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ELECTRODE-POLARIZATION STUDIES
IN HOT-CORROSION SYSTEMS

Progress Report
for period
1 June 1980 - 31 May 1981

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SUMMARY OF RESEARCH

The work reported herein is in compliance with the proposed technical scope of this project which stated:

"The work under this contract will be unclassified and will consist of polarization experiments on metals and alloys in sulfur-bearing molten salts under reducing atmospheres, liquid line corrosion studies in the same systems, and gas/metal reaction studies in sulfur-bearing reducing gases. Kinetic studies and metallographic analyses will be performed in each area."

As per agreement, principal investigator effort has constituted approximately 9 academic months at 10% of full time plus 3 summer months at full time.

PROGRESS REPORT

A. Overall Project

1. Personnel

a. Principal Investigator

Owen F. Devereux, Professor of Metallurgy

b. Graduate Assistants

Venkat Iyer - MS expected 1981.

Chien-Tung Liu - MS expected 1982.

Dane Wilson - PhD expected 1981.

Kook Sun Yeum - PhD expected 1982.

c. Current Employment of Former Graduate Assistants

Ross Boland - Howmet, Austenal Dover Division, Dover, New Jersey.

Richard Cooke - Gillette, Boston, Massachusetts.

Kyoo Young Kim - IITRI, Chicago, Illinois

2. Publications (cumulative list)

a. K. Y. Kim and O. F. Devereux, "Use of Alumina as a Sheath for the Pt, CO/CO_2 | Na_2CO_3 Reference Electrode", J. Electrochem. Soc. **125**, 1796 (1978). (2 reprint requests)

b. O. F. Devereux, "Polarization Curve-Fitting by Computer Modelling", Corrosion **35**, 125, (1979). (19 reprint requests)

c. R. Boland and O. F. Devereux, "Intergranular Sulfidation of Iron", Met. Trans. **10A**, 1959, (1979). (4 reprint requests)

d. O. F. Devereux and K. Y. Kim, "Computer Modelling of Polarization in Passive Systems", Corrosion **36**, 262 (1980). (2 reprint requests)

e. R. A. Cooke and O. F. Devereux, "Simulation of Coal Conversion Reactor Environments", Corrosion **36**, 167, (1980). (2 reprint requests)

f. K. Y. Kim and O. F. Devereux, "Reactions at the CO, CO_2 | Ni Electrode in Molten Sodium Carbonate". (Submitted)

3. Graduate Theses (Cumulative list)

- a. R. A. Cooke, "Coal Gas/Sodium Salt Equilibria", MS Thesis, University of Connecticut, 1978.
- b. Ross Boland, "High Temperature Intergranular Sulfidation of Armco Iron by Hydrogen Sulfide", MS Thesis, University of Connecticut, 1979.
- c. Venkatraman Iyer, "Liquid Line Corrosion of Ni-200 in Molten Sodium Carbonate", MS Thesis, University of Connecticut, 1981.
- d. Kyoo Young Kim, "Electrode Polarization Studies in Hot Corrosion Systems", PhD Thesis, University of Connecticut, 1981.

4. Presentations (Cumulative list)

- a. K. Y. Kim and O. F. Devereux, "A Pt,CO/CO₂ | Na₂CO₃ Reference Electrode for Use in Molten Sodium Carbonate and Other Salts", Fall Meeting of The Electrochemical Society, Pittsburgh, Oct. 1978.
- b. K. Y. Kim and O. F. Devereux, "Electrode Polarization Studies in Molten Sodium Carbonate under Reducing Environments", Fall Meeting of The Electrochemical Society, Los Angeles, Oct., 1979. (1 reprint request)
- c. K. Y. Kim and O. F. Devereux, "Electrode Polarization Studies under CO/CO₂ and CO/CO₂/H₂/H₂S in Molten Na₂CO₃", International Conference on High Temperature Corrosion, March 1981, Phoenix, Arizona. (To be presented; proceedings will be published.)

B. Task Summaries

1. Electrode Polarization Studies in Molten Sodium Carbonate (Kim, Yeum)

The area of greatest advance in this task has been the application of the concepts of absolute reaction rate theory to the interpretation of the empirical constants describing the polarization curves for the $\text{CO}, \text{CO}_2 \mid \text{Ni}$ electrode in molten sodium carbonate. Necessarily this is a trial-and-error process in which various reaction mechanisms are postulated and their rates predicted by kinetic theory. These predictions are then compared to the actual behavior of the empirical constants to confirm or refute the postulate. In the case of this electrode five different reactions have been identified as probably contributory to anodic current; oxidation of CO by two different paths, oxidation of nickel to the nickelous state and subsequently to a higher state, and oxidation of carbonate.

2. Electrode Polarization Studies in Molten Sodium Sulfide (Liu)

The suitability of Na_2S as an electrolyte at 1000°C has been explored and found to be poor in several respects: stability, safety, deliquescence, and cost. The use of Na_2S_4 , sodium polysulfide, at substantially lower temperatures, e.g., 300°C , has been discounted temporarily as a short-term project due to the necessity of developing a reference electrode employable in that temperature range. Current attention is focused upon the use of 75% FeS - 25% Na_2S at 1000°C as minimizing the disadvantages of Na_2S while introducing as a disadvantage only the possibility of current carried by $\text{Fe}^{++}/\text{Fe}^{+++}$ reactions.

3. Liquid Line Corrosion (Iyer)

This project has terminated with Mr. Iyer's MS thesis. The particular attack profiles seen on metal specimens at rest at the sodium carbonate/atmosphere interface were postulated to be the result of the interaction of

two transfer processes: diffusion of the oxidant from the liquid surface to the electrode surface and diffusion of the cationic product of the anodic reaction from the electrode surface into the bulk electrolyte, together with displacement of the electrolyte meniscus along the electrode surface due to evaporation. The mathematical problem thus presented is complex and was not deemed justified in the context of this project. As a simplification, the diffusion of reaction product away from the electrode was postulated as not rate-limiting, leaving approximate solution of the remaining two processes as tractable. Thus, rate of oxidant transport as a function of position along the electrode was established to within a proportionality constant (reflecting lack of knowledge of either boundary values or diffusivities of the oxidant in the electrolyte) and a displacement constant (reflecting uncertainty of the exact position of the junction of the meniscus and the electrode surface), and compared to the attack profile. A reduction of attack depth with increasing oxidant pressure was interpreted in terms of passivity.

4. Gas/Metal Reactions in Mixed Oxidants (Wilson)

Although considerable effort has been expended on this task during the report period, there has been little real progress. A key to rational modelling of attack of metals by mixed oxidants is an ability to describe phenomena in a single oxidant. As noted in the previous Progress Report, there are actually different types of kinetic behavior observed in the sulfidation of iron by different investigators. At that time, this had been roughly correlated with a size effect. During this report period, attempts have been made to express such an effect in terms of 1) growth stress in the scale and 2) gas phase transfer. Problems are presently being experienced in obtaining adequate numerical resolution in the matching of model to experiment to ensure a meaningful reproducibility.

C. Extended Discussion of Progress

1. Electrode Polarization Studies in Molten Carbonate (Yeum)

Experimental Procedure

Details of the apparatus and procedure were given previously.¹ In brief, nickel electrodes are polarized in molten sodium carbonate at 1000°C employing a platinum counter electrode and a previously described reference electrode reversible to reaction (1).

The reference gas composition, $P_{\text{CO}} = 0.382$ atm and $P_{\text{CO}_2} = 0.618$ atm, requires zero Nernstian correction. The stability of the equilibrium potential in the carbonate melt has already been found excellent.² Electrolytic contact between the cell and reference electrolyte is maintained by Na^+ ion conduction through the alumina tube jacketting the electrode. Potential is controlled and current measured via standard instrumentation, and output is plotted as an analog x-y plot of cell potential vs. log cell current. Sufficient points to define these polarization curves are input to a computer program and replotted on a graphics terminal together with a calculated curve. The parameters describing the latter are optimized through a series of successive guesses based on the degree of conformity to the experimental curves.

In a separate series of experiments, nickel specimens were held at particular anodic potentials for extended periods and then removed for x-ray diffraction analysis of the scales.

The feed gas used in this experiment was a mixture of 0.50 CO and 0.50 CO₂ and a mixture of 0.25 CO, 0.25 CO₂ and 0.50 H₂. Polarization curves obtained under the two gas atmospheres were compared to each other.

Results

The current, i_{aj} , carried by the j^{th} anodic reaction experiencing activation, concentration and resistance polarization is given by

$$i_{aj} = (1 - i_{aj}/i_{saj})^{RT/nFb_{aj}} \exp[(V - V_{aj}^0)/b_{aj}] \exp(-i_{aj}R_a/b_{aj}) \quad (2)$$

where i_{saj} is the limiting diffusion current; R , T and F the usual constants; n , the number of charges on the species controlling the limiting diffusion current; $2.303 b_{aj}$, the Tafel slope; V_{aj}^0 , a constant incorporating the concepts of the "rest potential" and the "exchange current"; and R_a is the cell resistance. Similarly, the current carried by the j^{th} cathodic reaction is given by

$$i_{cj} = (1 - i_{cj}/i_{scj})^{RT/nFb_{cj}} \exp[(V - V_{cj}^0)/b_{cj}] \exp(-i_{cj}R_c/b_{cj}) \quad (3)$$

The total cell current is given by

$$i = \sum_{j=1}^{n_a} i_{aj} - \sum_{j=1}^{n_c} i_{cj} \quad (4)$$

where n_a is the total number of anodic reactions possible and n_c the number of cathodic reactions. Not all reactions experience concentration polarization; for these the limiting diffusion current is simply an arbitrarily large value. Similarly, only the anodic and cathodic reactions dominant at the largest overpotentials are, in our model, assumed to be affected by resistance polarization; for the other reactions the resistance is set at zero. Cell resistance under anodic polarization was permitted to assume a different value from that under cathodic polarization because, in our experience, this provides for an optimum empirical fit of model to data. Passivation of anodic reactions is incorporated into the model by simply defining the current carried by that reaction above a particular potential, V_{pj} , to be a constant, i_{pj} .

Anodic and cathodic polarization curves obtained under an atmosphere of 0.50 CO and 0.50 CO₂ are shown in Figures 1 to 3, and the parameter values upon which these curves are based are listed in Table I. The dotted lines on the figures represent a series of data points taken from experimentally-determined potential vs. log current plots, and the solid line the curve calculated from the parameters chosen to ensure conformity to the data points. Comparison of the three figures and sets of parameters, obtained under the same conditions and procedures, show that the reproducibility of the data is satisfactory.

The cathodic polarization curves are represented by two reactions; the low current region is considered to have been affected by oxygen contamination of the cell atmosphere; however, the anodic behavior of the sample did not appear to be affected significantly. The anodic curves were reasonably well-defined by a total of four reactions, with two passive regions observed at 300 mV and 620 mV. If f is defined as $F/2.303 RT$, the Tafel slopes for the reactions are approximately $1/f$, $1/4f$, $1/3f \sim 1/2f$ and $1/4f$ respectively. The cell resistances obtained at the largest overpotential region show that the resistance under anodic polarization is higher than that under cathodic polarization by 0.8 ohm.

E/P_{CO₂} Diagram

All the thermal data necessary for the construction of the diagram were taken from the JANAF Tables³ except for NiO⁴ and NiCO₃. The data for NiCO₃ were available only in the temperature range, 298°K-700°K.⁵ The Gibbs free energy of formation for NiCO₃ at 1273°K was calculated from the data by extrapolation, ignoring the heat of fusion of NiCO₃ which does not seem to be established. $\Delta G_{1273}^0(\text{NiCO}_3)$ was computed as -87,201 cal./mole by following the procedure described in Appendix. The data used in constructing the diagram are listed in Table II.

Table I: Values of Empirical Constants

Sample No.	1	2	3
i_{a1}^S (ma/cm ²)	2	2	1.6
V_{a1}^0 (mV)	70	70	50
V_{a2}^0 (mV)	280	270	280
V_{a3}^0 (mV)	535	535	530
V_{a4}^0 (mV)	870	900	870
b_{a1} (mV)	110	120	110
b_{a2} (mV)	30	30	30
b_{a3} (mV)	40	40	50
b_{a4} (mV)	30	25	25
R_a (mV)	2.8	2.8	2.6
i_{c1}^S (ma/cm ²)	4.0	2.0	4.5
V_{c1}^0 (mV)	-80	-120	-80
V_{c2}^0 (mV)	-350	-390	-350
b_{c1} (mV)	130	160	120
b_{c2} (mV)	110	100	110
R_c (ohm)	2	2	2

Standard potentials have been calculated from the equation, $\Delta G^0 = -nFE^0$. Metal nobility is associated with a positive potential; similarly, a positive potential expresses oxidizing conditions in the melt. The potentials for some of the reactions are dependent on the pressure of CO_2 and CO in the gas phase. Thus for reaction (1) the potential is, if the activity of $\text{CO}_3^{=}$ ions is taken to be close to unity,

$$E = E^0 + 2.3 \frac{RT}{2F} \log \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}} \quad (5)$$

An investigation⁶ of the CO/CO_2 electrode in carbonate melts showed that the above relation is accurately obeyed. Relative to the CO/CO_2 reference electrode ($P_{\text{CO}} = 0.382 \text{ atm}$, $P_{\text{CO}_2} = 0.618 \text{ atm}$), Eq. (5) can be rewritten, for 1000°C ,

$$E = 0.1263 \log \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}} \quad (5a)$$

The E/P_{CO_2} diagram for the system nickel-sodium carbonate at 1000°C constructed by the method of Janz⁷ is shown on Figure 4. The Ni , NiCO_3 and NiO isoactivity lines divide the diagram into three parts, corresponding to immunity, corrosion and passivity of the metal, if it is assumed as by Pourbaix⁸ for aqueous solutions that the occurrence of corrosion implies an overall activity of ions exceeding 10^{-6} . However, it is to be noted that these lines are purely thermodynamic; in particular as far as passivation is concerned, its actual occurrence depends on number of properties of the oxide film, including primary adherence and coherence.

This diagram can be a rough guide to predict the corrosion behavior of nickel in a sodium carbonate melt. In our polarization cell, $\log P_{\text{CO}_2}$ will be nearly zero. Thus it is expected that NiO may be produced just above 240 mV and only gas reactions will be possible below the potential. Decompo-

sition of CO_3^- ions is considered to become possible above 800 mV. At sufficiently negative potentials carbon deposition may be observed. The dissolution of nickel into the melt is supposed to be negligible at any potential.

