is not a uniform barrier of homogeneous structure, but a rough inhomogeneous layer with distributed defects such as grain boundaries and small pores. Local penetration of the salt can happen at these defects, especially when the oxide layer is thin. Once the contact of the salt with the metal has been made, sulfidation of Ni (Eq. [118]) can drastically change the melt chemistry and the concentration profiles of the relevant species. As shown in Fig. 62a, the concentration of oxide ions (basicity) increases at the oxide/salt (O/S) interface, creating a basicity gradient across the salt film, because of the local sulfidation of exposed Ni. The excess oxide ions diffuse outward to the more acidic salt/gas interface (S/G), but the local basicity at O/S is still higher than that at S/G. At this stage, the chemistry of the salt film is dominated by the sulfidation reaction. The film chemistry at the two interfaces can be located schematically in the solubility plot as shown in Fig. 62b. Before active hot corrosion starts, both O/S and S/G are on the acidic dissolution side. Once the sulfidation reaction begins, both interfaces are shifted to the basic dissolution side. Because
of its dependences on basicity and oxygen activity, the solubility of NiO in the basic dissolution regime at the O/S interface is higher than that at the S/G interface due to a lower oxygen activity at O/S. Thus a negative solubility gradient is established. This condition satisfies the Rapp-Goto criterion (see Eq. [7]) for sustained hot corrosion.

When active hot corrosion is in progress, simultaneous scale fluxing and reprecipitation caused by the negative solubility gradient for the oxide in the salt film occurs. NiO dissolves at the O/S interface as basic NiO₂⁻ ions which migrate to a region of lower solubility, where a porous, non-protective oxide is precipitated. As suggested by Lee and Shores (63) when studying transport phenomena in the hot corrosion of Ni by molten alkali carbonates, a sufficient steady-state flux of dissolved NiO must be sustained to be consistent with the observed corrosion kinetics, i.e.,

\[ J_{\text{max}}(\text{dissolved NiO}) \geq R_{\text{corr}} \]

where \( J_{\text{max}} \) is the maximum flux of dissolved NiO, and \( R_{\text{corr}} \) the corrosion rate. From Fick’s first law,

\[ J_{\text{max}}(\text{dissolved NiO}) = D_{\text{NiO}} \frac{\partial C_{\text{NiO},0/S}}{\partial x} \]

From the data given by Gupta and Rapp (50) NiO solubility at the O/S is calculated to be \( 1.44 \times 10^{-5} \) mole/cm³. No information for NiO₂⁻ diffusion in molten Na₂SO₄ is available, but the diffusion coefficient of Ni²⁺ was found to be \( 3.3 \times 10^{-6} \) cm²/s
in a Li$_2$SO$_4$-K$_2$SO$_4$ melt at 873K (64). At 1200K, the diffusion coefficient of NiO$_2^-$ is estimated to be $5 \times 10^{-9}$ cm$^2$/s. Using the corrosion rate reported by Otsuka and Rapp (18) for the hot corrosion of Ni by a Na$_2$SO$_4$ film at 900°C ($\approx 3.7 \times 10^{-7}$ mole/cm$^2$-s), the effective diffusion length should be $2 \times 10^{-3}$ cm to satisfy Eq. [119], which is reasonable. Therefore, the dissolution flux is large enough to sustain the active hot corrosion. Fluxing of NiO due to a negative solubility gradient is an acceptable mechanism for the accelerated oxidation of Ni suffered in active hot corrosion in Na$_2$SO$_4$. 
Figure 62. Schematic diagrams representing the application of the Rapp-Goto criterion for fluxing. (a) concentration gradients, (b) solubility gradient.
CHAPTER VII
CONCLUSIONS

Hot corrosion of preoxidized Ni covered with a thin fused Na₂SO₄ film in a SO₂-O₂ gas atmosphere was investigated at 1200 K by AC impedance techniques. Preoxidation conditions as well as specimen purity were varied in order to study different reaction mechanisms for Ni in the thin salt film environment.

When 99.9975% pure Ni was preoxidized in oxygen at 1200K for 2 hours, the resulted oxide was thick and protective. After contact with a thin fused Na₂SO₄ film in a 0.1%SO₂-O₂ gas for 6 hours, no hot corrosion was observed for this sample. From the impedance data after cathodic polarization for 6 hours, a passive film model was proposed to explain the mechanism for this type of experiment. The total impedance of a metal/metal oxide/salt system can be treated as the sum of the impedances of metal/oxide interface, of oxide film itself, and of the oxide/salt interface. In this experiment, the interfacial reaction impedances of charged particles (Ni cation vacancies and holes) at the oxide/salt interface and the oxide film impedance are dominant. From the value for the charge transfer resistance in the oxide film, the conductivity
of NiO is calculated and agrees well with the reported value for similar experimental conditions. For the interfacial impedance at the oxide/salt interface, diffusion of $\text{SO}_3^-$ (as $\text{S}_2\text{O}_7^{2-}$ ions) plays an important role, which results in a Warburg behavior in the low frequency range.

