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ELECTRODE POLARIZATION STUDIES
IN HOT CORROSION SYSTEMS

Progress Report

for period

1 June 1979 - 31 May 1980

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ABSTRACT

Work on the following discrete tasks is reported: Electrode polarization studies in molten sodium carbonate: A comprehensive set of tests has been performed on iron, nickel, and types 304 and 316 stainless steel in gas mixtures of controlled P_{CO} , P_{CO_2} , P_{H_2} , and P_{H_2S} at a total pressure of one atmosphere and in a temperature range of 900 - 1000°C. The polarization curves thus derived have been reduced to a set of empirical kinetic constants via computer modelling. Gas/metal reactions in mixed oxidants: Oxidation of iron in gas mixtures of controlled P_{CO} , P_{CO_2} , P_{H_2} and P_{H_2S} at a total pressure of one atmosphere and a temperature of 900°C has been studied. In the P_{S_2} and P_{O_2} ranges employed sulfide scales were formed; P_{O_2} influenced the short term sulfidation kinetics. Specimen geometry was seen as a significant factor influencing long term kinetics. Liquid line corrosion: A reproducible corrosive attack is seen at the metal/molten carbonate/gas phase junction. This attack can be quantitatively evaluated and explained in terms of a diffusion model. Evaluation of reaction kinetics from polarization data (addendum): Previous modelling procedures have been expanded to include one or more anodic reactions displaying passive behavior.

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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 2 1/2 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 1980.

Kyooyoung Kim - PhD thesis in preparation, currently employed
by IITRI, Chicago, Illinois.

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.

Kyooyoung 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/CO₂ | Na₂CO₃ 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). (15 reprint requests)

c. R. Boland and O. F. Devereux, "Intergranular Sulfidation of Iron",
Met. Trans. 10A, 1959, (1979). (1 reprint request)

d. O. F. Devereux and K. Y. Kim, "Computer Modelling of Polarization
in Passive Systems", Corrosion (in press).

e. R. A. Cooke and O. F. Devereux, "Simulation of Coal Conversion
Reactor Environments", Corrosion (in press).

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.

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)

B. Task Summaries

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

The polarization cell and experimental procedure pertaining to this task were described in some detail in the Progress Report for the preceding period, 1 June 78 - 31 May 79.¹ During this report period this equipment and technique were used routinely to determine the polarization characteristics of Fe, Ni, and types 304 and 316 stainless steel in molten sodium carbonate at temperatures of 900, 950, and 1000°C. Atmospheres consisted of controlled mixtures of CO and CO₂; of CO, CO₂, H₂S, and H₂; or of CO, CO₂, H₂S, H₂, and H₂O at a total pressure of one atmosphere. All polarization curves have been reduced to sets of empirical constants corresponding to a theoretical equation incorporating the effects of activation, concentration, and resistance polarization on three or less anodic reactions and three or less cathodic reactions, together with the option of a passive region in each of the anodic reactions, using the previously described computer modelling technique.²⁻⁴

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

The recording gravimetric facility employed for oxidation studies is described in the previous report as are the procedures used.¹ During this report period the reaction of Armco iron with gases of controlled (Ar, H₂, H₂S, CO, CO₂) analysis was studied at 900°C, with the effective value of P_{S_2} being held at 1.2×10^{-5} atm while P_{O_2} was varied over the range 2×10^{-19} - 7×10^{-16} atm. In this range a sulfide scale was formed; however, short time kinetics was strongly influenced by P_{O_2} . Overall kinetic behavior was non-simple, and called attention to corresponding discrepancies in the literature which present results suggest are related to specimen size and/or geometry. While

the present investigation of this effect is very incomplete, such behavior could be rationalized in terms of the role of compressive stress in the scale in causing scale/substrate separation.

3. Liquid Line Corrosion (Iyer)

Reproducible profiles of liquid line attack have been obtained for nickel partially immersed in molten sodium carbonate under reduced air pressures at 1000°C. This profile is approximately circular in section, in some cases to a remarkable degree of accuracy. This is attributed to joint control of the process by 1) diffusion of oxygen to the reaction site and 2) diffusion of Ni^{++} from the reaction site. The geometry of the meniscus renders the problem mathematically unpleasant; a search for reasonable approximate methods of solution is underway.