Table II: Gibbs Free Energy of Formation at 1273°K

Compounds	$\Delta G_{1273}^0(\text{cal})$
CO (g)	- 53,565
CO ₂ (g)	- 94,696
NiO (s)	- 30,150
Na ₂ CO ₃ (l)	-184,485
Na ₂ O (l)	- 53,710
H ₂ O (g)	- 42,386
NiCO ₃ (l)	- 87,201

Reactions under CO/CO₂ Atmosphere

Four distinct stages in the anodic polarization curve designated as Stage 1, 2, 3, and 4, for convenience of discussion, are shown on Figure 5.

Nickel will not corrode at low anodic overpotentials as shown on Figure 4. In this range current is postulated to be carried by reaction (1) as observed by other investigators^{9,10} on non-corroding electrodes (gold and platinum). Borucka and Appleby¹¹, studying the dependence of the polarization curve on P_{CO_2} and P_{CO} suggested the following mechanism for the reaction

in which CO^+ and CO_2^- are transient intermediates. An application of electrode kinetics^{12,13} to this mechanism will give a Tafel constant value of 2.3 RT/F , i.e., $2.3 \times 110 \text{ mV}$ at 1000°C . Our experimentally determined parameter is consistent with this value.

Borucka¹⁰ demonstrated the existence of the CO_2^- ion in molten alkali carbonates by measuring relaxation time at various potentials after addition of Li_2O , and suggested that the reaction

occurs at higher current values. The behavior in Stage 2 may represent this reaction. Comparison of anodic polarization data for nickel to those for platinum or gold indicate that the succession of activity and passivity in Stage 2 is related to the surface characteristics of the metal. Inert electrodes did not show this passivation. Janz and Conte¹⁴ showed that passivation appears not only at this stage but also at higher overpotentials when nickel is anodically polarized in ternary eutectic alkali carbonate mixtures at 700°C ; however, they did not discuss the passivation observed at this stage. In the interpretation of passivation in aqueous solutions, at least two parallel reactions are considered. This treatment is presumed valid in the system nickel-sodium carbonate. Our suggested reactions at this stage are reaction (8) and

and reaction (8) is assumed to be inhibited due to complete coverage of nickel surface with NiO before the limiting current for reaction (8) is reached.

The second passivation, observed at 880 mV , is presumed to be caused by the formation of other oxides, although higher oxides such as Ni_2O_3 and NiO_2 are generally considered unstable.¹⁵ From x-ray diffraction analysis of the scale, NiO was identified in this region but other forms of oxide were not

detected. NiO is reported to have an NaCl structure (fcc) with $a = 4.177 \text{ \AA}$ ¹⁶ and also $a = 4.172 \text{ \AA}$.¹⁷ Among a number of other oxides reported, the formation of Ni_2O_3 (fcc, $a = 4.186 \text{ \AA}$)¹⁸ and Ni_2O_3 (hexagonal, $a = 4.61 \text{ \AA}$, $c = 5.61 \text{ \AA}$)¹⁹ are considered to be most probable; however, the latter was not found and the former would not be detected due to the very small difference in the lattice parameters between NiO and Ni_2O_3 (fcc). As a high anodic potential represents a highly oxidizing condition, the appearance of higher oxides is of significant possibility; however, it is considered that even though higher oxides may be formed in the passivation region, they might be transformed to stable NiO during the cooling period after the polarization run. It is, therefore, suggested that the Stage 3 passivation occurs by the reaction

At Stage 4 (above 800 mV), the electrode reaction is

The above reaction was verified by various investigators^{9,20} by anodic off-gas analysis which showed that the CO_2/O_2 ratio increases with increase in current in this potential range, reaching 1.8~2.0 at very high currents. The resistance value obtained from our data was 2.8 ohms and affects the polarization curve only in this stage. The resistance polarization term will be 28 mV at 10 ma and 280 mV at 100 ma. The Tafel slope obtained after subtracting this term was approximately $2.8 \text{ RT}/4\text{F}$. This reaction is also presumed to occur through a series of steps; however, the mechanism for the reaction, unlike oxygen evolution reaction from aqueous solution, is not known.

The cathodic polarization curve shows two reactions. At low currents, oxygen contamination is presumed to have shifted the polarization curve to the right as only one reaction is supposed to be significant under cathodic

polarization:

If the oxygen contamination is neglected, the Tafel constant obtained empirically is $2.3 \times 110 \text{ mV}$. This value is almost equal to the theoretical value.

Brocuka suggested that solid carbon is liable to deposit at high cathodic overpotentials. The application of her treatment to our system gives -549 mV as the lower limit for the potential of CO/CO_2 electrode, referred to as the Boudouard potential. Below this potential carbon deposition is favored and has been occasionally seen in our system.

Reactions under $\text{H}_2/\text{CO}/\text{CO}_2$ atmosphere

A polarization curve for nickel under an atmosphere of $P_{\text{H}_2} = 0.5 \text{ atm}$, $P_{\text{CO}} = P_{\text{CO}_2} = 0.25 \text{ atm}$ is shown in Figure 6, and the empirical parameters for the curve are listed in Table III. When a mixture of CO , CO_2 and H_2 is input to the cell, water will be produced by the reaction

for which the equilibrium constant, K , at 1000°C is

$$K = \frac{P_{\text{H}_2\text{O}} P_{\text{CO}}}{P_{\text{H}_2} P_{\text{CO}_2}} = 1.643 \quad (14)$$

By letting x be the amount of H_2 oxidized to H_2O , we get the relation

$$\frac{x (0.25 + x)}{(0.5 - x)(0.25 - x)} = 1.643 \quad (14a)$$

giving $x = 0.1481 \text{ atm}$. Thus the equilibrium gas composition will be $0.1481 \text{ H}_2\text{O}$, 0.3981 CO , 0.3519 H_2 and 0.1019 CO_2 .

At low anodic overpotentials, two electrochemical reactions can take place: oxidation of CO,

and oxidation of H₂,

The equilibrium potential for each reaction may be predicted by the Nernst relation

$$E = 0.1263 \log \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}} \quad (5a)$$

and

$$E = -0.0273 + 0.1263 \log \frac{P_{\text{H}_2\text{O}} P_{\text{CO}_2}}{P_{\text{H}_2}} \quad (16)$$

Substitution of the equilibrium composition in these equations gives a equilibrium potential value of -200 mV. The observed open circuit potential was -293 mV, suggesting that reaction (13) does not achieve equilibrium.

The gas mixture of the same H₂/CO/CO₂ composition was bubbled through water and input to the cell. The polarization curve obtained showed no difference in shape or open circuit potential when it was compared to the former curve. The small amount of water contained in the gas mixture (~3%) would not have a significant effect on the equilibrium composition determined by reaction (13). Calculation showed that this amount of water would displace the potential in the positive direction by 9 mV, a difference too small to be detected in our measurement.

Table III: Values of Empirical Constants for the Cell
in a $H_2/CO/CO_2$ Atmosphere

Anodic	$i_a^S (ma/cm^2)$	$V_a^0 (mV)$	$b_a (mV)$	$R_a (ohm)$
#1	1.7	-900	110	
#2	2.0	100	110	
#3	$9,000^{(*)}$	140	25	
#4	$9,000^{(*)}$	150	25	
#5	9,000	800	25	2.8
Cathodic	$i_c^S (ma/cm^2)$	$V_c^0 (mV)$	$b_c (mV)$	$R_c (ohm)$
	$9,000^{(*)}$	-180	160	1.8

(*) : The reactions were not found to be diffusion-limited; the large value was arbitrarily used for curve-fitting

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Figure 1.

Figure 2.

Figure 3.

Figures 1, 2 and 3. Experimental Data Points and Calculated Polarization Curves for Ni-200 obtained under an Atmosphere of 0.50 CO and 0.50 CO₂.

- a: Dissociation of carbonate*
 $E = 0.891 + 0.1263 \text{ Log } P_{\text{CO}_2} P_{\text{O}_2}^{1/2}$
- b: Formation of nickelous oxide*
 $E = 0.238 + 0.1263 \text{ Log } P_{\text{CO}_2}$
- c: Deposition of graphite*
 $E = -0.135 + 0.1895 \text{ Log } P_{\text{CO}_2}$

Figure 4. $E/\text{Log } P_{\text{CO}_2}$ Diagram For
 $\text{Ni}-\text{Na}_2\text{CO}_3$ At 1000°C

Figure 5. A Typical Anodic Polarization Curve. $P_{CO} + P_{CO_2} = 1 \text{ atm}$ And $P_{CO}/P_{CO_2} = 1$. The Curve Is Divided Into Four Distinguishable Stages.

Figure 6. Experimental Data Points and Calculated Polarization Curve for Ni-200 obtained under an Atmosphere of 0.25 CO_2 , 0.25 CO and 0.50 H_2 .

Appendix

ΔG_{1273}^0 of NiCO_3 was calculated by using the following data:⁵

$$\Delta H_{298}^0 = -162,500 \text{ cal}$$

$$S_{298}^0 = 20.4 \text{ e.u.}$$

$$C_p = 22.0 + 9.3 \times 10^{-3} T - 2.95 \times 10^5 T^{-2}$$

then

$$(H_{1273}^0 - H_{298}^0)_{\text{NiCO}_3} = \int_{298}^{1273} C_p dT = 27,814 \text{ cal}$$

and

$$S_{1273}^0 = S_{298}^0 + \int_{298}^{1273} \frac{C_p}{T} dT = 59.842 \text{ e.u.}$$

Thermochemical data for Ni, C and O_2 necessary for the calculation is summarized as follows:²¹

	Ni	C	O_2	NiCO_3
S_{1273}^0	17.87	7.09	60.22	59.843 (e.u.)
$H_{1273}^0 - H_{298}^0$	7,396	4,239	7,643	27,814 (cal/mole)

The enthalpy of formation will be

$$\begin{aligned} \Delta H_{1273}^0 &= \Delta H_{298}^0(\text{NiCO}_3) + (H_{1273}^0 - H_{298}^0)_{\text{NiCO}_3} - [(H_{1273}^0 - H_{298}^0)_{\text{Ni}} + (H_{1273}^0 - H_{298}^0)_{\text{C}} \\ &\quad + 3/2 (H_{1273}^0 - H_{298}^0)_{\text{O}_2}] \\ &= -157,786 \text{ cal} \end{aligned}$$

The Gibbs free energy of formation, ΔG_{1273}^0 , can be obtained from the equation

$$\begin{aligned} \Delta G_{1273}^0 &= \Delta H_{1273}^0 - 1273 [S_{1273}^0(\text{NiCO}_3) - S_{1273}^0(\text{Ni}) - S_{1273}^0(\text{C}) \\ &\quad - 3/2 S_{1273}^0(\text{O}_2)] = -157,786 + 70,585 = -87,201 \text{ (cal)} \end{aligned}$$

2. Electrode Polarization Studies in Molten Sodium Sulfide (Liu)

No extended discussion.

3. Liquid Line Corrosion of Ni-200 in Molten Sodium Carbonate (Iyer)

The molten salt cell and the experimental procedure pertaining to this work were described in some detail in the Progress Report¹ for the preceding period. During this report period the cell was used routinely and reproducible geometries of liquid line attack on Ni-200 were obtained under different reduced air pressures at 1000°C. In parallel, we developed a kinetic model describing the cathodic activity near the electrode surface in an attempt to define, if possible, the rate-determining factors influencing the anodic dissolution of nickel. The model with the necessary assumptions is described hereafter.

At the onset, we assume that

- i) The transport by convection can be neglected in the immediate neighborhood of the meniscus, but may occur in bulk.
- ii) Mass transfer in the gas phase (O_2 /air) and dissolution of O_2 is sufficiently rapid to ensure that the melt in immediate contact with the gas phase remains saturated with O_2 or $[O]$ at CO.
- iii) The diffusion of $[O]$ to the electrode and the migration of NiO away from it do not influence each other.

The final profile is assumed dependent only on three processes occurring in the thin film and meniscus region.

1) The diffusion of $[O]$ species through the electrolyte from the meniscus and thin film surface to the electrode/melt interface, where it reacts with the metal to form the corrosion product, NiO.

2) The diffusion of the corrosion product from the electrode surface towards the bulk of the electrolyte.

3) Due to evaporation losses resulting from the thermal decomposition of the sodium carbonate melt, there is a gradual lowering of the entire thin film and meniscus. However, the shape of the meniscus and thin film is assumed constant. Consequently, there is a continual change of the $[O]$ flux that

every point on the electrode near the liquid line region experiences and the resulting profile should reflect the summation of flux at that point. The extent of lowering is governed by the rate of evaporation of the melt. A schematic diagram illustrating the processes 1 and 2 are shown in Fig. 1.

Of the three processes, process 2 has been assumed not to play an important role in profile geometry. The following assumptions are also made for process 1.

i) Although a small but finite concentration of $[O]$ is present due to thermal decomposition of the melt i.e. $CO_3^{-2} \rightleftharpoons CO_2 + 1/2 O_2 + 2 e^-$, the initial concentration of $[O]$ is taken to be zero in this region.

ii) The concentration of the $[O]$ species at the meniscus boundary is a constant, C_0 for all times.

iii) The concentration of the $[O]$ species at the electrode/melt interface is zero for all times due to reaction with the metal.

iv) The concentration profile in the melt at any instant is given by the solution of the steady state Laplace equation $\nabla^2 C = 0$.

v) The flux J of $[O]$ at the electrode/melt interface in the direction perpendicular to the electrode surface governs the final profile of the specimen.

The coordinate system and the aforesaid boundary conditions are illustrated in Fig. 2. The equation for the meniscus and thin film on plane surfaces, optically verified for aqueous solutions is given by Maget and Rothlein (1). For our coordinate system, the equation is

$$x = \delta + A(y/h)^2$$

where

$$A = 1/2 \left(\frac{5+4\sqrt{2}}{4+3\sqrt{2}} \right) \left(\frac{2\sigma}{gd} \right)^{1/2}$$

and δ is the thickness of the thin film

σ is the surface tension of the molten carbonate

g is the gravitational acceleration - 980 cm/sec^2

d is the melt density

and h is the height of the meniscus and thin film and equals $(\frac{2\sigma}{gd})^{1/2}$.

