ELECTRODE POLARIZATION STUDIES
IN HOT CORROSION SYSTEMS

Progress Report
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ABSTRACT

Analysis of thermodynamic models pertaining to coal gasification is near completion. Model I, comprising a gas phase and a molten salt phase, pertains to laboratory materials testing; Model II incorporates as well a solid carbon phase and is intended to model typical gasifier environments. Anodic and cathodic polarization measurements on iron, 1018 steel, nickel, and 304 and 316 stainless steel have been performed in molten sodium carbonate under air and oxygen; tests under reducing environment are in progress. Preliminary metal/gas reactions tests involving iron, and hydrogen sulfide and nitrogen, have been performed. Reaction with nitrogen is minimal; reaction with hydrogen sulfide is very non-uniform, rendering kinetic analysis difficult.

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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 scope of 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. Parallel metallographic analyses and gas/metal reaction studies will be performed."

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.

A. Overall Project

1. Personnel

a. Principal Investigator

Owen F. Devereux, Professor of Metallurgy

b. Graduate Assistants

Ross Boland - MS expected May, 1978

Richard Cooke - MS expected May, 1978

Kyooyoung Kim - PhD expected May, 1979

Dane Wilson - PhD expected May, 1980

2. Publications - None

3. Results of Major Significance - Innovative Reference Electrode

a. Scientific Importance

Polarization studies in molten carbonates have traditionally used an oxygen electrode as reference electrode, either immersed in the cell electrolyte or in an electrolyte separated from the cell electrolyte by a defect oxide crucible. The latter configuration is necessary if the cell atmosphere is to be varied inasmuch as the atmosphere over the reference electrode must be invariant. However, transport through the defect oxide is by oxide ion and the maintenance of atmospheres of different oxide potential over the two electrolytes necessarily creates a liquid junction potential of unknown and variable magnitude. When the cell electrolyte and the reference electrode electrolyte are both sodium salts (e.g., sodium carbonate) this problem is avoided through housing the electrode in a commercially pure alumina crucible, in which the transport number of sodium

ion is essentially unity. Although studies on such electrodes are incomplete, they appear to have an adequately low resistance for use as reference electrodes, and to be stable. Figure 6 illustrates the use of an "alumina" electrode for polarization measurements in comparison to the traditional " Y_2O_3 -doped zirconia" electrode.

b. Relevance to Energy Technology

Electrode polarization studies have had a tremendous impact on the study of corrosion in aqueous systems, constituting the only logical alternative to lengthy exposure tests. This has been possible because of the availability of suitable reference electrodes such as the calomel electrode. Electrode polarization can have a similar impact on the study of corrosion in molten salts, but only if a truly invariant reference electrode is available. It is our hope that this electrode will prove suitable.

B. Task Summaries

1. Thermodynamic Analysis of Gasifier Models (Cooke)

This task was recognized as an important aspect of the original program of electrode polarization studies for two reasons: One, kinetic analyses of electrode reactions is meaningful only to the extent that the activities of the species participating in these reactions are established. Two, the viable means of experimental control of electrolyte activities is control of partial pressures in a gas phase equilibrated with the electrolyte. Hence, this task was scheduled for completion early in the program. A complete thermodynamic analysis of a simple two phase model describing the system employed in polarization studies has been completed; this is described in greater detail in section C, and a full report will be submitted to DOE shortly. A second model was derived from the first to include the effects of a third, solid carbon, phase and additional gas phase constituents

not included in the first model. Analysis of this model is progressing rapidly using the computational techniques established for the first model. Completion is anticipated prior to the end of this report period.

This task is on schedule with respect to earlier progress, other tasks, and the overall goals of the project.

Completion of this task early in the life of the project was intended; there are no new or modified objectives.

2. Electrode Polarization Studies in Molten Sodium Carbonate (Kim)

The prime objective during the previous year was to achieve a status in the experimental program whereby polarization data obtained under full environmental control were being generated on a routine basis. We have not achieved this status; this is attributed to underestimation of the time required for the solution of a number of anticipated experimental problems. Gas handling apparatus, electronic instrumentation, and materials of construction have presented no significant problem. Proper electrode mounting to insure against interfacial effects required considerable trial-and-error testing prior to selection of a suitable design. Choice of a reference electrode was given considerable importance; we believe this problem solved subject to final testing. Finally, effective sealing of the polarization cell against the ambient environment has been elusive; we believe this problem has been solved through use of a soft sealing wax at the interface between the mullite retort housing the cell and the aluminum flange supporting access to the cell and instrumentation, but final tests are not complete.