4. Evaluation of Reaction Kinetics from Polarization Data (Devereux)

A visual regression procedure to optimize fit of theoretical curve to polarization data through selection of up to fourteen linear and nonlinear empirical kinetic parameters has been described.¹⁻³ Subsequent polarization studies revealed a necessity for expansion of this capability to include up to three anodic reactions and up to three cathodic reactions, together with the possibility that each of the anodic reactions may display passive behavior. This has been accomplished and reported.⁴

REFERENCES

1. "Electrode Polarization Studies in Hot Corrosion Systems", Progress Report for period 1 June 1978 - 31 May 1979, DOE Contract No. EY-76-S-02-2960.A002, (Feb. 1979).

2. O. F. Devereux, "Polarization Curve-Fitting by Computer Modelling", Corrosion 35, 125, (1979).
3. O. F. Devereux, "Computer Modelling of Electrode Polarization", Internal Report, Institute of Materials Science, University of Connecticut, (Aug. 1978).
4. O. F. Devereux and K. Y. Kim, "Computer Modelling of Polarization in Passive Systems", Corrosion (in press).

C. Extended Discussion of Progress

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

Mr. K. Y. Kim has completed his experimental work on this task and is presently employed at IITRI, Chicago, Ill., on a somewhat similar program in a training position. At the same time, he is analyzing the results of his experimental program and writing his doctoral thesis. In the interest of efficiency of effort, we would like to defer any detailed discussion of these results and their meaning pending completion of that writing. Mr. K. S. Yeum, a new PhD candidate, has assumed Mr. Kim's position in this project and has familiarized himself with the experimental aspect of the program.

One aspect of this task that should be reported at this time, however, is that of the analysis of the effluent gas from the polarization cell. We have just performed a few analyses, but this has been sufficient to establish that the gas is not achieving equilibrium as it passes through the cell although significant reaction does occur. A major premise of this work has been that equilibrium would occur, thereby establishing precisely the environment of the electrode. As this is not the case, we will have to determine through additional analyses the extent to which we can approximate the cell environment as the incoming gas.

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

The continuous recording gravimetric facility described in the previous progress report is fully operational. The experimental procedure is as reported except for a change in the termination of a corrosion test; the specimen is quenched in the reactive gas mixture (as a result of the removal of the hinged furnace) rather than cooled in an argon environment.

This report covers work performed on iron in Ar/H₂/H₂S/CO/CO₂ gas mixtures at 900°C. Individual flow rates of Ar, (H₂/H₂S), and (CO/CO₂) were held constant. The gas mixtures were composed as follows: Ar 10%, (H₂/H₂S) 50%, and (CO/CO₂) 40%. The H₂S/H₂ ratio was held constant at 0.01 and the CO₂/CO ratio varied. In order to clarify certain features of the observed kinetic behavior tests were also performed in the absence of CO and CO₂. In these instances, the argon flow rate was increased so that the total flow rate as well as that of the H₂S/H₂ mixture was held constant at the previous values. Also, an additional H₂S/H₂ ratio of 0.1 was used. Experiments were performed at least in duplicate.

Only scales from long time reactions have been analysed. In all cases, the scales were two-layered, the outer layer being coarser. Both layers were identified as FeS (troilite or pyrrhotite) by x-ray diffraction analysis.

Kinetic data for iron in Ar/CO/CO₂/H₂/H₂S gas mixtures with H₂S/H₂ = 0.01 are presented in Figure 1. The effect of varying the CO₂/CO ratio is most pronounced during the early time behavior. As the CO₂/CO ratio is increased the individual curves change from exhibiting 1) an initially slow, but increasing, rate which finally breaks into the long time rate to 2) a fast initial rate which decreases with time to the long time rate. The former early time behavior is also exhibited in the absence of CO₂ and CO for this same H₂S/H₂ ratio as shown in Figure 2. This behavior exists for scale thicknesses up to $1.1 \times 10^5 \text{ \AA}$ (2 mg/cm^2), a thickness that is beyond that normally associated with thin film growth. As can be seen in Figure 3 this behavior is not observed for H₂S/H₂ = 0.1.