Using (2)

$$\sigma = 269.8 - 0.0514 T (^{\circ}\text{K}) = 204.4 \text{ dyne/cm and}$$

$$d = 2.4797 - 0.4487 \times 10^{-3} T = 1.91 \text{ gm/cm}^3$$

T being equal to 1273°K , we get the equation of the meniscus and thin film as

$$x = \delta + 0.302 (y/h)^2$$

and $h = 0.22 \text{ cm}$.

In mathematical notation we have the Laplace equation $\nabla^2 C = 0$ with the following restraint

- i) $C = 0, t = 0$ for all interior (x, y)
- ii) $C = c_0$ for all t at $n = \delta + 0.302 (y/h)^2$
- iii) $C = 0, x = 0$ for all t

The solution to the equation furnishes $C = C(x, y)$ and $J(x, y)$ for the region.

The horizontal flux at the melt/electrode interface which describes this profile geometry is thus $J_{x=0}(y)$.

The situation above is analogous to the steady state heat loss in a bounded region, whose surface is kept at zero temperature and heat is produced in it. The solution to the Laplace equation is, in this case formulated by using the method of images or in general, the Green's function of potential theory.³

In effect, the temperature due to a point source at (x', y') in a two-dimensional region, which emits Q units of heat per unit time, is

$$u = \frac{Q}{4\pi K} \left[\frac{1}{\sqrt{(x-x')^2 + (y-y')^2}} - \frac{1}{\sqrt{(x+x')^2 + (y-y')^2}} \right]$$

where K is the thermal conductivity of the medium. In applying the above result to our system, we consider the meniscus to be comprised of many such

point-sources, each point source (x', y') transferring $[O]$ at the rate of Q moles/sec. The electrode surface at $x = 0$ is at zero concentration. The concentration of $[O]$, $C(x, y)$ analogous to temperature in the above expression is then given by

$$C(x, y) = \frac{Q}{4\pi D} \left[\frac{1}{\sqrt{(x-x')^2 + (y-y')^2}} - \frac{1}{\sqrt{(x+x')^2 + (y-y')^2}} \right]$$

where D is the diffusion coefficient of $[O]$ (analogous to the thermal conductivity, K). The above solution satisfies all the boundary conditions.

The flux of $[O]$ in the region $J(x, y)$ is given by Ficks first law i.e.

$$J = -D \nabla C$$

The horizontal flux $J(y)$ at the electrode surface $x = 0$ which governs the geometry of the final experimental profile of the specimen is then

$$J_{x=0}(y) = -D \left. \frac{\partial C}{\partial x} \right|_{x=0} = -\frac{Q}{2\pi} \left[\frac{x'}{[x'^2 + (y-y')^2]^{3/2}} \right]$$

The expression above is then the horizontal flux distribution due to a point source at (x', y') transferring Q moles/sec of $[O]$. The flux distribution due to all such point sources distributed along the meniscus is the summation of the fluxes generated by the point sources as they move along the meniscus i.e. as x' varies according to the equation

$$x' = \delta + 0.302 (y'/h)^2$$

where h is the intrinsic meniscus height. If $y' = u \delta$, then the flux distribution is given by the expression

$$J(y) = -\sum_{u=0}^{u=h/\delta} \frac{Q}{2\pi} \left[\frac{x'}{[x'^2 + (y-u\delta)^2]^{3/2}} \right]$$

$$\text{and } x' = \delta + 0.302 \left(\frac{u \delta}{h} \right)^2$$

The expression above considers the flux generated at the electrode surface due to the transfer of [O] from the meniscus boundary the transfer of [O] across the boundary at $y=0$ has been so far neglected. The [O] species introduced through this boundary will contribute predominantly to the flux at the electrode surface in the thin film and upper region of the meniscus. A solution supplementing the contributions to the flux due to this boundary would be complicated owing to the discontinuity at the point $x=0, y=0$ where the boundary ($C = C_o$) meets the electrode surface.

Thus we postulate the existence of an hypothetical meniscus located as a mirror image of the actual meniscus about the x -axis ($y=0$), the meniscus consisting of hypothetical point sources as in the derivation heretofore. In mathematical notation we therefore calculate

$$J(y) = - \sum_{u=-h/\delta}^{u=h/\delta} \frac{Q}{2\pi} \left[\frac{x'}{[x'^2 + (y-u\delta)^2]^{3/2}} \right]$$

where

$$x' = \delta + 0.302 \left(\frac{u\delta}{h} \right)^2$$

The above expression would then give us the flux distribution along the electrode surface (from $y=0$ to $y=h$) due to both the boundary at $y=0$ and the meniscus.

The negative sign in the expression indicates that the horizontal flux at the electrode surface is directed in the negative x -direction, as it should be. The factor $Q/2\pi$, where Q is the rate of transfer of [O] in moles/sec is just a multiplier and does not affect the shape of the flux distribution at the electrode surface. The value of Q is, however, dependent on

- i) The concentration C_o at the meniscus and
- ii) The diffusion coefficient D of [O] in the melt

The concentration C_o is dependent on the solubility of oxygen in the melt, which varies with the partial pressure of oxygen over the melt. Few data are available in the literature as regards this variation. Appleby and Van Drunen⁴ conclude that typical first order Henry's Law ($C_o = kP_{O_2}$) should not be obeyed

because of the chemical solubility (O_2^{-2} , O_2^{-}) of oxygen. The variation of Q or C_O with the partial pressure of oxygen is therefore assumed unclear. The factor $Q/2\pi$ is therefore deleted from the expression.

The expression has also neglected process 3, i.e., the occurrence of melt loss due to evaporation resulting from the thermal decomposition of the carbonate. This would mean gradual lowering of the profile of attack. Once the horizontal flux in the region from $y=0$ to $y=h$ has been calculated using the expression, the flux distribution for a certain amount of lowering can be found out by simply adding the existent flux at that point after lowering to the flux existent prior to lowering.

A Fortran program was written for the purpose of calculating the flux values at different points on the electrode surface. The points were chosen at intervals of 0.025 in the thin film and meniscus region, i.e., as y/h varies from 0 to 1. Thereby 40 values of flux are calculated corresponding to increasing values of y/h in increments of 0.025. Thereafter the profile is displaced incrementally and the flux values are summed up at the different points. The theoretical results are as shown in Fig. 3.

The experimentally observed profiles are as shown in Figure 4 for different reduced air pressures. Table 1 features the variation in the maximum depth of attack as a function of the different air pressures employed. Whereas no attack is seen in pure N_2 and in air, the values indicate the possible existence of a maximum in corrosion in the total pressure range of 5 to 150 Torr.

Discussion

Liquid line corrosion in fused salts takes place, as in aqueous systems, via two processes occurring locally on the electrode surface in the meniscus and thin film region, viz.,

- i) the anodic dissolution of nickel $Ni \rightleftharpoons Ni^{+2} + 2 e^{-}$
- ii) the cathodic reduction of the dissolved oxygen, or species thereof.

In the molten salt environment, in addition we have to account for the contribution to corrosion due to the reaction

which is dependent on the thermal decomposition of the melt. Though this may be significant it is assumed in the present study that it does not play a rate-determining role in the corrosion process. However, the decomposition leads to evaporation losses which may affect profile geometry as seen in Fig. 3.

The anodic dissolution of nickel should be dependent on initiation on the fluxing of the oxide layers present at the high temperatures employed. Even during the course of corrosion, this product should inhibit corrosion to some extent. It was observed that whereas most specimens exhibited only small amounts of oxide in the meniscus region presumably due to its diffusion to the bulk melt subsequent to formation, the specimens corroded in the melt at the higher partial pressures of oxygen did have a reasonable thickness of oxide layer.

Our experimental results show declining attack with increasing oxygen pressure, thereby suggesting the role of the oxide layer in inhibiting corrosion. The rate of reaction seems to be governed by solid state diffusion through the oxide scale. As the diffusion distance increases due to oxide layer growth, the rate of reaction decreases with time. Oxide layer growth on nickel takes place due to preferential diffusion of nickel in the oxide towards the oxide surface. We propose therefore that the maximum in corrosion which occurs at low oxygen pressures is due to a thin oxide layer, which is easily fluxed by the melt (possibly due to the reaction (a) $\text{NiO} \rightleftharpoons \text{Ni}^{++} + \text{O}^-$ or (b) $\text{NiO} + \text{CO}_2 \rightleftharpoons \text{Ni}^{++} + \text{CO}_3^-$) or that the amount of nickel diffusing through the thin oxide film is sufficiently large to offset its presence. At higher oxygen pressures the film thickness provides effective corrosion control.

The mechanism of the cathodic reaction occurring in the vicinity of the electrode is unclear. Whereas the NiO formation is likely to take place due to the reaction

the roles of the superoxide (O_2^-) and peroxide (O_2^{-2}) ions, resulting from the chemical solubility of oxygen in the melt is unclear. Their reduction may, however, occur^{5,6} via

where O^- is a transient species.

The kinetics of the corrosion process is governed by the horizontal flux of the diffusing species $[\text{O}]$ at the electrode surface. The diffusion model developed in an attempt to define the anodic dissolution by substantiating the cathodic activity of $[\text{O}]$ in the vicinity of the electrode. A comparison between the theoretical flux distribution at the electrode surface and the observed corrosion profile should render definition to the kinetics.

The model developed satisfies the following:

a) The maximum flux of $[\text{O}]$ is in the thin film and upper regions of the meniscus.

b) The flux decreases as we move along the electrode surface towards the bulk of the melt.

As seen in Fig. 3, the flux profile does resemble the observed profiles to a reasonable degree. This is possible, however, only by accounting for the lowering of meniscus profile due to evaporation losses. The solution thereby just defines the shape of the flux distribution. The model is insufficient in that nothing could be said about the rate of dissolution.

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TABLE 1

MEASURED MAX. DEPTH OF ATTACK AS A FUNCTION OF THE PARTIAL
OXYGEN PRESSURE OVER THE MELT

Poxygen TORR	DEPTH cm
0.00	0.00000
1.00	0.01125
1.00	0.01167
1.00	0.01208
1.00	0.01667
1.00	0.02000
15.00	0.01367
15.00	0.01250
15.00	0.01167
30.00	0.01083
30.00	0.01000
30.00	0.00625
60.00	0.00833
60.00	0.00667
60.00	0.00542
152.00	0.00000

FIGURE # 1
PROCESSES 1 AND 2 OCCURRING IN THE THIN
FILM AND MENISCUS REGION

FIGURE # 2

PROCESS 1 : DIFFUSION OF (C)

FIGURE # 3

THE THEORETICAL FLUX DISTRIBUTION ALONG THE ELECTRODE SURFACE FOR VARIOUS MENISCUS DISPLACEMENTS.

THE NUMBERS ON THE CURVES INDICATE THE DISPLACEMENT VALUES (Y/H). THE DASHED LINES SHOW THE CURRENT POSITION OF THE MENISCUS/THIN FILM FOR THAT DISPLACEMENT. THE ELECTRODE EXPERIENCES NO FLUX TO THE LEFT OF THIS DASHED LINE.

FIGURE # 4
THE OBSERVED CORROSION PROFILE
FOR VARIOUS REDUCED AIR PRESSURES.

4. Gas/Metal Reactions in Mixed Oxidants (Wilson)

Introduction

The complexity of the corrosion kinetics of iron in sulfidizing and mixed oxidant (sulfidizing/oxidizing) atmospheres was presented in the previous report (1). This report concerns itself with modeling of the corrosion kinetics. In particular, a single equation is needed that will allow for long time parabolic or linear kinetics each of which has been observed. A general model is presented which with a simplifying assumption allows a tractable solution.

General Model for Corrosion

Consider iron covered with a layer of sulfide as indicated in Figure 1. As is generally indicated, the corrosion process is assumed to occur by the outward diffusion of cations rather than an inward diffusion of anions (2). It is also assumed that the reaction proceeds under steady state conditions.

The following processes occur:

- (1) Metal ions are transferred from the base metal to the growing scale.
- (2) The cations are transported across the scale to the scale/gas interface.
- (3) The cations react at the scale/gas interface to form additions to the scale.
- (4) Gaseous species are transferred from the gas to the scale at the scale/gas interface where they react or are absorbed.

The flux of metal ions from the base metal to the metal/scale interface is given by

$$F_1 = L(C_M^* - C_{M1}), \quad (1)$$

where L is a linear transport coefficient, C_M^* is the equilibrium concentration of metal ions in the scale, and C_{M1} is the actual metal ion concentration at the metal/scale interface. An underlying assumption is that of ideal solution.

The flux of metal ions across the scale is obtained from Fick's law as

$$F_2 = D(C_{M1} - C_{M2})/x, \quad (2)$$

where D is the diffusion coefficient, x is the thickness of the scale, and C_{M2} is the concentration of cations at the scale/gas interface.

The flux of oxidant to the scale/gas interface is

$$F_3 = h(C_0^* - C_{O2}) , \quad (3)$$

where h is the transport coefficient, C_0^* is the equilibrium concentration of gaseous species in the scale, and C_{O2} is the actual concentration of gaseous species at the scale/gas interface.

The flux corresponding to the scaling reaction is taken as first order in ionic concentrations. Namely,

$$F_4 = kC_{M2}C_{O2} . \quad (4)$$

Using equations 1, 2, and 3, it can be shown that the flux is

$$F = F_1 = F_2 = F_4 + (C_M^*kC_{O2})/(1 + kC_{O2}/L + xkC_{O2}/D) . \quad (5)$$

This equation is similar to that of Deal and Grove (3) for $kC_{O2} = a$ constant. Their solution to that equation allows for short time linear kinetics and parabolic kinetics at long times. Substitution for C_{O2} in terms of the known concentrations and desired reaction constants leads to an equation for F, the solution of which is non-trivial.

A simpler solution can be derived assuming that the process at the metal/scale interface is very rapid. Using equations 2, 3, and 4, the flux F is obtained from

$$F^2 - (a + b/x)F + c/x = 0 , \quad (6)$$

where $a = hC_0^*$

$$b = D(h/k + C_{M1})$$

$$\text{and } c = DhC_{M1}C_0^* .$$

under the assumed conditions $C_{M1} \approx C_M^*$.