This task is approximately three months behind schedule, both with respect to its previous progress and with respect to project goals. Inasmuch as it is supported by the other tasks in the project, the other tasks are not adversely affected by this delay.

The original objectives of this task remain unchanged; however, additional emphasis has been given the use of a true reference electrode. This simply means that if, as noted above, the new reference electrode is truly suitable, it will be used routinely.

3. Gas/Metal Reaction Studies (Boland, Wilson)

The study of gas/metal reactions in the absence of any electrolytic phase was initiated as a new task last year to be supportive of the electrode polarization studies. Work to date has been exploratory, primarily intended to test the feasibility of using simple manometric apparatus to follow reaction extent either continuously, where suitable, by monitoring gas consumption, or intermittently through periodic removal of specimens. These objectives, in essence, have been completed, but have indicated the need for additional means of reaction rate study.

Although progress on this project is consistent with its recent initiation, effort will be accelerated in view of the fact that further exploratory studies seem indicated before a routine data collection capability is established. To the extent that these further studies had not been anticipated, the task is somewhat behind in relation to the polarization task and, therefore, in relation to the overall project.

An immediate, and new, task objective will be the establishment of a continuous gravimetric gas phase reaction facility suitable for use in gas mixtures containing hydrogen sulfide.

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

This task was not separately identified prior to the obtaining of initial results from the polarization phase of the project. Examination of initial current/potential curves indicated that the minimal kinetic expression needed to describe these data contained ten linear and non-linear empirical

constants and was transcendental in current. Prior experience has indicated that fitting of such curves via simple statistical means is very difficult and fraught with pitfalls, whereas simple polarization data may be adequately evaluated by graphical means. Hence, a decision was made to analyze these results by an interactive computer graphics procedure. We are in the process of procuring a graphics terminal and of learning the necessary programming skills.

This task is on schedule with respect to initial progress, other tasks, and the overall goals of the project.

This task has only recently been separately identified as such.

C. Extended Discussion of Progress

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

Initial exploratory polarization studies involving Fe, 1018 steel, 304 and 316 stainless steels, and Ni 200 in molten Na_2CO_3 were performed under ambient atmosphere, using in essence the apparatus and procedure described in the previous progress report (ERDA C00-2960-1). Anodic and cathodic curves, obtained at 940°C with a stepping increment of 2mv/20sec are shown in Figs. 1 and 2, respectively.

Under anodic polarization the Ni 200 is seen to be significantly noble relative to the ferrous alloys. Amongst the ferrous materials, unalloyed Fe displays the highest corrosion rate with 1018 steel possibly slightly less corrosion-prone at high anodic potentials, and the stainless alloys falling between Ni and Fe. The relative merit of alloy 316 vs alloy 304 seems to depend upon potential. The stainless steels and nickel show an abrupt reduction of current with increasing anodic potential that could be indicative of a passivation phenomenon; a less abrupt current reduction at higher anodic potentials is also seen; this is especially marked in the stainless alloys. In general, the initial anodic current appears to follow

mixed electrode behavior, while the high-potential current seems to approach a constant, diffusion-limited value independent of the electrode.

The cathodic polarization curves show two distinct regions of behavior, suggestive of two distinct cathodic reactions. The reaction active at low cathodic overpotentials exhibits simple mixed electrode behavior followed by a concentration polarization, or diffusion-limited, region. A second reaction showing simple Tafel behavior becomes dominant as the overpotential is further increased. The electrodes differ in their suitability as cathodes, with Fe again showing the higher current. The polarization curves also display a fine structure of uncertain origin.