When the preoxidation time was shortened to 1 hour in air at 1200K, 99±% pure Ni with a thinner oxide than the previous passive case remained passive until external cathodic polarization was applied. When the cathodic polarization brought the melt chemistry to the region of nickel sulfide stability, a drastic increase in basicity shifted the melt from the acidic dissolution regime to the basic dissolution regime for NiO. Hot corrosion was evident both from the potentiometric trace of basicity and oxygen activity and from the final sample examination. This pseudo-passive behavior can be explained as follows. When the melt chemistry is in the NiO stability region, no direct contact between the base metal and salt film has been made. From the impedance spectroscopy obtained during this period, one dominant process is the diffusion of the $\text{S}_2\text{O}_7^{2-}$ ions in the salt; probably the diffusion of nickel cation vacancies in the oxide is also important, but cannot be exclusively decided by EIS. Because the oxide layer is thin, the passive state only lasts until cathodic polarization coupled with oxide dissolution forces the sulfidation of Ni to occur upon salt/metal contact. After that, active hot corrosion proceeds and causes the impedance
spectroscopy to change to a chemical reaction/diffusion-
controlled behavior.

The active hot corrosion behavior was also observed for
99+\% pure Ni preoxidized in air for only 5 minutes at 1200 K
without the preceding passive behavior as in the pseudo-
passive case. Although the fast changing nature of this
active state caused some scatter in the impedance data, the
basic features bear a good resemblance to the active part of
the pseudo-passive case. The overall reaction is suggested to
be a preceding electrochemical reaction (oxidation of nickel)
coupled with a chemical reaction (basic dissolution of nickel
oxide). Computer-simulated impedance based on the suggested
reaction scheme fits the experimental data quite well.

In this research, the negative solubility gradient
criterion for self-sustaining hot corrosion proposed by Rapp
and Goto is confirmed. For the active hot corrosion state,
the chemistry of the melt is located in the range of the basic
dissolution of NiO, thereby establishing the basicity gradient
across the thin fused salt film. The basicity gradient
creates the negative solubility gradient for NiO and thus
maintains the self-sustaining hot corrosion for Ni. The
analysis of the transport rate of dissolved oxide through the
salt film also supports the Rapp-Goto fluxing criterion.
APPENDIX

A. Simulation For Bounded Diffusion Impedance

The following computer program was written based on Eq. [B1] which describes impedance of a bounded (limited) diffusion process. In the program, ARG = \( \delta / \sqrt{2D} \) and RR = \( RT^6/(n^2F^2DC) \), so \( ZW \) in Eq. [B1] can be expressed as

\[ RR \cdot \tanh(\text{ARG} \cdot \sqrt{\omega})/(\text{ARG} \cdot \sqrt{\omega}). \]

```plaintext
DIMENSION X(250,3)
OPEN(10,FILE='Z.DAT',STATUS='NEW')
DO 100 J=1,250
  W=10**(-2+(8.*J/250.))
  CALL LIMITED(ARG,W,FF,XX,YY)
  X(J,1)=FF
  X(J,2)=XX
  X(J,3)=YY
  WRITE(10,'(2F15.8)')X(J,2),X(J,3)
100 CONTINUE
END

C THIS SUBROUTINE CALCULATE RR*TANH(Z)/Z
C WARBURG COEFF. SIG = RR/ARG
SUBROUTINE LIMITED(ARG,W,X11,X12,X13)
COMPLEX*16 A,B,CTAHN,ZZ,ZIZZ
REAL*8 XI,X2,RR,ARG,W,ARGG
A=(1.,0.)
B=(0.,1.)
ARGG=ARG*DSQRT(W)
IF(DABS(ARGG).GT.85.0) THEN
  CTANH=(1.,0.)
ELSE
  XI=DTANH(ARGG)
  X2=DTAN(WARGG)
  CTANH=(XI+B*X2)/(A+B*XI*X2)
END IF
ZZ=A*ARGG+B*ARGG
XI1=W/(2*3.14159)
ZIZZ=CTANH/ZZ
```

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XI2=RR*DREAL(ZZZ)
XI3=-1*RR*DIMAG(ZZZ)
RETURN
END