The growth rate of the scale is given by the differential equation

$$\Omega dx/dt = [(ax + b)/2x] \pm 1/2[a^2 + (2ab - 4c)/x + (b/x)^2]^{1/2}, \quad (7)$$

where Ω is the number of oxidant species per unit volume of the scale. For $b/x \ll a$ and $4c/x \ll a$, i.e., long times, equation 7 reduces to

$$\Omega dx/dt \rightarrow a/2 \pm a/2.$$

giving linear long time kinetics for the plus sign, i.e., gas phase control.

Equation 7 is not integrable in closed form. Further, the equation is ill-behaved and as such, a , b , and c cannot directly be evaluated. That a solution exists can be demonstrated as follows:

Following the least squares method, the quadratic error function q is

$$q = \sum_{i=1}^n [Y_i^2 - (a + b/x_i)Y_i + c/x_i]^2,$$

where $Y_i = d(\Omega x_i)/dt = F$ for film thickness x_i .

Setting the partial derivatives of q with respect to a , b and c equal to zero leads to

$$\sum_{i=1}^n [Y_i^2 - (a + b/x_i)Y_i + c/x_i](-Y_i) = 0 \quad (8a)$$

$$\sum_{i=1}^n [Y_i^2 - (a + b/x_i)Y_i + c/x_i](-Y_i/x_i) = 0 \quad (8b)$$

$$\sum_{i=1}^n [Y_i^2 - (a + b/x_i)Y_i + c/x_i](1/x_i) = 0 \quad (8c)$$

The above equations are not linearly related; the rank of the coefficient matrix as well as that of each augmented matrix is three. As these matrices are also third order a solution exists. The poor behavior of this set of equations apparently arises from the magnitude of one of the parameters. At present an interactive computer graphics technique is being developed to evaluate the parameters via regression. No results will be presented at this time.

Equation 7 as developed above is for one of the cases presented in the previous report (1); namely, a fast initial rate which decreases with time to the long time rate. In agreement with Worrell and Turkdogan (4), a surface chemical reaction is invoked to account for the initial linear region. There must exist cation diffusion through the scale. The use of the gas transport parameter is detailed as follows:

Gas transport to the outer surface of the scale is not considered as rate-limiting. If it were, separation of the linear surface chemical parameter from the linear gas transport parameter would be impossible. Instead, the latter is included to allow for behavior when: 1) a protective outer layer is ruptured due to growth stresses (5), or 2) an inner porous layer is formed between the outer scale and the base metal (6).

In the first instance, Figure 2, it is assumed that microfissures occur and extend to the scale/gas interface. Transport of gas down these fissures will determine whether these microfissures are healed and may be rate-determining for so long as they exist. In the second instance, Figure 3, it is postulated that the pores may be filled by a change in stoichiometry of the sulfide on the high sulfur side of the pore. This change in stoichiometry will release gas at the "sulfur" side of the pore for consumption at the 'metal' side of the pore without the concurrent release of an iron ion that may diffuse to the scale/gas interface. The occurrence of the latter would simply result in scale growth with pores at a fixed distance from the outer surface, i.e. parabolic growth. While transport across a pore is incorrectly modeled by the gas transport equation used, a complex model is not warranted at this time.

Parabolic behavior for long times will occur only if microfissures do not develop in the outer scale layer or, if they develop, are either rapidly healed or do not change in extent with time. If microfissures are not healed and the intact inner layer maintains constant thickness, long-time kinetics

will be linear. This association of an inner porous layer and parabolic kinetics, and an outer porous layer and linear kinetics, is consistent with the literature review and observations previously presented (1).

Conclusion

A general equation for the growth of sulfide scales on iron has been developed. This equation allows for short time linear kinetics, long time linear or parabolic kinetics, and behavior that lies between the two.

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Figure 1

Model For The Corrosion Of Iron.

Figure 2

*Two Layer Sulfide Scale On Iron Displaying
An Outer Fissured Layer.*

Figure 3

*Two Layer Sulfide Scale On Iron Displaying
An Inner Porous Layer.*

D. Appendix

Attached in order are the following:

1. Abstract: K. Y. Kim, "Electrode Polarization Studies in Hot Corrosion Systems", PhD Thesis, University of Connecticut, 1981.
2. Abstract: Venkatraman Iyer, "Liquid Line Corrosion of Ni-200 in Molten Sodium Carbonate", MS Thesis, University of Connecticut, 1981.
3. Manuscript: K. Y. Kim and O. F. Devereux, "Reactions at the $\text{CO}, \text{CO}_2 | \text{Ni}$ Electrode in Molten Sodium Carbonate", submitted for publication.
4. Manuscript: O. F. Devereux and K. Y. Kim, "Reactions at the Corroding Nickel Electrode in Molten Sodium Carbonate under CO, CO_2 Atmospheres", to be submitted for publication.

ELECTRODE POLARIZATION STUDIES IN HOT CORROSION SYSTEMS

Kyoo Young Kim, Ph.D.

The University of Connecticut, 1981

Hot corrosion processes on the specimens of nickel, Armco iron, 1018 steel, and types 304 and 316 stainless steels were evaluated through electrode polarization study in the systems of molten sodium carbonate under oxidizing atmospheres ($0.2 \lesssim P_{O_2} \lesssim 1$), under reducing CO/CO₂ atmospheres ($10^{-18} \lesssim P_{O_2} \lesssim 10^{-12}$), and under sulfur bearing CO/CO₂/H₂/H₂S/H₂O atmospheres ($10^{-11} \lesssim P_{S_2} \lesssim 10^{-6}$) at temperatures between 1173 and 1273°K. An "Alumina sheathed Pt, CO/CO₂|Na₂CO₃" electrode was used as a reference electrode, and proved to be a relevant reference electrode to monitor the potential of a corroding electrode independently of cell pressure and cell contamination. On nickel, the most thoroughly studied of those electrodes, a single cathodic reaction, reduction of CO₃⁼, and three anodic reactions are seen under reducing CO/CO₂ environments. The latter include oxidation of CO at the nickel surface, oxidation of nickel to nickelous state, and, possibly, oxidation of CO at the nickel oxide surface. In the sulfur bearing environments, the effect of H₂S on the polarization kinetics at lower anodic overpotentials is attributed to adsorption of sulfur species on the nickel electrode surface; at higher anodic overpotentials, it is attributed to alteration of the transport properties of nickel oxide scale in the P_{S₂} range between 10⁻¹¹ and 10⁻⁹ atm, and to formation and disso-

Kyoo Young Kim - The University of Connecticut, 1981

lution of nickel sulfide at P_{S_2} in the vicinity of 10^{-6} atm. All ferrous materials show very similar polarization behavior with small difference in degree depending on the alloying elements, and experience severe corrosion attack by even simple immersion in molten sodium carbonate. Morphological changes of nickel specimens are more significantly dependent on the electrode potential than the variation of either P_{O_2} or P_{S_2} and of temperature. The current/overpotential relationship for these systems is very closely described by combined activation, concentration, and resistance polarization incorporating passive region. The corresponding empirical parameters are determined via an interactive computer graphics procedure. Fundamental kinetic parameters are, in turn, derived from these parameters and their dependence upon temperature and gas phase composition via absolute rate theory.

Liquid Line Corrosion of Ni-200 in Molten Sodium Carbonate

Venkatraman Iyer

Abstract

Liquid line corrosion is a phenomenon well known in aqueous systems wherein electrodes partially immersed in an electrolyte experience enhanced corrosion at the line of contact of the electrode surface and the electrolyte/gas interface. This work is a study of this process on Ni-200 specimens semi-immersed in molten sodium carbonate at 1000°C under reduced air pressures. Several Ni-200 specimens were exposed to various air pressures to delineate the conditions under which significant corrosion occurs. The specimens showed maximum liquid line attack in the pressure range of 5-150 Torr and decreasing attack when higher pressures were employed. No attack was seen at near zero oxygen pressures (1 atm. N₂). A simplistic diffusion model has been developed relating the cathodic activity of the [O] species in the vicinity of the electrode at the liquid line, i.e., in the thin film and meniscus regions, to the anodic behavior of Ni-200 in this region. The latter was observed by recording the profile of corroded specimens.

REACTIONS AT THE CO, CO₂/Ni ELECTRODE IN MOLTEN SODIUM CARBONATE

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ABSTRACT

Reactions at the nickel electrode in molten sodium carbonate at 1000°C under CO/CO₂ atmospheres were studied by electrode polarization. The polarization curves were analysed by means of a previously described computer model, which in turn was interpreted in terms of the absolute rate expressions for postulated reactions. In agreement with previous workers observations for inert electrodes, the dominant anodic reactions were found to be oxidation of CO at low and intermediate anodic overpotentials, and oxidation of CO₃⁼ at high anodic overpotentials. The cathodic reaction was found to be reduction of CO₃⁼. The form of the polarization curves was described by activation, concentration, and resistance polarization of these reactions; however, anomalous anodic behavior was observed which was attributed to corrosion reactions at the electrode and accurately described through the use of additional anodic reactions displaying passivity.

Key words: Nickel, sodium carbonate, polarization

Introduction

Research on electrode reactions in molten carbonates has been pursued in large part in the context of fuel cell development. With few exceptions such studies have involved the CO, CO_2 or O_2, CO_2 electrodes at gold or other "noble" metals, including such materials as platinum and silver.¹⁻¹⁵ However, with the exception of gold and an 80% Au, 20% Pd alloy these materials were found to react to some degree, exhibiting either dissolution or oxide film formation.⁷ Even in the case of gold, limited oxidation of the electrode metal has been suggested.^{4,10} Relatively little attention has been given electrodes experiencing significant corrosion, and studies reported have been of a primarily qualitative nature.^{4,6,16,17} A number of authors have used electrode polarization to study corrosion in molten sulfates, again analysing the results in an essentially qualitative manner.¹⁸⁻²³ Concern for these systems originated with the discovery of the major role played by sodium sulfate in the hot corrosion of turbine components.²⁴ In another process of current interest, coal gasification, a molten salt phase containing sulfate, sulfide, carbonate, oxide and/or hydroxide may occur, with carbonate and sulfide being the more likely dominant anions.²⁵ Although not even the binary phase diagrams representative of this complex system have been established, it is reasonable to assume that these salts are miscible in the liquid phase, creating a wide range of environments that are of potential concern in their effects on the integrity of structural materials. The present study has been restricted to the behavior of the $\text{CO}, \text{CO}_2 | \text{Ni}$ electrode in molten sodium carbonate. The development of computer modelling techniques has enabled the separate contributions of the various reactions to the net electrode current to be distinguished and studied as distinct entities.^{26,27}

Kinetic Analysis of Electrode Reactions

Borucka has identified three distinct anodic reactions occurring at the $\text{CO}, \text{CO}_2 | \text{Au}$ electrode.¹³ The first of these may be written

Reaction (1) is also a possible cathodic reaction under conditions of temperature and gas composition not favoring the Boudouard, or Deville, equilibrium:^{12,28}

Assuming unit carbonate activity and a simple, one-step reaction the anodic current carried by reaction (1) under purely activation control may be written:

$$i_{a1} = z_1 F k_{a1} P_{\text{CO}} e^{(1-\beta_1) z_1 F (V - V_1^0) / RT} \quad (3)$$

and the cathodic current carried by the same reaction is

$$i_{c1} = z_1 F k_{c1} P_{\text{CO}_2}^2 e^{-\beta_1 z_1 F (V - V_1^0) / RT} \quad (4)$$

where z_1 is the number of electronic charges passed for each occurrence of reaction (1); F , the Faraday; P_{CO} and P_{CO_2} , the partial pressures of CO and CO_2 ; k_{a1} and k_{c1} , the "chemical" reaction rate constants; β_1 , the symmetry of the activation barrier; V , the applied potential; V_1^0 , the equilibrium potential; R , the gas constant; and T , the temperature. The equilibrium potential is given by the Nernst equation:

$$V_1^0 = E_1^0 + \frac{RT}{z_1 F} \ln \frac{P_{\text{CO}_2}^2}{P_{\text{CO}}} \quad (5)$$

where E_1^0 is the standard electrode potential for reaction (1) and $a_{\text{CO}_3^{2-}}$ has been assumed equal to unity. Substituting, equations (3) and (4) become

$$i_{a1} = z_1 F k_{a1} P_{CO} (P_{CO}/P_{CO_2}^2)^{(1-\beta_1)} e^{-z_1 F(1-\beta_1)E_1^0/RT} e^{z_1 F(1-\beta_1)V/RT} \quad (6)$$

and

$$i_{c1} = z_1 F k_{c1} P_{CO_2}^2 (P_{CO_2}^2/P_{CO})^{\beta_1} e^{z_1 F\beta_1 E_1^0/RT} e^{-z_1 F\beta_1 V/RT} \quad (7)$$

The chemical reaction rate constants may be written

$$k_{a1} = f_{a1} e^{\Delta S_{a1}^*/R} e^{-\Delta H_{a1}^*/RT} \quad (8)$$

$$k_{c1} = f_{c1} e^{\Delta S_{c1}^*/R} e^{-\Delta H_{c1}^*/RT} \quad (9)$$

where ΔS_{a1}^* , ΔS_{c1}^* , ΔH_{a1}^* and ΔH_{c1}^* are the entropy changes and enthalpy changes associated with the anodic and cathodic activation barriers, and f_{a1} and f_{c1} include attempt frequency and appropriate geometric factors. Equations (6) and (7), together with equations (8) and (9), constitute a complete description of the activation polarization of the CO, CO_2 /metal electrode in terms of fundamental physical parameters according to the simplest model commensurate with reaction (1).