Effect of Oxygen Pressure

The foregoing polarization studies were conducted in a quiescent electrolyte equilibrated with air. An exploratory study of the effect of oxygen on the anodic and cathodic reactions was conducted by comparing this work to polarization curves taken while air was bubbled through the electrolyte and while oxygen was bubbled through the electrolyte. The results were flow-rate sensitive, indicating that equilibrium between the gas and the electrolyte was not attained; consequently, the data may be taken only as indicative of a trend. Both anodic and cathodic behavior, at 940°C and 1000°C, are shown in Figs. 3 and 4, respectively. The cathodic current shows an expected increase on bubbling oxygen through the electrolyte instead of air, while the relatively low current seen with the quiescent electrolyte is indicative that that electrolyte is not able to maintain equilibrium with the atmosphere. The data also suggest that only the cathodic reaction occurring at low overpotential is dependent on oxygen pressure, e.g.,

or

while that occurring at high cathodic overpotential is not, e.g.,

However, both reactions are clearly dependent upon P_{CO_2} and the latter, upon P_{CO} ; thus a firm conclusion cannot be drawn at this point inasmuch as control on these parameters was not exerted.

The anodic polarization behavior also displays a dependence on P_{O_2} , but only in the activation-limited region. This is more marked at 940°C. No clear reason is presented for this behavior; it is quite possibly artificial.

Effect of Temperature

A significant temperature dependence is evident on comparison of Figs. 3 and 4. This is especially evident in the diffusion-limited region of the low-overpotential cathodic reaction, while the diffusion-limited region of the anodic reaction appears temperature insensitive.

Reference Electrode

The data discussed were obtained using a standard three electrode configuration, with a reference electrode consisting of platinum immersed in molten Na_2O_3 in a Y_2O_3 -doped ZrO_2 crucible. This material is presumed to have an oxide transport number of essentially unity. This electrode experiences two difficulties. First, and most apparent, the zirconia is degraded by long-term exposure to molten Na_2CO_3 , becoming friable and failing after several runs of 15-20 hours each. Secondly, since transport through the ceramic occurs by oxide transport, absence of a liquid junction potential depends upon maintenance of equal oxide ion activities within and without

the crucible. In a predominantly carbonate salt, oxide ion activity is maintained via control of P_{CO_2} , i.e.,

while the electrode reaction,

or

or

is fixed by the establishment of an additional partial pressure, P_{O_2} or P_{CO} . Thus it is not possible using this electrode to at once eliminate a liquid junction potential, maintain a constant half-cell potential, and vary the values of P_{CO} and P_{CO_2} over the cell itself. While this did not present a problem in obtaining the above data inasmuch as environment control was not exerted, it presents an impossible restriction on the bulk of the planned program.

An appropriate reference electrode for this particular system will allow independent control of the electrode EMF and provide for electrical contact with the cell electrolyte by means of species unaffected by the planned atmospheric variations. These conditions are satisfied by a reference half-cell consisting of platinum immersed in Na_2CO_3 through which a gas of fixed P_{CO}/P_{CO_2} ratio is bubbled, the whole being contained in a vessel permeable to sodium ion. The latter condition is met by commercially-obtainable cast alumina (99.8%) refractory. Published data for alumina suggest that at $1000^\circ C$, D_{Al} and D_O are of the order of $10^{-19} \text{ cm}^2 \text{ sec}^{-1}$ whereas $D_{Na} \sim 5 \times 10^{-11} \text{ cm}^2 \text{ sec}^{-1}$ (J. F. Stringer, AGARD-AG-200). For alumina containing 0.005% Na_2O (a typical analysis), the conductivity is $\sim 5 \times D$ at $1000^\circ C$ or $2.5 \times 10^{-10} \text{ ohm}^{-1} \text{ cm}^{-1}$. The actual electrode configuration in use has a geometric factor of $\sim 60 \text{ cm}$, yielding an effective expected electrode re-

sistance of $60M\Omega$, well within the acceptable range of input impedance for an electrometer. Figure 5 shows current passed by such an electrode as a function of potential; the behavior is essentially ohmic with a resistance of $35K\ \Omega$. The origin of this discrepancy is not clear, nor is it important. Two factors may contribute to the increased conductivity: An increased concentration of Na^+ in the alumina, and erroneous extrapolation of high temperature data to $1000^\circ C$. In the latter respect Oishi and Kingery (J. Chem. Phys. 33, 905 (1960)) show a reduced activation energy for $O^=$ diffusion below $1400^\circ C$, a factor not taken into account in the above extrapolations. Figure 6 shows polarization curves obtained using the alumina reference electrode, as well as curves obtained using the zirconia reference electrode. Any discrepancy between the electrodes does not appear to be significantly different from the reproducibility obtained with a given electrode.