While nucleation can no longer be a rate limiting factor at these thicknesses, it is proposed that islands associated with nucleation sites may be growing laterally over a sulfide base film during this period. Such sites may be associated with grain boundaries; preferential attack at grain boundaries has been demonstrated for Armco iron in H_2S (1). It is likely that a surface controlled reaction is also rate limiting; this is necessary to explain the initial linear regions for the cases where the initial reaction is fast. Worrell and Turkdogan (2) invoked a similar mechanism in describing their work.

Bartlett (3) has presented a detailed discussion of oxidation kinetics for lateral oxide growth coupled with a linear process. For such lateral growth the fraction f of the total surface area covered at time t is given by $f = [1 - \exp(-kt^n)]$. The value of n is determined by the nucleation rate. In this case the density of nuclei or islands is considered fixed and, therefore, $n = 2$. This is not strictly correct since all the islands will not impinge on each other at the same time. This expression may be coupled with the equation representing the surface chemical reaction, namely:

$$\frac{d(m/A)}{dt} = k_L c_g$$

where m/A is the weight change per unit area, c_g is the gas concentration at the surface and k_L is the linear rate constant; giving

$$\frac{d(m/A)}{dt} = k_L c_g [1 - \exp(-kt^2)]$$

In this treatment, the contribution of a diffusional process, later seen to be important, to the growth normal to the surface has been neglected. If the islands grow simultaneously at a linear rate normal to the surface, e.g., by a surface controlled process, and laterally according to $f = [1 - \exp(-kt^n)]$ the reaction rate will initially increase and eventually become linear when the surface becomes flat. Alternatively, if growth normal to the surface is

parabolic, e.g., diffusion controlled, the corrosion rate will initially increase and eventually decrease according to a parabolic rate. The mathematical solution to the differential equation accounting for the diffusional process is non-trivial. These hypotheses are in agreement with observation.

At 900°C Hayward and Trapnell (4) find that CO_2 is dissociated and adsorbed on the surface as CO and O, and also that the chemisorption of one gas can assist and create sites for the adsorption of a second gas. The effect of the CO_2/CO gas mixtures may then be due solely to the partial pressure of CO_2 , that is, a kinetic rather than a thermodynamic effect. The atomic oxygen created may greatly increase the number of nucleation sites, causing a higher initial rate and little lateral growth of the sulfide scale. The atomic oxygen is then desorbed. (No oxides have been found in these scales.)

The long time linear kinetic behavior of iron in these gas mixtures is different from the parabolic behavior reported for the same $\text{H}_2\text{S}/\text{H}_2$ ratio by Zelouf (5). Further, examination of the literature over a wide range of $\text{H}_2\text{S}/\text{H}_2$ ratios and gas flow rates, and a temperature range from 250 to 900°C, revealed two different classes of observation. While the initial behavior is much the same in all cases, the long time behavior is reported as either linear (6,7,8) or, parabolic (5,9). The two layered scales formed also reflect this difference in kinetic behavior. The inner layer is always fine grained and the outer layer coarse grained; however, porosity is reported for the outer scale when the long time kinetic behavior is linear, but for the inner scale when the kinetic behavior is parabolic. A significant variable appears to be the specimen geometry. In the last two papers (5,9) cited, flat plates of surface area 6 and 20 cm^2 were used, while in the former studies (6,7,8) either a flat plate of surface area 2 cm^2 or a cylindrical ring of surface area 5 cm^2 was used. Haycock's use of the cylindrical ring further complicates the geometric effect, since tensile stresses will develop on the outer surface of the ring while compressive stresses will occur on the inner surface

as growth proceeds. The present gravimetric system does not permit the use of a larger specimen (due to total weight and weight gain limitations), thus it was decided to test this effect at the higher H_2S/H_2 ratio of 0.1 at which ratio, as previously reported, parabolic kinetics were observed.