In the more general case the overall reaction (1) occurs in a number of discrete steps, one of which is assumed to be rate-determining while the others are at equilibrium. If there are n_1 steps, of which γ_1 precede the rate-determining step, and the rate-determining step is repeated ν_1 times for each occurrence of the overall reaction and carries z_1 electrons each of the ν_1 times, the kinetic expressions corresponding to equations (3) and (4) are:²⁹

$$i_{a1} = n_1 F k_{a1} \prod_{i=1}^{\gamma_1} (K_i)^{1/\nu_1} (P_{CO})^{1/\nu_1} e^{[(\gamma_1/\nu_1)+z_1(1-\beta_1)]F(V-V_1^0)/RT} \quad (10)$$

and

$$i_{c1} = n_1 F k_{c1} \prod_{i=n_1-\gamma_1-z_1\nu_1}^{n_1} (K_i)^{1/\nu_1} (P_{CO_2}^2)^{1/\nu_1} e^{-[(n_1-\gamma_1)/\nu_1-z_1(1-\beta_1)]F(V-V_1^0)/RT} \quad (11)$$

where the K_i represent the equilibrium constants for the various component

steps of the reaction.* Defining the transfer coefficients

$$\alpha_{a1} \equiv \gamma_1/\nu_1 + z_1(1-\beta_1) \quad (12)$$

and

$$\alpha_{c1} \equiv (n_1 - \gamma_1)/\nu_1 - z_1(1 - \beta_1) \quad (13)$$

with $\alpha_{a1} + \alpha_{c1} = n_1/\nu_1$, equations (10) and (11) become

$$i_{a1} = n_1 F k_{a1} \prod_{i=1}^{\gamma_1} (K_i)^{1/\nu_1} (P_{CO})^{1/\nu_1} e^{\alpha_{a1} F(V-V_1^0)/RT} \quad (14)$$

and

$$i_{c1} = n_1 F k_{c1} \prod_{i=n_1-\gamma_1-z_1\nu_1}^{n_1} (K_i)^{1/\nu_1} (P_{CO_2}^2)^{1/\nu_1} e^{-\alpha_{c1} F(V-V_1^0)/RT} \quad (15)$$

respectively. Now substituting equation (5), with n_1 replacing z_1 ,

$$i_{a1} = n_1 F k_{a1} \prod_{i=1}^{\gamma_1} (K_i)^{1/\nu_1} P_{CO}^{1/\nu_1} (P_{CO}/P_{CO_2}^2)^{\alpha_{a1}/n_1} e^{-\alpha_{a1} F E_1^0/RT} e^{\alpha_{a1} F V/RT} \quad (16)$$

and

$$i_{c1} = n_1 F k_{c1} \prod_{i=n_1-\gamma_1-z_1\nu_1}^{n_1} (K_i)^{1/\nu_1} (P_{CO_2}^2)^{1/\nu_1} (P_{CO_2}^2/P_{CO})^{\alpha_{c1}/n_1} e^{\alpha_{c1} F E_1^0/RT} e^{-\alpha_{c1} F V/RT} \quad (17)$$

At higher current densities the anodic reaction is limited by the rate at which CO can diffuse to the electrode surface.¹³ Such concentration polarization is described by

$$\eta_{a1}^d = - \frac{RT}{n_1 F} \ln (1 - i_{a1}/i_{a1}^s) \quad (18)$$

where η_{a1}^d is the potential difference necessary to cause current i_{a1} across the diffusion barrier, and i_{a1}^s is the limiting current, given by

$$i_{a1}^s = \frac{D_{a1} n_1 F}{t_{a1} \delta} a_{a1}^o \quad (19)$$

* Our i_{a1} , i_{c1} , and γ_1 correspond to the $\bar{i}$, $\bar{i}$, and $\bar{\gamma}$, respectively, of Bockris and Reddy.²⁹

where D_{a1} and a_{a1}^0 are the diffusivity and bulk activity of the rate-limiting reactant, CO in this case, and $t_{a1} = 1 - t'_{a1}$, where t'_{a1} is its transport number. The thickness of the diffusion layer is given by δ . Joint control of reaction (1) by activation and diffusion control may be treated by expressing the total overpotential of the electrode, $V - V_1^0$, as the sum of the potential difference across the diffusion barriers, η_{a1}^d , and the potential difference across the activation barrier, η_{a1}^a . The preceding equations, which were written assuming that the reaction rate was wholly under activation control, must be rewritten with η_{a1}^a substituted for $V - V_1^0$. To a first approximation, equation (19) predicts a limiting anodic current proportional to P_{CO} , assuming molecular solubility of CO, with a temperature dependence largely governed by that of the diffusivity of CO in the electrolyte. The cathodic reaction is also subject to rate limitation by the diffusion of CO_2 to the surface, for which

$$\eta_{c1}^d = \frac{RT}{n_1 F} \ln (1 - i_{c1}/i_{c1}^s) \quad (20)$$

with

$$i_{c1}^s = \frac{D_{c1} n_1 F}{t_{c1} \delta} a_{c1}^0 \quad (21)$$

Thus, approximate linear dependence between i_{c1}^s and P_{CO_2} is expected.

Empirically, Lorenz and Janz found the dominant cathodic reaction to be

above 875°C, and

below that temperature.¹² Reaction (22) is distinct from reaction (1) only if it is assumed that the oxide ion thus formed is not at equilibrium with the cell atmosphere via the reaction

Under this condition the rate of reaction (22) is given by

$$i_{cl} = n_1 F k_{cl} \frac{n_1}{\prod_{i=n_1-\gamma_1-z_1}^{n_1}} (K_i)^{1/\nu_1} e^{-\alpha_{cl} F(V-V_1^0)/RT} \quad (25)$$

with

$$V_1^0 = E_1^0 - \frac{RT}{n_1 F} \ln P_{\text{CO}} a_{\text{O}}^2 \quad (26)$$

Substituting,

$$i_{cl} = n_1 F k_{cl} \frac{n_1}{\prod_{i=n_1-\gamma_1-z_1}^{n_1}} (K_i)^{1/\nu_1} a_{\text{O}}^{-\alpha_{cl}/n_1} P_{\text{CO}}^{-\alpha_{cl}/n_1} e^{\alpha_{cl} E_1^0 F/RT} e^{-\alpha_{cl} VF/RT} \quad (27)$$

Similarly, the rate due to reaction (23) is also given by equation (25),

but with

$$V_1^0 = E_1^0 - \frac{RT}{n_1 F} \ln a_{\text{O}}^3 \quad (28)$$

thus

$$i_{cl} = n_1 F k_{cl} \frac{n_1}{\prod_{i=n_1-\gamma_1-z_1}^{n_1}} (K_i)^{1/\nu_1} a_{\text{O}}^{-3\alpha_{cl}/n_1} e^{\alpha_{cl} E_1^0 F/RT} e^{-\alpha_{cl} VF/RT} \quad (29)$$

In neither case would a significant overpotential due to diffusion be expected due to the omnipresence of $\text{CO}_3^{=}$.

At higher anodic overpotentials Borucka shows evidence for the equilibrium¹³

followed by

Clearly, if the activity of $\text{O}^{=}$ is expressed in terms of reaction (24) the overall reaction reduces to reaction (1). Thus, the equation for the multi-step reduction, equation (16), should remain valid with, however, the parameters describing the reaction sequence assuming the new values, γ_2 , ν_2 , z_2 and β_2 . This reaction may experience concentration polarization

due to diffusion of $\text{CO}_2^=$ from the bulk electrolyte, with

$$n_{a2}^d = - \frac{RT}{n_2 F} \ln (1 - i_{a2}^s / i_{a2}^s) \quad (32)$$

with

$$i_{a2}^s = \frac{D_{a2} n_2 F}{t_{a2} \delta} a_{a2}^o \quad (33)$$

In this case the limiting current is proportional to the activity of $\text{CO}_2^=$, or to the ratio $P_{\text{CO}}/P_{\text{CO}_2}$.

At sufficiently high overpotentials Borucka observes oxidation of the carbonate according to¹³

The rate of this reaction may be expressed

$$i_{a3} = n_3 F k_{a3} \prod_{i=1}^3 (K_i)^{1/\nu_3} e^{\alpha_{a3} F(V-V_3^0)/RT} \quad (35)$$

with

$$V_3^0 = E_3^0 + \frac{RT}{n_3 F} \ln P_{\text{CO}_2} P_{\text{O}_2}^{1/2} \quad (36)$$

Invoking the equilibrium

for which

$$K_{37} = \frac{P_{\text{CO}_2}}{P_{\text{CO}} P_{\text{O}_2}^{1/2}} \quad (38)$$

the equilibrium potential becomes

$$V_3^0 = E_3^0 + \frac{RT}{z_3 F} \ln \frac{P_{\text{CO}_2}^2}{K_{37} P_{\text{CO}}} \quad (39)$$

Substituting,

$$i_{a3} = n_3 F k_{a3} \prod_{i=1}^3 (K_i)^{1/\nu_i} K_{37}^{\alpha_{a3}/n_3} (P_{CO}/P_{CO_2}^2)^{\alpha_{a3}/n_3} e^{-\alpha_{a3} FE_3^0/RT} e^{\alpha_{a3} FV/RT} \quad (40)$$

with

$$k_{a3} = e^{\Delta S_{a3}^*/R} e^{-\Delta H_{a3}^*/RT} \quad (41)$$

and

$$K_{37} = e^{\Delta S_{37}/R} e^{-\Delta H_{37}/RT} \quad (42)$$

Due to the ubiquitous presence of $CO_3^{=}$ reaction (34) would not, a priori, be expected to experience concentration polarization; however, at sufficiently high currents resistance polarization may occur according to

$$\eta_a^r = iR_a \quad (43)$$

where R_a is the applicable cell resistance and η_a^r is the portion of the total potential difference which occurs across the cell resistance (exclusive of the effective resistance of activation and diffusion zones). The cell resistance is inversely proportional to the electrolyte conductivity, σ , given by

$$\sigma = \sum_i D_i \frac{c_i z_i^2 F^2}{kT} \quad (44)$$

summed over all of the ionic species in the electrolyte, where D_i , c_i and z_i are the diffusivity, molar concentration, and valence of species i , respectively. The temperature dependence of σ is largely due to the diffusivity,

$$D_i = D_i^0 e^{-\Delta H_i^{\ddagger}/RT} \quad (45)$$

Resistance polarization of the cathodic reaction may be similarly described by

$$\eta_c^r = iR_c \quad (46)$$

For obvious reasons, it is convenient to rewrite equation (16) as

$$i_{a1} = e^{(V-V_{a1}^0)/b_{a1}} \quad (47)$$

where

$$e^{-V_{a1}^0/b_{a1}} = n_1 F k_{a1} \prod_{i=1}^{\gamma_1} (K_i)^{1/\nu_i} P_{CO}^{1/\nu_1} (P_{CO}/P_{CO_2}^2)^{\alpha_{a1}/n_1} e^{-\alpha_{a1} FE_1^0/RT} \quad (48)$$

and

$$b_{a1} = \frac{RT}{\alpha_{a1} F} \quad (49)$$

It will be noted that in simple systems equation (47) can also be written

$$i_{a1} = i_1^0 e^{(V-V_1^0)/b_{a1}} \quad (50)$$

where

$$e^{-V_{a1}^0/b_{a1}} = i_1^0 e^{-V_1^0/b_{a1}} \quad (51)$$

Traditionally, V_1^0 has the connotation of "rest potential"; i_1^0 , of "exchange current"; and $2.303 b_{a1}$, Tafel slope. Similarly, equation (17) becomes

$$i_{c1} = e^{-(V-V_{c1}^0)/b_{c1}} \quad (52)$$

with

$$e^{V_{c1}^0/b_{c1}} = n_1 F k_{c1} \prod_{i=1}^{\gamma_1} (K_i)^{1/\nu_i} (P_{CO_2}^2)^{1/\nu_1} (P_{CO_2}^2/P_{CO})^{\alpha_{c1}/n_1} e^{\alpha_{c1} FE_1^0/RT} \quad (53)$$

and

$$b_{c1} = \frac{RT}{\alpha_{c1} F} \quad (54)$$

If however, the cathodic reaction is reaction (22) or reaction (23), equations (52) and (54) remain valid, but equation (53) must be replaced by

$$e^{V_{c1}^0/b_{c1}} = n_1 F k_{c1} \prod_{i=1}^{n_1} (K_i)^{1/\nu_i} a_0^{-\alpha_{c1}/n_1} P_{CO}^{-\alpha_{c1}/n_1} e^{\alpha_{c1} FE_1^0/RT} \quad (55)$$

or

$$e^{V_{c1}^0/b_{c1}} = n_1 F k_{c1} \prod_{i=1}^{n_1} (K_i)^{1/\nu_i} a_0^{-3\alpha_{c1}/n_1} e^{\alpha_{c1} E_1^0 F/RT} \quad (56)$$

respectively. When reaction (1) occurs via the intermediary $CO_2^=$ equation (16) is written

$$i_{a2} = e^{(V-V_{a2}^0)/b_{a2}} \quad (57)$$

with

$$e^{-V_{a2}^0/b_{a2}} = n_2 F k_{a2} \prod_{i=1}^{\gamma_2} (K_i)^{1/\nu_i} P_{CO}^{1/\nu_2} (P_{CO}/P_{CO_2}^2)^{\alpha_{a2}/n_2} e^{-\alpha_{a2} FE_2^0/RT} \quad (58)$$

and

$$b_{a2} = \frac{RT}{\alpha_{a2} F} \quad (59)$$

Equation (40) becomes

$$i_{a3} = e^{(V-V_{a3}^0)/b_{a3}} \quad (60)$$

with

$$e^{-V_{a3}^0/b_{a3}} = n_3 F k_{a3} \prod_{i=1}^{\gamma_3} (K_i)^{1/\nu_i} K_{37}^{\alpha_{a3}/n_3} (P_{CO}/P_{CO_2}^2)^{\alpha_{a3}/n_3} e^{-\alpha_{a3} FE_3^0/RT} \quad (61)$$

and

$$b_{a3} = \frac{RT}{\alpha_{a3} F} \quad (62)$$

In the most general case it is necessary to consider joint control of the first anodic reaction by activation, equation (47), and diffusion, equation (18). This may be done by recognizing that the effect of concen-

tration polarization is to lower the effective potential difference for activation polarization by the amount η_{a1}^d . Substituting $V - \eta_{a1}^d$ for V in equation (47),

$$i_{a1} = (1 - i_{a1}/i_{a1}^s)^{RT/n_1 F b_{a1}} e^{(V-V_{a1}^0)/b_{a1}} \quad (63)$$

Similarly,

$$i_{a2} = (1 - i_{a2}/i_{a2}^s)^{RT/n_2 F b_{a2}} e^{(V-V_{a2}^0)/b_{a2}} \quad (64)$$

In the foregoing two expressions it has been tacitly assumed that the current regime described is sufficiently low for resistance polarization to be insignificant. However, for the cathodic reaction and the third anodic reaction an ohmic potential drop in the electrolyte may be taken into account through substituting $V - \eta_a^r$ and $V - \eta_{c1}^d - \eta_c^r$ for V in equations (60) and (52), respectively, leading to

$$i_{a3} = e^{(V-V_{a3}^0)/b_{a3}} e^{-i_{a3} R_a / b_{a3}} \quad (65)$$

and

$$i_{c1} = (1 - i_{c1}/i_{c1}^s)^{RT/n_1 F b_{c1}} e^{-(V-V_{c1}^0)/b_{c1}} e^{-i_{c1} R_c / b_{c1}} \quad (66)$$