Atmospheric Control

The results presented above represent preliminary studies inasmuch as atmospheric control was not exerted over the polarization cell. Current and planned tests involve control of P_{CO} , P_{H_2} and P_{H_2S} over the cell, and P_{CO} and P_{CO_2} over the reference electrode. These parameters are sufficient, with temperature and total pressure control, to fix the thermodynamic state of each system.

Data Analysis

It is recognized that a verbal description of curve shapes is not optimum output for this study. Polarization curves of the type shown in Fig. 1-4, 6 can be described by a sum of terms describing both activation-limited and diffusion-limited behavior; unfortunately, the resulting expression is transcendental in nature and involves 10 disposable constants. Estimation of the values of these constants and their temperature - and environment -

dependence is considered one of the most valuable results of this program. This is currently being attempted via interactive graphic computer programming.

2. Thermodynamic Analysis of Gasifier Models (Cooke)

Work on the thermodynamic modelling of coal gasification systems has progressed along two distinct paths since the previous progress report (ERDA C00-2960-1). First, a concentrated effort has been channelled towards developing a more sophisticated computer graphics capability in order to simplify and improve presentation of the complex equilibria in this system. Second, an additional gasifier model has been developed which includes additional components and spans a wider temperature range, thus having increased applicability.

As of the previous report date (February, 1977) analysis of the gas phase of the two phase Model I was complete. This model comprises a gas phase containing CO , CO_2 , H_2 , H_2O , H_2S , S_2 , SO_2 , and SO_3 and a liquid phase containing the sodium salts of $\text{CO}_3^{=}$, $\text{O}^{=}$, $\text{S}^{=}$, $\text{SO}_4^{=}$, and OH^- . Several series of plots representing isobars of the gaseous components in P_{CO} , P_{H_2} , and $P_{\text{H}_2\text{S}}$ space were presented. Since then computer techniques for isometric representation of three dimensional plots have been developed, yielding diagrams typified by those in Figure 7. Figure 7 shows isobaric surfaces for carbon dioxide at 1300°K and 1 atm total pressure. This technique yields a concise, readable solution, with enhanced $P_{\text{H}_2\text{S}}$ resolution in comparison with the previous plotting method. Although the equations describing these equilibria are not linear with total pressure, to a good approximation the individual partial pressures are linear with pressure in the total pressure range of 1 - 10 atm.

Solution of the liquid phase equilibrium for Model I is now also complete. The useful output of this solution consists of activity ratios of the various anions as functions of the independent composition parameters, i.e., $a_{O^{2-}}/a_{CO_3^{2-}}$, $a_{S^{2-}}/a_{CO_3^{2-}}$, $a_{SO_4^{2-}}/a_{CO_3^{2-}}$, and $a_{OH^-}/a_{CO_3^{2-}}$ vs P_{CO} , P_{H_2} , and P_{H_2S} . Typical output is shown in Figure 8, depicting $a_{O^{2-}}/a_{CO_3^{2-}}$ vs P_{H_2} and P_{CO} for constant values of P_{H_2S} . A schematic summary of one aspect of the liquid phase behavior is shown in Figure 9, in which regions of anionic dominance are given as a function of gas phase composition.

Model II is based upon the above Model I computations, but includes an additional phase, solid carbon, and two additional components in the gas phase, CH_4 and COS . Methane is the dominant hydrocarbon in coal gases and, to some extent, representative behaviorwise of less abundant hydrocarbons; carbonyl sulfide was added to the model when it was discovered to be at least as significant as the simple oxides of sulfur. The addition of gas phase components simply increases the number of equations to be solved simultaneously in determining the gas phase equilibrium; however, the addition of a third phase reduces the number of degrees of freedom in the system to four: temperature, pressure, and two compositional variables being obvious choices. Solution of this model is in an advanced stage of completion.

Full documentation of both models will be reported shortly.

3. Gas/Metal Reaction Studies (Boland)

A manometric apparatus was constructed to observe the gas-solid reaction kinetics for iron and various gases. It is capable of recording volume changes from 0.01 cc to 111.00 cc as determined from pressure changes on an absolute manometer with a sensitivity of 0.02 mm mercury. The reaction chamber is capable of maintaining specimens at temperatures up to $1000 \pm 1^\circ C$.