The results are presented in Figure 3. The smaller specimen used had a width 1/2 that normally employed, the other dimensions being held at approximately the usual values. As is seen in Figure 3, the smaller specimen gave rise to a faster corrosion rate and a long time linear kinetic behavior, while long time parabolic behavior of the larger specimen is evident. These specimens were reacted to about 65% of possible weight gain. It should also be noted that an edge effect, whereby the decrease in the area of the boundary between scale and metal during scaling gives rise to an artificial decrease in scaling rate, is not seen. The porosity or lack of it, has not been assessed as of this writing due to difficulties in handling these friable scales.

The rupturing of a protective outer layer is due to stresses within the scale. These stresses, as outlined by Kofstad (10), may be related to epitaxial mismatch, to formation of pores in the scale, metal, or at the metal/scale interface, or to the growth morphology of the scale. In polycrystalline materials large stresses may also be developed at grain boundaries owing to differences in the corrosion rates of neighboring grains and crystal surfaces, and preferential diffusion and corrosion product formation along the grain boundaries. At high temperatures, rupture and fragmentation are counteracted by plastic flow and sintering. The latter is facilitated by such processes as volume, grain boundary and surface diffusion, the rates of which increase with temperature and partial pressure of the oxidant. Thus a complex interaction between specimen geometry, partial pressure, and temperature can be expected. In the absence of rupturing, the formation of an inner porous layer can be explained by the formation of pores and dissociative growth mechanism of Dravnieks and McDonald (11).

Although it can not be experimentally demonstrated for $H_2S/H_2 = 0.01$, the linear behavior of the long time kinetics is presumed due to a geometric constraint. As such, this linear rate is associated with diffusion through a compact inner layer of constant thickness as treated by Haycock (7). The linear corrosion constant at long times, with or without CO and CO_2 , is approximately $7.2 \times 10^{-2} \text{ mg cm}^{-2} \text{ min}^{-1}$.

Summary

It has been demonstrated that the specimen geometry can change the kinetic behavior of Armco iron in H_2S/H_2 gas mixtures. The smaller the specimen becomes, the faster is the corrosion rate and eventually the long time kinetic behavior changes from parabolic to linear. The implications for corrosion testing and design criteria are obvious. The effect of CO_2/CO mixtures on the kinetic behavior is most pronounced at short times. The early time behavior is postulated to be governed by a combined surface reaction and lateral growth of islands of corrosion product on a film of corrosion product. The latter effect is not seen when the partial pressure of CO_2 is raised.

References

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3. R. W. Bartlett, J. Electrochem. Soc. 111, 903, (1964).
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5. S. Zelouf, "The Sulfidation of Iron and Iron Chromium Base Alloys with Hydrogen Sulfide -- Hydrogen Gas Mixtures." PhD. Pennsylvania State University 1970.
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11. A. Dravnieks and H. McDonald, J. Electrochem. Soc. 94, 139, (1948).

Figure 1

EFFECT OF CO/CO_2 ON
CORROSION KINETICS. ARMCO
IRON IN 10% Ar, 50% ($\text{H}_2\text{S}/\text{H}_2=0.01$)
& 40% CO/CO_2 GAS MIXTURES
AT 900°C.

Figure 2

LINEAR PLOT OF CORROSION.
ARMCO IRON IN A 50% Ar &
50% ($H_2S/H_2=0.01$) GAS
MIXTURE AT 900°C.

Figure 3

EFFECT OF SPECIMEN AREA
ON CORROSION KINETICS.
ARMCO IRON IN A 50% Ar & 50
% ($H_2S/H_2 = 0.1$) GAS MIXTURE AT
900°C.

3. Liquid Line Corrosion (Iyer)

Introduction

In accordance with the objectives stated in the research proposal submitted for the fiscal period June 1978 - May 1979, the design, fabrication, and testing of a molten salt cell for the study of liquid line corrosion has been accomplished. The apparatus, similar in construction to that employed in polarization studies on fully immersed samples, is now in routine use.

Although the cell design has the capability of employing varied gas atmospheres, present use is restricted to partial vacuum. A series of runs on Ni 200 specimens, made under identical conditions, has produced satisfactorily reproducible geometries of attack.