Finally, the net cell current is the sum of that carried by the cathodic reaction and each of the three anodic reactions. Arbitrarily denoting the cathodic current as negative,

$$i = i_{a1} + i_{a2} + i_{a3} - i_{c1} \quad (67)$$

Although insoluble in closed form, equations (63) through (67) constitute a prediction of the current passed by the CO, CO_2 |metal electrode for non-corroding systems. A means of solving these equations for a given set of experimental data, with evaluation of the constants therein, has been described in detail.^{26,27}

In the system presently reported, the $\text{CO}, \text{CO}_2 | \text{Ni}$ electrode, oxidation and subsequent passivation of nickel are known to occur in approximately the potential range in which reaction (30) is significant.⁴ If the oxidation of nickel is the more rapid reaction, the "second" anodic reaction can be replaced by

for the lower potentials in this range, and

after the onset of passivation. To a first approximation (a necessary approximation because time has not been explicitly considered in this analysis) the formation of a solid oxide on the electrode surface can be treated as concentration polarization, with the pertinent diffusivity representative of processes within the solid oxide rather than the salt. Reaction (68) will, thus, follow equation (64), with

$$e^{-V_{a2}^0/b_{a2}} = n_2 F k_{a2} \prod_{i=1}^{\gamma_2} (K_i)^{1/\nu_2} p_{\text{CO}_2}^{2/\nu_2} (p_{\text{CO}_2}/p_{\text{CO}})^{\alpha_{a2}/n_2} (a_{\text{Ni}^{++}} \text{CO}_3^-)^{-\alpha_{a2}/n_2} e^{-\alpha_{a2} E_2^0/RT} \quad (70)$$

while reaction (69) will follow equation (64) with

$$e^{-V_{a2}^0/b_{a2}} = n_2 F k_{a2} \prod_{i=1}^{\gamma_2} (K_i)^{1/\nu_2} p_{\text{CO}}^{1/\nu_2} (p_{\text{CO}_2}/p_{\text{CO}})^{\alpha_{a2}/n_2} e^{-\alpha_{a2} E_2^0/RT} \quad (71)$$

and the system parameters n_2 , ν_2 , α_{a2} and E_2^0 possessing values characteristic of reaction (68) or reaction (69), rather than reaction (1).

Experimental Apparatus and Procedure

A three-electrode polarization cell was used to obtain anodic and cathodic current-potential curves to be compared to the equations derived in the foregoing section. Measurements were made for the $\text{CO}, \text{CO}_2 | \text{Ni}$ electrode in molten sodium carbonate for a range of p_{CO} and p_{CO_2} values ($p_{\text{CO}} + p_{\text{CO}_2} = 1 \text{ atm}$) and temperature. The cell components were housed in a 3 1/2" OD closed

end mullite tube inserted into a vertical glow-bar furnace controlled with negligible temperature variation by a solid state proportioning controller. The open upper end of the mullite tube was cemented to a gasketed flange, in turn closed by a cover plate containing the electrical and gas feed-throughs. The plate, flange, and adjacent mullite were water-cooled. The electrolyte was contained in a commercial crucible of recrystallized 99.8% alumina, nominal OD 2 1/4", height 2 3/4"; this rested on an alumina disc suspended from the cover plate by Inconel 82 rods. Alumina and, in the cooler regions of the furnace, 304 stainless steel radiation shields reduced heat loss from the cell. Working and counter electrodes were fashioned from Ni 200 (nominal composition: 99.5% Ni, 0.25% Mn, 0.15% Fe, 0.06% C) and 99.995% platinum rod, respectively. Cylinders of nominal dimension 1/4" dia. x 5/8" long were polished on a lathe through 600 grit metallographic paper, washed, attached to 20 mil platinum lead wires, and cemented to alumina support tubes with a high temperature alumina cement (Ultra Bond 552, Aremco Products, Inc.). The lead wires were, thus, threaded through the tubes, which were vacuum-sealed to the cover plate. This arrangement precluded any anomalous effects attributable to the solid-liquid-gas contact line. A CO,CO₂ mixture was bubbled directly over the working electrode. The reference electrode has been previously described.²⁹ In brief, it consisted of a platinum wire immersed in molten sodium carbonate contained in a closed-end 99.8% alumina tube. The reference environment, distinct from that of the cell proper, was controlled by maintaining a flow of reference gas, 38.2% CO, 61.8% CO₂, over the surface of the reference electrolyte.*

*This reference mixture was suggested by Borucka⁷ in defining a standard potential scale for the CO,CO₂|metal electrode inasmuch as at a total pressure of 1 atm the Nernstian correction for the standard electrode potential is zero.

Due to its high Na^+ conductivity, the alumina functions as a salt bridge between the cell electrolyte and the reference electrolyte. As the Na^+ concentration in the two electrolytes is, to a first approximation, unaffected by changes in the anionic concentrations, there is no correction necessary for liquid junction potential. Cell temperature was measured directly by a thermocouple in a closed-end alumina well immersed in the electrolyte. This cell is shown schematically in Figure 1.

The cell electrolyte was prepared from reagent grade sodium carbonate. To minimize gas lift of this material during initial evacuation of the cell, it was previously melted and crushed, so that it could be placed in the cell in the form of coarse chips. Gas mixtures were in most cases purchased directly (Matheson certified mixtures) or derived from admixing bottled carbon monoxide (Matheson C. P. purity) or carbon dioxide (Norwich medical grade) with a purchased mixture. Individual and total flow rates were measured with rotameter flow gauges. Although individually calibrated for the gases employed, these gauges introduce discernable uncertainty into flow rate measurements, as discussed in detail by Borucka.⁷ Although cell potential was affected by total gas flow rate, variations in gas composition were of greater significance and were minimized to the extent possible through the use of purchased mixtures. In normal use, the cell was outgassed overnight at 250°C at 10^{-3} torr. It was then pumped with an oil diffusion pump during subsequent heat-up until approximately 800°C (m.p. of Na_2CO_3 : 858°C) at which point the desired gas environment was introduced. This procedure was adopted to optimize the removal of water without excessive decomposition of carbonate. After reaching test temperature the cell was allowed to stand until a stable rest potential obtained, then both anodic and cathodic polarization curves were measured. Current readout and potential control were provided by a Wenking #68TS3 Potentiostat, with a Wenking #69 Stepping

Motor Potentiometer providing a fixed scan rate of 2 mv/20 sec. The curves were directly recorded as log (current) vs. potential by means of a log converter and an x-y recorder. Sufficient points manually chosen from these plots to define the curves were then input into the computer programs previously described^{26,27} for determination of the pertinent empirical constants.

Results

Anodic and cathodic polarization curves obtained for four different P_{CO}/P_{CO_2} values ($P_{CO} + P_{CO_2} = 1$ atm.) are shown in Figures 2 through 5, along with the corresponding curves calculated according to equations (63) through (67). The parameter values upon which these curves are based are listed in Table I. Each set of parameter values represents an optimum choice for a single sample; the selection of values was not prejudiced by the values selected for previous samples.

Kinetic parameters were determined to the extent possible from the empirical parameters listed in Table I through the use of appropriate equations from the preceding section. This information is summarized in Table II. In all cases, $v_i = 1$ was found to yield the best correlation. Plots for the determination of α/n values are shown in Figures 6 through 9; the lines drawn in each Figure were determined by least squares fit to all of the plotted points, calculated from the data in Table I. The values of α were determined from arithmetic averages of b values. Attempts to correlate the second anodic reaction with reactions (68) and (69) and the cathodic reaction with reaction (1) resulted in negative and, therefore, impossible values for α/n , while reaction (23) is inconsistent with any cathodic dependence on gas composition. The empirically determined values of saturation current, i^s , and of electrolyte resistance, R , did not show a sufficiently consistent dependence on environment for meaningful analysis.

Table I
Values of Empirical Constants

<u>Sample No.</u>	<u>90</u>	<u>91</u>	<u>82</u>	<u>81</u>	<u>83</u>	<u>75</u>	<u>78</u>
P_{CO}/P_{CO_2}	5/95	5/95	25/75	50/50	50/50	95/5	95/5
i_{a1}^S (ma/cm ²)	2.0	2.5	1.8	1.5	1.5	2.8	3.0
i_{a2}^S (ma/cm ²)	11	7	9	9	9	9	9
V_{a1}^0 (mv)	150	190	160	40	90	-110	-40
V_{a2}^0 (mv)	280	300	270	230	250	235	300
V_{a3}^0 (mv)	830	870	750	740	810	820	750
b_{a1} (mv)	25	40	25	60	50	40	70
b_{a2} (mv)	25	20	30	30	30	70	30
b_{a3} (mv)	20	20	20	18	20	25	20
R_a (ohm)	0.9	0.9	1.2	1.5	1.3	2.5	2.0
i_{c1}^S (ma/cm ²)	*	*	*	*	*	*	*
V_{c1}^0 (mv)	30	-90	0	-150	-140	-95	-40
b_{c1} (mv)	160	160	120	130	130	90	70
R_c (ohm)	1.9	0.5	0.3	0.4	0.3	1.5	1.5

* The cathodic reaction was found not to be diffusion-limited; the value of i_{c1}^S used in curve-fitting was large but otherwise arbitrary.

Table II
Determination of Kinetic Constants

<u>Electrode Reaction</u>	<u>Described by Reaction ()</u>	<u>α/n given by Equation ()</u>	<u>α given by Equation ()</u>	<u>Inconsistent with Reaction ()</u>
1st anodic	(1)	(48)	(49)	-
2nd anodic	(1)	(58)	(59)	(68),(69)
3rd anodic	(34)	(61)	(62)	-
cathodic	(22)	(55)	(54)	(1),(23)

The values of α/n and of α thus calculated are listed in Table III. The obvious scatter in the magnitude of these values precluded further analysis.

Table III: Values of α/n and α

<u>Reaction</u>	<u>α/n</u>	<u>α</u>
1st anodic	0.4604	2.477
2nd anodic	0.3488	3.134
3rd anodic	0.7711	5.370
cathodic	0.2714	0.893

Discussion

The results given in the foregoing section represent an initial study of electrode reactions in molten sodium carbonate at a corroding electrode. As such, they display significantly poorer reproducibility than data obtained by previous investigators working with relatively inert electrodes, although the correlation between data and model is good. Despite this, there is sufficient consistency in the empirical parameters which describe these polarization curves to infer that the reactions seen at inert electrodes also dominate at the corroding electrode. Manifestations of corrosion are

seen in the fine structure, or "blips", that occur primarily in the polarization region described by the second anodic reaction. The model used to describe these polarization curves, leading to the solid curves in Figures 2 through 5, is deliberately naive in that only three anodic reactions are considered and the kinetic behavior of each reaction is considered to be totally described by activation, concentration, and resistance polarization. This is shown to be adequate to provide a general description of the polarization behavior and to provide an initial assessment of the nature of the reactions involved. It is possible, however, to more precisely model these curves by 1) considering additional reactions, and 2) incorporating passivity into the model.²⁷ For example, Figure 10 shows the experimental polarization curve for specimen #75 (Figure 5 and Table I) plotted together with a curve calculated for a model similar to the foregoing, but containing five distinct anodic reactions, three of which exhibit passive behavior. The degree of correlation between the two curves is excellent, the calculated curve displaying all of the essential features seen by experiment. It is our intention to examine in detail in a subsequent paper this fine structure peculiar to the corroding electrode through the use of the more complex model.

Conclusions

In agreement with the findings of Borucka¹³ for inert electrodes, we have found the anodic reactions at the corroding nickel electrode in molten sodium carbonate under CO/CO₂ atmospheres at 1000°C to be

at low overpotentials and also, via a different reaction mechanism, at intermediate overpotentials, and to be

at high anodic overpotentials. In agreement with the work of Lorenz and

Janz¹² on inert electrodes, we have found the cathodic reaction to be

provided that the oxide ion is presumed not to be in equilibrium with the cell atmosphere. In general, the polarization behavior of this electrode is described by activation and concentration polarization of these reactions, together with resistance polarization. However, the anodic curves display anomalies which are attributable to corrosion of the electrode and which may be described by incorporating additional reactions, with passive behavior, into the model.

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FIGURE CAPTIONS

1. Schematic diagram of polarization cell.
2. Experimental (dotted) and calculated (solid) polarization curves for $P_{CO} = 0.05 \text{ atm.}$, $P_{CO_2} = 0.95 \text{ atm.}$
3. Experimental (dotted) and calculated (solid) polarization curve for $P_{CO} = 0.25 \text{ atm.}$, $P_{CO_2} = 0.75 \text{ atm.}$
4. Experimental (dotted) and calculated (solid) polarization curves for $P_{CO} = 0.50 \text{ atm.}$, $P_{CO_2} = 0.50 \text{ atm.}$
5. Experimental (dotted) and calculated (solid) polarization curves for $P_{CO} = 0.95 \text{ atm.}$, $P_{CO_2} = 0.05 \text{ atm.}$
6. Linear plot of equation (48) using values in Table I.
7. Linear plot of equation (58) using values in Table I.
8. Linear plot of equation (61) using values in Table I.
9. Linear plot of equation (55) using values in Table I.
10. Replot of experimental polarization curve for $P_{CO} = 0.95 \text{ atm.}$, $P_{CO_2} = 0.05 \text{ atm.}$, together with calculated curve employing five anodic reactions and three regions of passivity.