B. Simulation for Passive State Impedance

The following program was written based on the equivalent circuit shown in Fig. 33b for Ni WE in passive state.

```plaintext
REAL*8 COS,CMO,RH,R,SIGM,W,RS,LOGF,THE
COMPLEX*16 ZMO,ZOS,ZTOT,A,B
DIMENSION X(250,10)
OPEN(10,FILE='OX.DAT',STATUS='NEW')
OPEN(12,FILE='OB.DAT',STATUS='NEW')
A=(1.,0.)
B=(0.,1.)
COS=500.E-6
CMO=100.E-6
RS=1.654
RH=1.
R=10.
SIGM=62.07
DO 100 J=1,250
  W=10**(-2+(8.*J/250.))
  ZMO=1./RH+B*W*CMO
  ZOS=1./(R+SIGM*(A-B)/SQRT(W))+B*W*COS
  ZTOT=RS+1./ZMO+1./ZOS
  X(J,1)=DREAL(ZTOT)
  X(J,2)=-1.*DIMAG(ZTOT)
  WRITE(10,'(2F15.8)')X(J,1),X(J,2)
  LOGF=DL0G10(W/(2*3.14159))
  THE=-1.*ATAND(X(J,2)/X(J,1))
  WRITE(12,'(2F15.8)')LOGF,THE
100 CONTINUE
END
```

C. Simulation for Pseudo-Passive Reaction Impedance

Computer simulation program for impedance behavior described in the equivalent circuit shown in Fig. 43 is listed below.

```plaintext
DIMENSION X(250,8)
COMPLEX*16 ZWA,ZWC,ZTAL
```
REAL*8 RRA,ARGA,RRC,ARGC,W
OPEN(10,FILE='ZWA.DAT',STATUS='NEW')
OPEN(11,FILE='ZWC.DAT',STATUS='NEW')
OPEN(12,FILE='ZTAL.DAT',STATUS='NEW')
A=(1.,0.)
B=(0.,1.)

C CALCULATE THE ANODIC BRANCH

DO 100 J=1,250
W=10.*-(2+(8.*J/250.))
CALL LIMITED(ARGA,W,FA,XA,YA)
X(J,1)=FA
X(J,2)=XA
X(J,3)=YA
WRITE(10,'(2F15.8)')X(J,2),X(J,3)
ZWA=A*X(J,2)+B*X(J,3)

C CALCULATE THE CATHODIC BRANCH

CALL LIMITED(ARGA,W,FC,XC,YC)
X(J,4)=FC
X(J,5)=XC
X(J,6)=YC
WRITE(11,'(2F15.8)')X(J,5),X(J,6)
ZWC=A*X(J,5)+B*X(J,6)

C CALCULATE THE TOTAL IMPEDANCE

ZWA=1./ZWA
ZWC=1./ZWC
ZTAL=ZWA+ZWC+B*W*C
ZTAL=1./ZTAL+RS
X(J,7)=DREAL(ZTAL)
X(J,8)=DIMAG(ZTAL)
WRITE(12,'(2F15.8)')X(J,7),X(J,8)
100 CONTINUE
END

D. Simulation for Active Hot Corrosion Impedance

The following computer program was written based on the equivalent circuit shown in Fig. 59. The impedance for the anodic reaction is described by Eq. [112] and the impedance for the cathodic reaction is the diffusion impedance shown in Eq. [81].
REAL*8 CDL, RV, ARGV, RNI2, ARG2, RC, ARGC, W
REAL*8 SKA, KA, SG
COMPLEX*16 ZZN, ZZC, ZZT, A, B, SJ
DIMENSION X(250,14)
A=(1.,0.)
B=(0.,1.)
DO 200 J=1,250
W=10.*(-2.+B.*J/250)
G=SKA/W
SG=G**2+1
SGG=SQR(SQR(SG)+G)/SQR(SG)
GSS=SQR(SQR(SG)-G)/SQR(SG)
CALL LIMITED(ARGV,W,FF,XX,YY)
X(J,2)=RV*XX
X(J,3)=RV*YY
CALL LIMITED(ARG2,W,FFF,XXX,YYY)
X(J,8)=RNI2*XXX
X(J,9)=RNI2*YYY
CALL LIMITED(ARGC,W,FFFF,XX,XX,YY,YY)
X(J,11)=RC*XX
X(J,12)=RC*YY
ZZC=A*X(J,11)+B*X(J,12)
X(J,5)=X(J,8)*KA/(KA+1.)+X(J,8)/(KA+1.)*SGG+X(J,2)
X(J,6)=X(J,9)*KA/(KA+1.)+X(J,9)/(KA+1.)*GSS+X(J,3)
ZZN=A*X(J,5)+B*X(J,6)
SJ=B*W
ZZT=CDL*SJ+1./ZZN+1./ZZC
ZZT=1./ZZT+RS
XJ12=DIMAG(SJ)/(2*3.14159)
X(J,13)=DREAL(ZZT)
X(J,14)=DIMAG(ZZT)
200 CONTINUE
STOP
END
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