Current attention is primarily devoted to understanding the mechanism of corrosion and development of a kinetic model that will predict the profile seen in a corroded specimen. At this stage, the model is dependent on the successful solution of appropriate diffusional equations, subject to pragmatic boundary restraints.

Experimental

A schematic diagram of the molten salt cell is shown in Figure 1. Ni 200 specimens employed were cylindrical in shape to avoid edge effects. (Ht. = 1.5 cm, Radius = 0.32 cm) Volume contraction on melting, and small losses due to decomposition of the melt (sodium carbonate: Fisher reagent grade) necessitated specimen introduction only after fusion (m.p. = 858°C) of melt.

Partial immersion was ensured by maintaining an arbitrary potential between the specimen and a platinum electrode to signal contact with the conductive molten sodium carbonate. Following immersion, the Pt electrode was withdrawn from the melt and a dynamic partial vacuum of 75 Torr was established. The specimens were thereafter left exposed to the melt for 48 hours at 1000°C.

Experimental Results

The corroded specimens, after removal from the molten salt cell, were left immersed in a mercuric chloride solution for 48-96 hours. This procedure, in conjunction with post-ultrasonic cleaning in double-distilled water, ensured complete removal of the oxide films found adherent to the electrode surface above and below the meniscus and thin film region. The meniscus and thin film region showed no evidence of this corrosion product. Fig. 2 illustrates the typical corrosion profile of such a specimen. The attack geometry is perceptibly circular in profile.

Discussion

(a) Literature Survey

In recognition of the similarity between partially immersed specimens and gas-diffusion electrodes used in fuel cells exploratory work done in the latter field was studied. Whereas the processes are well understood in aqueous systems, conditions prevalent in the present work are more closely akin to that in oxygen electrodes operating in high temperature fuel cells involving use of molten carbonates as electrolytes, wherein severe corrosion of the structural materials has precluded operation beyond six months.

Janz et al (1) investigated the stability of Pt, Au and Ag in $(\text{Li}, \text{K}, \text{Na})_2\text{CO}_3$ at 900°C. Au showed little if any attack, Pt was definitely attacked, and Ag actually dissolved to a small but finite extent. Work done by Rahmel, and by Davis and Kinnibrugh on some metals and alloys has already been cited (2). Janz and Conte (3), in studying the full immersion of nickel in the ternary mixture of carbonates at 600°C and 700°C, ascertained that NiO is the corrosion product. In addition they propose the formation of a thermodynamically unstable NiCO_3 as a soluble product during corrosion. In subsequent work (4), they observed that, although anodic polarization curves showed metal passivation at 600°C, post-inspection exhibited marked attack of nickel. At 700°C however, no passivation was noted, but a similar

dark film covered the electrode surface and the electrode was embrittled. A thermodynamic treatment by Ingram and Janz (5) predicted oxide film formation on nickel in preference to the carbonate unless the CO_2 pressure over the melt is increased to 10^5 atm., or the O_2 pressure reduced to 10^{-19} atm. Our observation on the submerged portion of the Ni 200 electrode are in agreement.

In the region of the electrode surface totally exposed to the atmosphere, gaseous oxidation occurs. Green NiO in contact with O_2 consumes considerable amounts of oxygen and changes color to black; however, no phase change is reported (6). Our observations are in agreement.

The electrode surface adjacent to the meniscus and thin film displays the most pronounced rate of attack. For corrosion to occur two processes must take place locally:

(1) The anodic dissolution of nickel: $\text{Ni} \rightleftharpoons \text{Ni}^{+2} + 2\text{e}^-$

(2) The cathodic reduction of oxygen according to either reaction

1: $\text{CO}_2 + \frac{1}{2} \text{O}_2 + 2 \text{e}^- \rightleftharpoons \text{CO}_3^{-2}$, or reaction

2: $2\text{O}_2 + 4\text{e}^- \rightleftharpoons 2\text{O}^{-2}$

The presence of CO_2 near the electrode surface is dependent only on the slow thermal decomposition of the carbonate melt at high temperatures viz.