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Figure 1

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

Figure 6

Figure 7

Figure 8

Figure 9

FIGURE 10

REACTIONS AT THE CORRODING NICKEL ELECTRODE IN
MOLTEN SODIUM CARBONATE UNDER CO, CO₂ ATMOSPHERES

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ABSTRACT

Anodic reactions at the CO,CO₂|Ni electrode in molten sodium carbonate at 1000°C are examined in detail. Experimental polarization curves are fit via a computer graphics procedure to a model employing five anodic reactions with activation, concentration and resistance polarization, and passivation. The resultant empirical parameters are interpreted in terms of absolute rate expressions describing possible anodic reactions. At low anodic overpotentials reaction according to the sequence $\text{CO} + \text{O}^{2-} \rightleftharpoons \text{CO}_2 + 2 \text{e}^-$ is postulated; the next reaction can be kinetically described either by $\text{CO} + \text{CO}_3^{2-} \rightleftharpoons 2 \text{CO}_2 + 2 \text{e}^-$ or $\text{CO}_3^{2-} \rightleftharpoons \frac{1}{2} \text{O}_2 + \text{CO}_2 + 2 \text{e}^-$; the third reaction follows $2 \text{Ni} + \text{CO}_3^{2-} \rightleftharpoons 2 \text{NiO} + \text{CO} + 2 \text{e}^-$; the fourth reaction is apparently oxidation of NiO to a higher oxidation state, e.g., $2 \text{NiO} + \text{CO}_3^{2-} \rightleftharpoons \text{Ni}_2\text{O}_3 + \text{CO}_2 + 2 \text{e}^-$; and the fifth, at highest anodic overpotentials, is kinetically described by $\text{CO}_3^{2-} + \text{CO}_2 \rightleftharpoons \frac{3}{2} \text{O}_2 + 2 \text{CO} + 2 \text{e}^-$. The cathodic polarization curve follows $\text{CO}_3^{2-} + 2 \text{e}^- \rightleftharpoons \text{CO} + 2 \text{O}^{2-}$.

Key words: anodic, polarization, molten carbonate, nickel.

Introduction

In a recent paper¹ we described polarization measurements on the $\text{CO}, \text{CO}_2 | \text{Ni}$ electrode in molten sodium carbonate. These measurements were analyzed via a previously described computer modelling technique^{2,3} in terms of three anodic reactions, two of which experience diffusional effects, and a single cathodic reaction. This superficial analysis suggested that the observed behavior was in agreement with that observed by other investigators at non-corroding electrodes^{4,5}, namely that at low anodic overpotentials anodic current is carried by

at intermediate anodic overpotentials anodic current is carried by

and

and at high anodic overpotentials anodic current is carried by

Cathodic current is carried by

It was noted that, assuming the equilibrium

reactions (2) constitute an alternate route for reaction (1).

It was noted in the previous paper¹ that the anodic polarization curve showed a "fine structure" that was presumed representative of corrosion reactions at the nickel electrode. Consequently these data have been re-analyzed, taking into account possible contributions to the anodic current of up to five reactions and including passivation in the computer model. This analysis is presented in the following.

Experimental

Details of apparatus and procedure were given previously.¹ In brief, nickel electrodes were polarized in molten sodium carbonate at 1000°C employing a platinum counter electrode and a previously described⁶ reference electrode reversible to reaction (1). The reference atmosphere was held fixed, independent of the cell atmosphere, with $P_{CO} = 0.38$ atm and $P_{CO_2} = 0.62$ atm and electrolytic contact between the cell and reference electrolytes maintained by Na^+ conduction through the alumina jacketing the reference electrode. Potential was controlled and current measured via standard instrumentation, and output as an analog x-y plot of cell potential vs. log cell current. Sufficient points to define these polarization curves were input to a computer program and replotted on a graphics terminal together with a calculated curve. The parameters describing the latter were optimized through a series of successive guesses based on the degree of conformity of the experimental and calculated curves, i.e., via "visual regression".

In a separate series of experiments, nickel specimens were held at particular anodic potentials for extended periods, then removed for x-ray diffraction analysis of the scale thus formed.

Results

Data are reported for seven polarization runs involving four different P_{CO}/P_{CO_2} ratios, with $P_{CO} + P_{CO_2} = 1$ atm. The current, i_{aj} , carried by the j th anodic reaction experiencing activation, concentration, and resistance

polarization is given by

$$i_{aj} = (1 - i_{aj}/i_{saj})^{RT/nFb_{aj}} \exp[(v - v_{aj}^0)/b_{aj}] \exp(-i_{aj}R_a/b_{aj}) \quad (6)$$

where i_{saj} is the limiting diffusion current; R , T , and F , the usual constants; n , the number of charges on the species controlling the limiting diffusion current; $2.303 b_{aj}$, the Tafel slope; v_{aj}^0 , a constant incorporating the concepts of the "rest potential" and the "exchange current"; and R_a is the cell resistance. Similarly, the current carried by the j th cathodic reaction is given by

$$i_{cj} = (1 - i_{cj}/i_{scj})^{RT/nFb_{cj}} \exp[-(v - v_{cj}^0)/b_{cj}] \exp(-i_{cj}R_c/b_{cj}) \quad (7)$$

The total cell current is given by

$$i = \left| \sum_{j=1}^{n_a} i_{aj} - \sum_{j=1}^{n_c} i_{cj} \right| \quad (8)$$

where n_a is the total number of anodic reactions possible and n_c the number of cathodic reactions. Not all reactions experienced concentration polarization; for these the limiting diffusion current is simply an arbitrarily large value. Similarly, only the anodic reaction and cathodic reaction dominant at the largest overpotentials were, in our model, assumed affected by resistance polarization; for the other reactions the resistance was set at zero. Cell resistance under anodic polarization was permitted to assume a different value from that under cathodic polarization because, in our experience, this provided for an optimum empirical fit of model to data. Passivation of anodic reactions is incorporated into the model by simply defining the current carried by that reaction above a particular potential, v_{pj} , to be a constant, i_{pj} .

The polarization data reported are represented by sample numbers 90 and 91 ($P_{CO}/P_{CO_2} = 0.05/0.95$), 82 ($P_{CO}/P_{CO_2} = 0.25/0.75$), 81 and 83 ($P_{CO}/P_{CO_2} = 0.50/0.50$), and 75 and 78 ($P_{CO}/P_{CO_2} = 0.95/0.05$). With the exception of sample 91 the cathodic polarization curves are clearly represented by a single reaction; the slight anomaly for sample 91 was associated with an oxygen contamination of the cell atmosphere and was ignored. The anodic behavior of this sample did not appear to be affected significantly. Samples 90, 91, 82, 81, and 83 were reasonably well-described by a total of four anodic reactions; sample 75 showed clearly an additional reaction in the low anodic overpotential region and there is a less clear suggestion of this same reaction in sample 78. The empirical parameters chosen as "visually optimum" to represent these polarization data are listed in Table I; the experimental and calculated polarization curves are shown in Figures 1 through 7.

Figure 6 has three points, A, B, and C, identified on the anodic branch of the polarization curve. These indicate potentials at which specimens were held for x-ray diffraction analysis of scale. All diffraction patterns indicated nickel⁷, unavoidably included during sample removal. The sample obtained at point A contained only nickel; that obtained at point B contained nickel and nickelous oxide (NiO).⁸ Two specimens were prepared at point C; one of these contained only nickel and NiO, while the other produced a diffraction pattern which included three additional lines not characteristic of nickel or NiO. These lines corresponded to d spacings of 2.59, 2.21 and 1.92 Å°. Nickelous oxide (NiO) is reported to have an NaCl structure (fcc) with $a = 4.177 \text{ Å}^\circ$ ⁸ and also $a = 4.172 \text{ Å}^\circ$ ^{9,10}. A number of other oxides have been reported, including Ni_xO_y (rhombohedral, $y/x - 1 = 0 - 0.2$)¹¹, $Ni_{15}O_{16}$ (tetragonal, $a = 5.911 \text{ Å}^\circ$, $c = 8.360 \text{ Å}^\circ$)¹², Ni_2O_3 (fcc, $a = 4.186 \text{ Å}^\circ$)⁹, Ni_2O_3 (hexagonal,

$a = 4.61 \text{ \AA}$, $c = 5.61 \text{ \AA}$)¹³, a solid solution of NiO in Ni₂O₃,⁹ and NiO₂ (cubic, $a = 4.620 \text{ \AA}$)⁹. The additional lines observed do not match the patterns of hexagonal Ni₂O₃, fcc Ni₂O₃, nor cubic NiO₂. However, the lines at $d = 2.57$ and $2.21 \text{ \AA}$ do correspond to the (111) and (200) lines for a cubic crystal with $a = 4.4 \text{ \AA}$, and the 1.92 line could be construed as a second order diffraction from the NiO (331) plane.

Discussion

Empirical parameters describing the cathodic branch of the polarization curves were not significantly altered by the inclusion of additional anodic reactions in the model; thus, the conclusion previously given¹ that the cathodic current is carried by the reaction

with the oxide ion not at equilibrium with the cell atmosphere, remains valid. The anodic branch requires significant reanalysis, however.

We may postulate the following anodic reactions as possible:

Oxidation of CO:

Oxidation of CO via the intermediary CO₂⁼:

Oxidation of CO₃⁼ (or O⁼):

which reduces to reaction (1) if the oxygen is at equilibrium with the cell atmosphere. Oxidation of CO₃⁼ with CO formation:

Oxidation of nickel to the +2 state:

Oxidation of nickel to the +2 state with scale formation:

and

Oxidation of nickel to the +3 state with scale formation:

and

Oxidation of nickelous oxide to nickelic oxide:

and

Let us, as an example, consider reaction (1) in detail. For currents appreciably less than any saturation current and for which the ohmic potential drop is negligible equation (6) reduces to

$$i_{a1} = \exp[(v - v_{a1}^0)/b_{a1}] \quad (17)$$

It was shown in the previous paper¹ that the empirical constants v_{a1}^0 and b_{a1} could be represented as

$$e^{-v_{a1}^0/b_{a1}} = n_1 F k_{a1} \prod_{i=1}^{\gamma_1} (K_i)^{1/\nu_1} P_{\text{CO}}^{1/\nu_1} (P_{\text{CO}}/P_{\text{CO}_2}^2)^{\alpha_{a1}/n_1} e^{-\alpha_{a1} FE_1^0/RT} \quad (18)$$

and

$$b_{a1} = \frac{RT}{\alpha_{a1} F} \quad (19)$$

where k_{a1} is the chemical reaction rate constant, n_1 is the number of steps comprising the overall reaction, γ_1 is the number of steps preceding the rate-limiting step, ν_1 is the number of times the rate-limiting step occurs in a single reaction sequence, z_1 is the number of electrons carried by

the rate-limiting step, the K_i are the equilibrium constants for the various component steps of the reaction, E_1^0 is the standard half-cell potential for the reaction, and α_{a1} is a transfer coefficient defined by

$$\alpha_{a1} \equiv \gamma_1/\nu_1 + z_1(1 - \beta_1) \quad (20)$$

where β_1 represents the symmetry of the activation barrier controlling the reaction. The transfer coefficient reduces to $\alpha_{a1} = z_1(1 - \beta_1)$ for a single step reaction in which necessarily $\nu_1 = 1$ and $\gamma_1 = 0$. In equation (18) the factor P_{CO}^{1/ν_1} has simple kinetic origins, while the factor $(P_{CO}/P_{CO_2}^2)^{\alpha_{a1}/n_1}$ represents a Nernstian correction for the equilibrium potential. If P_{CO} is increased the reaction rate will increase both because of the increase in interaction frequency of CO with the electrode surface and also because the equilibrium potential for the reaction will be made more negative. Without laboriously deriving a comparable expression for each of the foregoing possible anodic reactions, we may thus readily infer the dependence of this parameter upon P_{CO} and P_{CO_2} as shown in Table II. Also listed in Table II is the tendency for each of these reactions to experience passivation or a diffusion-limited behavior (concentration polarization). These terms are being used somewhat loosely inasmuch scale formation is, typically, a passivation phenomenon; yet, it is also an extreme case of concentration polarization. Use of the latter term in this paper has been restricted to diffusion-limited transport in the electrolyte. In attempting to match the component reactions of the anodic polarization curve with the foregoing possible anodic reactions we may, thus, make use of the displacement of these reactions with change in P_{CO}/P_{CO_2} values and of the occurrence of passivation or concentration polarization.

Accordingly, let us consider the anodic reactions in order of their occurrence, starting with the lowest anodic overpotentials. This has been denoted A1 in Table I and is seen only at the highest P_{CO} values, hence we

may infer that $\frac{d}{dP_{CO}}(e^{-v_{a1}^0/b_{a1}})$ is positive. This reaction appears to display passivation, yet this occurs well below potentials or currents at which a scale is seen by x-ray diffraction. Reaction A2 clearly has a positive value for $\frac{d}{dP_{CO}}(e^{-v_{a2}^0/b_{a2}})$ and displays concentration polarization, but not passivation. Reaction A2 must be, therefore, either reaction (1) or reaction (2) from the characteristics listed in Table II. It is reasonable to propose that reaction A2 is, in fact, reaction (1) as suggested in our earlier analysis¹. Necessarily, reaction A1 must be reaction (2) since reaction (3), being simply oxidation of $CO_3^{=}$, should show neither concentration polarization nor passivation, and the remaining reactions showing positive values for $\frac{d}{dP_{CO}}(e^{-v_{aj}^0/b_{aj}})$ involve scale formation. Although reaction (2) should not inherently passivate, similar behavior would be seen if $CO_2^{=}$ formation is slow; i.e., on reaching adequate overpotentials the $CO_2^{=}$ formed during previous equilibration of the cell would be consumed and, if not replenished, the reaction would cease. Values pertaining to reaction A2 in Table I are plotted according to Table II for reaction (1) in Figure 8 for $v_2 = 1$, in Figure 9 for $v_2 = 2$, and in Figure 10 for large v_2 , i.e., $1/v_2 = 0$. The latter clearly affords the better fit. This can be interpreted as indicative that the rate-determining step is repeated a large number of times, which does not seem likely, or that the surface region is essentially saturated with CO at all P_{CO} values employed. Although the latter inference is contrary to ultimate control of the reaction by CO diffusion, the observed concentration polarization could be also attributable to diffusion of CO_2 away from the electrode. If this is the case, then reaction (3) could also exhibit concentration polarization and a plot of these data according to this reaction, Figure 11, show an equally good fit. Reaction A3 shows a negative value for $\frac{d}{dP_{CO}}(e^{-v_{a3}^0/b_{a3}})$ and clear passivation; furthermore, in the region described by this reaction an NiO scale is seen by x-ray diffraction. These features

are unique to reaction (12). Interestingly, this suggests that reaction (10), direct formation of Ni^{++} in solution, is of little significance and that nickel oxidation in this potential region occurs by NiO formation. At currents too low to maintain passivity, this species must immediately dissolve in a non-rate-limiting step. Values pertaining to reaction A3, plotted according to reaction (12), are shown in Figure 12. Reaction A4 clearly represents the oxidation of NiO to a higher oxidation state inasmuch as a current peak is seen in this region. Were this reaction to be oxidation of nickel to a state higher than +2, its rate would be controlled by diffusion through the scale already formed by reaction A3; i.e., a peak would not be seen. The parameter values seem scattered for this reaction, but do show a positive value for $\frac{d}{dP_{\text{CO}}}(e^{-v_{\text{a4}}^0/b_{\text{a4}}})$ suggesting reaction (15). The corresponding plot is given in Figure 13. The scatter is more apparent than real in view of the very small slope of this plot. The x-ray diffraction results pertaining to this region of the polarization curve are not definitive, but imply the presence of an additional oxide. Close examination of the polarization curves for several specimens shows that more than one reaction may be occurring in this region, suggesting that, in fact, a multi-stage oxidation to the +3 state may occur. Reaction A5 is affected by resistance polarization, does not show passivity nor concentration polarization, and has a negative value for $\frac{d}{dP_{\text{CO}}}(e^{-v_{\text{a5}}^0/b_{\text{a5}}})$. In contrast to our earlier conclusion¹ based on a total of three, non-passivating anodic reactions, that simple oxidation of $\text{CO}_3^{=}$ to oxygen is occurring at these potentials, the P_{CO} dependence seen with the present more complete analysis suggests that reaction (9), involving concurrent formation of CO , rather than reaction (3) is occurring. This suggestion is strengthened by the observation¹⁴ in gas adsorption studies that at elevated temperatures CO_2 adsorbs on nickel as $\text{CO} + \text{O}$, i.e., that CO_2 is not stable at the nickel surface. Data for reaction A5 are plotted according to reaction (9) in Figure 14. Although the general dependence is

correct, there is definite curvature evidence in the plotted points that suggests a stronger dependence such as that afforded by reaction (21):

for which a plot of $-\nu_{a5}^0/2.3b_{a5} - 1/\nu_5 \log P_{\text{CO}_2}$ versus $\log P_{\text{CO}_2}/P_{\text{CO}}^2$ should yield a straight line of slope α_{a5}/n_{a5} . This is shown in Figure 15 for $\nu_5 = 1$, and in Figure 16 for $\nu_5 = 2$. The degree of fit is substantially better for reaction (21), but is not especially sensitive to ν_5 .

The results of the foregoing paragraph and the values of α_{aj}/n_{aj} thus obtained are summarized in Table III, together with average values of α_{aj} calculated from the b_{aj} values given in Table I and equation (19). Relating these values yields a value for n_{aj} , which should be a small integer. For the curves for which the "Visual degree of fit" is denoted "good", only n_{a4} has an unreasonable value, 39. This is indicative either that reaction (15) is a totally inappropriate choice for reaction A4 (oxidation of NiO to any other oxidation state by a comparable reaction would shown the same dependence, however) or that the reaction choice is correct and its mathematical description is correct, but the model leading from the reaction to the mathematical description is wrong. The expressions of the form of equation (18) derive from the treatment of Bockris and Reddy¹⁵ for reactions experiencing simple activation control at an interface, resulting in an exponential dependence of rate upon field. Reaction A4 clearly does not occur at a well-defined interface, but throughout the bulk of a thin layer, and is possibly controlled by diffusion of either ionic or electronic defects within this layer, a process which would display an exponential dependence on field if the field is sufficiently high. We also note that the α_{aj} values reported in Table III are average values for the $P_{\text{CO}}/P_{\text{CO}_2}$ values studied; in fact, b_{a2} , b_{a3} , and b_{a5} show a clear decrease with increasing P_{CO} . There are insufficient data to draw any conclusion regarding P_{CO} dependence of b_{a1} , and

the accuracy of the b_{a4} values is poor in view of the small portion of the polarization curve affected by this parameter. Thus, there appears to be a shift in the symmetry of the activation barrier affecting these reactions at the electrode/electrolyte interface which, in very general terms, may be related to an adsorption phenomenon. A priori, the passivation potentials should be amenable to a thermodynamic interpretation; however, there is no apparent trend in these parameters.

Cell resistance during anodic polarization, R_a , increases with increasing P_{CO} , i.e., with decreasing P_{CO_2} . The most obvious interpretation of this change is in terms of equilibrium (5), i.e., a decrease in P_{CO_2} corresponds to an increase in $O^{=}$ concentration at the expense of the $CO_3^{=}$ concentration. Thus, the Table I data are in accord with an electrolyte resistivity that increases with increasing Na_2O/Na_2CO_3 ratio. We have no independent data with which to compare this observation, but it might be rationalized in terms of relative anionic size, i.e., the relatively smaller size of the oxide anion implies a higher concentration of charge and higher local fields which, in turn, cause a greater degree of anion/cation interaction and a correspondingly reduced mobility. While this is not borne out with pure salts (the Na^+ halides show a steady increase in resistance with increase in anion size¹⁶ in accord with the Stokes-Einstein equation¹⁷), there is some indication that binary salt mixtures exhibit a "conductivity depression" somewhat analagous to freezing point depression, i.e., the conductivity of the salt is reduced with respect to the pure salt by the addition of a solute irrespective of its nature.^{16,17} Resistance values during cathodic polarization show the same trend with P_{CO} , but are typically smaller, possibly due to local changes caused by CO evolution in accord with reaction (4).

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Table I
Values of Empirical Parameters

ecimen	90	91	82	81	83	75	78	
$\frac{CO}{P_{CO_2}}$	0.05/0.95	0.05/0.95	0.25/0.75	0.50/0.50	0.50/0.50	0.95/0.05	0.5/0.05	atm/atm
i_{sa1}	*	*	*	*	*	-	-	ma/cm ²
i_{sa2}	1.8	1.8	3.0	1.3	1.3	3.0	2.7	ma/cm ²
i_{sa3}	-	-	-	-	-	-	-	ma/cm ²
i_{sa4}	-	-	-	-	-	-	-	ma/cm ²
v_{oa1}	*	*	*	*	*	-55	0	mv
v_{oa2}	235	260	220	60	125	-50	-25	mv
v_{oa3}	245	270	265	230	260	300	315	mv
v_{oa4}	415	440	390	410	430	420	400	mv
v_{oa5}	770	810	690	700	775	840	735	mv
b_{a1}	*	*	*	*	*	60	70	mv
b_{a2}	80	70	60	50	50	40	50	mv
b_{a3}	80	60	60	55	55	60	50	mv
b_{a4}	80	80	80	80	80	80	80	mv
b_{a5}	40	40	40	30	30	27	23	mv
R_a	0.8	0.9	1.1	1.3	1.3	2.1	2.1	ohm
v_{p1}	*	*	*	*	*	5	-10	mv
i_{p1}	*	*	*	*	*	0.1	0.1	ma/cm ²
v_{p2}	-	-	-	-	-	-	-	mv
i_{p2}	-	-	-	-	-	-	-	ma/cm ²
v_{p3}	450	445	400	400	425	460	450	mv
i_{p3}	8	3	4	6	7	3	3	ma/cm ²
v_{p4}	600	550	560	535	555	610	600	mv
i_{p4}	1	0.1	1	0.1	0.1	4	4	ma/cm ²
i_{sc1}	-	-	-	-	-	-	-	ma/cm ²
v_{oc1}	25	-90	-10	-165	-135	-100	-40	mv
b_{c1}	160	160	120	125	140	90	70	mv
R_c	1.0	0.5	0.3	0.3	0.3	1.5	1.5	ohm
$v_{a1}/2.3b_{a1}$	*	*	*	*	*	-0.398	0	-
$v_{a2}/2.3b_{a2}$	1.276	1.613	1.592	0.521	1.086	-0.543	-0.217	-
$v_{a3}/2.3b_{a3}$	1.330	1.954	1.918	1.816	2.053	2.171	2.736	-
$v_{a4}/2.3b_{a4}$	2.253	2.389	2.117	2.226	2.334	2.280	2.171	-
$v_{a5}/2.3b_{a5}$	8.360	8.794	7.492	10.133	11.219	13.511	13.879	-
$i_{c1}/2.3b_{c1}$	0.068	-0.244	-0.036	-0.573	-0.419	-0.483	-0.248	-

* This reaction was not employed in determining an empirical fit.

- Not applicable.

Table II

Dependence of $e^{-v_{aj}^0/b_{aj}}$ on P_{CO} for $(P_{CO} + P_{CO_2}) = 1 \text{ atm.}$

Reaction	$\frac{d}{dP_{CO}}(e^{-v_{aj}^0/b_{aj}})$	For a linear plot		slope	Passivates	Diffusion limited
		y	x			
1	positive	$-v_{aj}^0/2.3b_{aj} - 1/v_j \log P_{CO}$	$\log P_{CO}/P_{CO_2}^2$	α_{aj}/n_{aj}	no	yes
*2	positive	$-v_{aj}^0/2.3b_{aj} - 1/v_j \log P_{CO}$	$\log P_{CO}/P_{CO_2}^2$	α_{aj}/n_{aj}	***	yes
**3	positive	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO_2}$	$-\alpha_{aj}/n_{aj}$	no	no
**9	negative	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO}$	$-\alpha_{aj}/n_{aj}$	no	no
10	0	-	-	-	yes	no
11	positive	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO_2}$	$-\alpha_{aj}/n_{aj}$	yes	no
12	negative	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO}$	$-\alpha_{aj}/n_{aj}$	yes	no
13	positive	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO_2}$	$-\alpha_{aj}/n_{aj}$	yes	no
14	negative	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO}$	$-\alpha_{aj}/n_{aj}$	yes	no
15	positive	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO_2}$	$-\alpha_{aj}/n_{aj}$	yes	no
16	negative	$-v_{aj}^0/2.3b_{aj}$	$\log P_{CO}$	$-\alpha_{aj}/n_{aj}$	yes	no

* Assumes equilibrium O_2 and CO_2

** Assumes that O_2 is not equilibrium

*** As noted in Discussion, this reaction could lend the appearance of passivation if CO_2 production is slow.

Table III
Correlation Summary

<u>Reaction</u>	<u>Reaction</u>	<u>α_{aj}/n_{aj}</u>	<u>α_{aj}</u>	<u>n_{aj}</u>	<u>v_j</u>	<u>Visual degree of fit</u>
A1	(2)	-	1.686	-	-	-
A2	(1)	0.199	1.919	9.643	1	poor
A2	(1)	0.352	1.919	5.452	2	fair
A2	(1)	0.506	1.919	3.792	large	good
A2	(3)	1.435	1.919	1.337	-	good
A3	(12)	0.545	1.827	3.352	-	good
A4	(15)	0.035	1.371	39.171	-	poor
A5	(9)	3.590	3.337	0.929	-	fair
A5	(21)	1.063	3.337	3.139	1	good
A5	(21)	1.226	3.337	2.722	2	good

Figure Captions

1. Anodic and cathodic polarization curves for specimen 90 ($P_{CO} = 0.05$ atm; $P_{CO_2} = 0.95$ atm). Dotted - experimental; solid - calculated.
2. Anodic and cathodic polarization curves for specimen 91 ($P_{CO} = 0.05$ atm; $P_{CO_2} = 0.95$ atm). Dotted - experimental; solid - calculated.
3. Anodic and cathodic polarization curves for specimen 82 ($P_{CO} = 0.25$ atm; $P_{CO_2} = 0.75$ atm). Dotted - experimental; solid - calculated.
4. Anodic and cathodic polarization curves for specimen 81 ($P_{CO} = 0.50$ atm; $P_{CO_2} = 0.50$ atm). Dotted - experimental; solid - calculated.
5. Anodic and cathodic polarization curves for specimen 83 ($P_{CO} = 0.50$ atm; $P_{CO_2} = 0.50$ atm). Dotted - experimental; solid - calculated.
6. Anodic and cathodic polarization curves for specimen 75 ($P_{CO} = 0.95$ atm; $P_{CO_2} = 0.05$ atm). Dotted - experimental; solid - calculated.
7. Anodic and cathodic polarization curves for specimen 78 ($P_{CO} = 0.95$ atm; $P_{CO_2} = 0.05$ atm). Dotted - experimental; solid - calculated.
8. Plot of $-v_{a2}^0/2.3b_{a2} - \log P_{CO}$ (Y) versus $\log P_{CO}/P_{CO_2}^2$ (X).
9. Plot of $-v_{a2}^0/2.3b_{a2} - \frac{1}{2} \log P_{CO}$ (Y) versus $\log P_{CO}/P_{CO_2}^2$ (X).
10. Plot of $-v_{a2}^0/2.3b_{a2}$ (Y) versus $\log P_{CO}/P_{CO_2}^2$ (X).
11. Plot of $-v_{a2}^0/2.3b_{a2}$ (Y) versus $\log P_{CO_2}$ (X).
12. Plot of $-v_{a3}^0/2.3b_{a3}$ (Y) versus $\log P_{CO}$ (X).
13. Plot of $-v_{a4}^0/2.3b_{a4}$ (Y) versus $\log P_{CO_2}$ (X).
14. Plot of $-v_{a5}^0/2.3b_{a5}$ (Y) versus $\log P_{CO}$ (X).
15. Plot of $-v_{a5}^0/2.3b_{a5} - \log P_{CO_2}$ (Y) versus $\log P_{CO_2}/P_{CO}^2$ (X).
16. Plot of $-v_{a5}^0/2.3b_{a5} - \frac{1}{2} \log P_{CO_2}$ (Y) versus $\log P_{CO_2}/P_{CO}^2$ (X).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Figure 12

Figure 13

Figure 14

Figure 15

Figure 16

INSTITUTE OF MATERIALS SCIENCE

The Institute of Materials Science (IMS) was established at The University of Connecticut in 1966 in order to promote academic research programs in materials science. To provide requisite research laboratories and equipment, the State of Connecticut appropriated \$5,000,000, which was augmented by over \$2,000,000 in federal grants. To operate the Institute, the State Legislature appropriates over \$500,000 annually for faculty and staff salaries, supplies and commodities, and supporting facilities such as an electronics shop, instrument shop, a reading room, etc. This core funding has enabled IMS to attract over \$2,500,000 annually in direct grants from federal agencies and industrial sponsors.

IMS fosters interdisciplinary graduate programs in Alloy Science, Biomaterials, Corrosion Science, Crystal Science, Metallurgy, and Polymer Science. These programs are directed toward training graduate students while advancing the frontiers of knowledge and meeting current and long-range needs of our state and our nation.