$\text{Na}_2\text{CO}_3 \rightleftharpoons \text{Na}_2\text{O} + \text{CO}_2\uparrow$. Even if small amounts of CO_2 are available, it is reasonable to assume that reaction 1 plays a negligible part in the corrosion process due to the proximity of the gas phase. However, Lorenz and Janz (7) studying the electrochemical reduction of oxygen in carbonate melts maintain that reaction 1 is predominant in the low cathodic polarization region at high temperatures.

The occurrence of reaction 2 presupposes the diffusion of O_2 molecule from the meniscus and thin film surface of melt to the electrode/melt interface. Appleby and Nicholson (8) propose that O_2 dissolves in CO_3^{-2} via the reaction:

$O_2 + 2CO_3^{-2} \rightleftharpoons 2O_2^{-2} + 2CO_2$, followed by: $O_2 + O_2^{-2} \rightleftharpoons 2O_2^-$. In support, Andersen (9) produced experimental evidence that the peroxide and superoxide ions were indeed present in significant amounts in the melt. Recently Andersen (10) concluded that O_2 does not dissolve in sodium carbonate as molecules. The diffusion species in our model will be denoted as [O] in acknowledgement of this ambiguity. The possible roles of O_2^{-2} and O_2^- in the corrosion mechanism are as yet unclear.

(b) Theoretical Treatment

The intent in this section is to describe the circular profile observed with the aid of kinetic equations. The real situation, however, does not lend itself towards the development of a simple diffusion model without certain assumptions. In the actual situation one encounters a profile constantly changing with time, resulting in a moving boundary problem. Simultaneous changes in meniscus geometry are expected. These complexities have been neglected. Also, the processes are considered only in two dimensions. The final profile is assumed dependent only on two processes occurring in the thin film and meniscus regions:

I. The diffusion of the [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 a non-adhering corrosion product.

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

A schematic diagram illustrating the two processes is shown in Fig. 3. The two cases will be treated separately, assuming no mutual dependence.

CASE I

The following assumptions are made:

(i) Although a small but finite concentration of [O] is present due to thermal decomposition of the melt, 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' at all times, due to reaction with the metal.

(iv) The flux at any point in the region does not alter with time. This permits use of the steady state Laplace equation, $\nabla^2 C = 0$.

(v) The flux 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. 4. The equation of the meniscus and thin film on plane surfaces, optically verified for aqueous solutions, is given by Maget and Rothlein (11). For our coordinate system, the equation is

$$x = \delta + A[y/h]^2$$

where

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

and σ is the surface tension of carbonate

g is the gravitational acceleration

d is the melt density

δ is the thickness of thin film

h is the meniscus height above melt surface

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

(i) $C = 0$, $t = 0$ for all (x, y)

(ii) $C = C_0$ for all t at $x = \delta + A[y/h]^2$

(iii) $C = 0$; $x = 0$ for all t

The solution furnishes $C = C(x,y)$ for the region. Using Ficks first law of diffusion

$J_x(y) = D[C] \frac{dC(x,y)}{dx}$ at $x = 0$ yields the horizontal flux at the melt/electrode interface, which in turn describes the profile geometry.

The above problem is analogous to the steady state heat loss from a cable buried in the ground. This has been treated by Schofield (12) and Aubery (13). A similar solution is in progress for this system.

CASE II

The following are assumed:

(i) The concentration of the corrosion product in the region is initially zero.

(ii) Any point on the electrode profile is a line source of a constant concentration, C_s , of the corrosion product NiO , at all times.

(iii) The amount of NiO that diffuses into the bulk of the electrolyte or melt is sufficiently small so as to regard the melt as a sink of zero concentration, at all times.

(iv) The flux of the corrosion product perpendicular to the meniscus surface is zero.

(v) The flux in the region is constantly changing with time. Thus the non-steady state equation i.e. the Ficks Second Law equation $D\nabla^2 C = dC/dt$ must be used.

(vi) The flux at the electrode surface ($C = C_s$) of the corrosion product governs the final profile geometry.

The coordinate axes and the boundary conditions are as illustrated in Fig. 5.

We have, therefore, the equation $D\nabla^2 C = dC/dt$ with following mathematical boundary restraints:

- (i) $C = 0$; $t = 0$ for all $(x > 0, y)$
- (ii) $C = C_s$; $x = 0$ for all t
- (iii) $J_1 = 0$ at $x = \delta + A[y/h]^2$ for all t
- (iv) $C = 0$ for $x = \infty$, $y = \infty$ for all t

The solution furnishes $C = C(x, y)$, whence the required $J(x, y)$ at $x = 0$ can be obtained.

The situation as presented is a complex one, necessitating further simplifications. The problem is reduced to a steady state problem by the following geometrical construction (see Fig. 5).

A tangent is drawn from a point P on the electrode surface to the meniscus. The area enveloped within the tangent and the electrode surface is a sector of a circle of apex angle θ , with a point source $C = C_s$ at the apex. Such a solution for Laplace's equation $\nabla^2 C = 0$, available in Carslaw and Jaeger (14), gives $C(r, \theta)$ in cylindrical coordinates. [$C = 0$ at $r = \infty$ represents bulk conditions.] Integration over all points on the electrode surface, i.e., for different θ 's, would give us the cumulative flux at any point in the region. However, this solution is not strictly valid, as each solution (i.e. for a point) disregards the existence of any other point source in the neighborhood. Nevertheless, the solutions should give some indication of the shape of the final profile. A successful solution of the equations is still being attempted.

Conclusions

The combined solutions for the two cases should result in an equation for the final profile of the corroded specimen. The equation would involve relevant parameters such as the oxygen or CO_2 partial pressure in the atmosphere over the melt, the oxide content in the melt, the diffusion coefficient of $[O]$, and the time of exposure.

The correlation between the experimental and theoretical profiles with the aid of a curve-fitting program should render definition and evaluation of the above parameters and establish their significance on the kinetics of liquid line corrosion.

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FIGURE 1
MOLTEN SALT CELL

Figure 2

Corrosion profile of Ni 200 partially immersed in Na_2CO_3 (1000°C , 75 torrs, 48 hours). The white line is an arc of a circle.

FIGURE 3
THE TWO PROCESSES OCCURRING IN
THE THIN FILM & MENISCUS REGION.

FIGURE 4
PROCESS I: DIFFUSION OF (0)

FIGURE 5
PROCESS II: DIFFUSION OF NiO

4. Evaluation of Reaction Kinetics from Polarization Data (Devereux)
(The text of the previously cited reference 4 is reproduced below)

COMPUTER MODELLING OF POLARIZATION CURVES IN PASSIVE SYSTEMS

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We have recently described our success in the use of interactive computer graphics to model rather complex experimental electrode polarization curves.^{1*} In that paper the current due to a single cathodic reaction experiencing activation, concentration, and resistance polarization was described by:²

$$i_c = \left[1 - \frac{i_c}{i_{sc}}\right]^{RT/nFb_c} \exp\left[-\frac{v-v_c^0}{b_c}\right] \exp\left[-\frac{i_c R_c}{b_c}\right] \quad (1)$$

and, similarly, that due to a single anodic reaction was

$$i_a = \left[1 - \frac{i_a}{i_{sa}}\right]^{RT/nFa} \exp\left[\frac{v-v_a^0}{b_a}\right] \exp\left[-\frac{i_a R_a}{b_a}\right] \quad (2)$$

The total observed current was considered to be the sum of that due to one or two cathodic reactions and one or two anodic reactions, i.e.,

$$i = i_{a1} + i_{a2} - i_{c1} - i_{c2} \quad (3)$$

In these equations v is the applied potential and i , the observed current. Each reaction is characterized by three disposable parameters, for example, i_{sa1} , b_{a1} , and v_{a1}^0 characterize the first anodic reaction. A resistance polarization term, characterized, e.g., by R_a , is applied only to one of the anodic reactions and one of the cathodic reactions.

*Reference 1 contains a misprint. The expression following equation (1) should read:

$$\exp\left[\frac{v_c^0}{b_c}\right] = i_c^0 \exp\left[\frac{v_c^0}{b_c}\right]$$

Despite the number of empirical parameters (up to fourteen) each is resolvable and can be optimized by the procedures discussed.

This procedure has been significantly expanded in its capabilities. Aside from a trivial extension to include a greater number of contributing reactions, we have found it feasible to include passive behavior in the anodic reactions routinely. This is accomplished through the inclusion of two new parameters for each anodic reaction, a potential, e.g., v_{pa1} for the first anodic reaction, which marks the onset of passive behavior, and a corresponding current, e.g., i_{pa1} , characteristic of the passive region. Thus, the current attributable to that particular reaction is given by equation (2) for $v < v_{pa1}$, and by

$$i = i_{pa1} \quad (4)$$

for $v \geq v_{pa1}$. Equation (3) remains valid. An example of the application of this technique is shown in Figure 1. The data shown (dotted line) were obtained by potentiostatic polarization of a specimen of Ni 200 in molten sodium carbonate at 1000°C continuously flushed with a gas mixture of nominal composition 95% CO, 5% CO₂ at 1 atm. The procedural details are given elsewhere.^{1,3} The Figure shows a very close fit to these data by the model described above (solid line), incorporating three anodic reactions, two of which display passivation, and a single cathodic reaction. The values of the empirical constants for the calculated curve are given in Table I. As noted in the Table, the model is not very sensitive to the values chosen for the various saturation currents for this particular experiment due to the over-riding nature of the passivation phenomenon (1st and 2nd anodic reactions) and the significance of the resistance polarization (3rd anodic reaction and cathodic

Table I

Values of Empirical Constants

(Run #75, Ni 200 in Na_2CO_3 , 1000°C, 95% CO/5% CO_2)

i_{sa1}	3.5	mA/cm^2	(*)
i_{sa2}	100	mA/cm^2	(*)
i_{sa3}	1000	mA/cm^2	(*)
i_{sc2}	9000	mA/cm^2	(*)
b_{a1}	15	mV	
b_{a2}	85	mV	
b_{a3}	35	mV	
b_{c2}	80	mV	
v_{a1}^0	-100	mV	
v_{a2}^0	250	mV	
v_{a3}^0	820	mV	
v_{c2}^0	-100	mV	
v_{pa1}	10	mV	
v_{pa2}	490	mV	
i_{pa1}	2.8	mA/cm^2	
i_{pa2}	9	mA/cm^2	
R_a	2	ohm	
R_c	2	ohm	

(* As discussed in the text, the fit of the model to these data is not especially sensitive to these parameters.)

reaction). The current components due to the individual anodic and cathodic reactions are plotted separately along with the data in Figure 2; also shown in this Figure is the total anodic current and, since there is a single cathodic reaction, the total cathodic current.

The corrosion current and rest potential are clearly, albeit graphically, defined on this plot.

The previous paper¹ cited considerable success and lack of ambiguity in the selection of values for the various curve parameters to optimize the fit of model to data. Now, with the inclusion of parameters pertaining to passivation, there has appeared a certain degree of ambiguity with respect to similarity in the effects of passivation and concentration polarization as manifested in the curve of total current versus potential. The data shown herein display a characteristic drop in current at the onset of passivation; however, in other data we have examined there appears merely an abrupt change in the magnitude of the slope of the curve, but not the sign. In such cases both phenomena provide satisfactory empirical correlations. We have also found that model optimization becomes increasingly difficult as the number of disposable parameters increases, as might be expected. The data herein require eighteen parameters to be chosen by repetitive guesswork. This can be increased to 21 or 24 parameters through the inclusion of a second or third cathodic reaction if necessary, but in our opinion and experience the use of more than three reactions to describe either branch of the polarization curve would be difficult and of questionable validity.

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Figure Captions

- Fig. 1. Experimental polarization curve (dotted line) with calculated curve (solid line) using the constants in Table I. Model employs a single cathodic reaction and three anodic reactions, two of which display passive behavior.
- Fig. 2. The experimental data and model plot of Figure 1, showing the total anodic and cathodic currents, and the separate contributions of the three anodic reactions to the total current.

FIG. 1

FIG. 2