In this apparatus Armco iron (commercially pure) specimens were reacted with nitrogen gas (Matheson pink label) at 650, 900, 950 and 1000°C at pressures of 200, 440 and 620 mm mercury. The specimens were cold rolled from 0.25 inch round stock to flat strips 0.36 mm x 10.00 mm x 50.00 mm which were mechanically polished to a 600 grit finish before use. The nitrogen showed a single impurity of 0.1 percent oxygen when analyzed on a mass spectrometer. In the reactions run at 900, 950 and 1000°C at 200 and 440 mm mercury no measurable volume consumption was recorded for two specimens run for time intervals to 1110 minutes. When two specimens were reacted at 650°C and 620 mm mercury a volume consumption of 1.64 cc was observed after 1395 minutes. Assuming a reaction product of Fe_4N on the surface of the specimen suggests a maximum observed corrosion rate of 1.202 mpy at 650°C and 620 mm mercury and a corrosion rate of less than 0.0929 mpy (based on a 0.01 cc volume change) in the other cases.

The same apparatus was used to conduct iron-hydrogen sulfide reactions at 850 and 950°C at 220 and 440 mm mercury, although manometric monitoring was impossible due to the nature of the reaction ($\text{H}_2\text{S} + \text{Fe} \rightleftharpoons \text{FeS} + \text{H}_2$). Three specimens, differing only in length (38 mm vs 50 mm) from those used with the nitrogen, were reacted for different time intervals at the same temperature and pressure. The weight changes of the specimens were recorded to obtain a relation between weight gain, film thickness and time of reaction. The reaction product, shown by x-ray diffraction analysis to be FeS, was of a non-coherent nature. Reacted specimens exhibited intergranular attack, pitting, spalling and a general non-uniform (Figure 10) attack. Kinetic measurements were, of course, not possible. The general trend observed was that the overall degree of corrosion and maximum penetration depth increased with increased pressure and/or temperature. A maximum local corrosion rate of 3185.37 mpy was observed at 950°C and 220 mm mercury, as calculated from

a maximum film thickness in a minimum time. A maximum general corrosion rate of 474.13 mpy was observed at 950°C and 440 mm Hg as calculated from a maximum weight gain in a minimum time.

Table I
Reaction of Fe with H₂S

950°C 440 mm Hg				
Run #	Time (min)	Weight Gain (gm)	Max. Film (mm)	Ave. Film (mm)
8	7440	--	0.21	--
15	7270	--	0.07	0.03
20	2105	0.0482	0.15	0.07
21	1140	0.0537	0.20	0.01
22	540	0.0512	0.09	0.01
950°C 220 mm Hg				
Run #	Time (min)	Weight Gain (gm)	Max. Film (mm)	Ave. Film (mm)
16	3840	0.0291	0.07	0.01
17	2835	--	0.05	0.01
18	2270	0.0257	0.10	0.05
7	1830	--	0.19	0.01
19	625	0.0421	0.15	0.07
850°C 440 mm Hg				
Run #	Time (min)	Weight Gain (gm)	Max. Film (mm)	Ave. Film (mm)
10	3520	--	0.015	--
11	1170	--	0.18	--
13	990	--	0.09	--
12	470	--	0.10	0.01
850°C 220 mm Hg				
Run #	Time (min)	Weight Gain (gm)	Max. Film (mm)	Ave. Film (mm)
23	--	0.0217	0.05	0.01
24	1575	0.0217	0.05	0.01
25	515	0.0236	0.04	0.01

4. Gas/Metal Reaction Studies (Wilson)

The following is a survey of the salient aspects of the oxidation literature pertaining to the program.

Introduction

The kinetics and mechanism of the reactions of metals with gases have in the main been reported for metals or alloys with a single oxidant, for example O_2 , S_x , N_2 . Oxidation and to lesser extent sulphidation has been the subject of numerous investigations.

Metals, however, are seldom exposed to a single gas in industrial processes. Fossilic fuels such as coal, oil and gas are the world's main sources of energy. During the combustion of these fuels, materials are exposed to reactive gases containing molecular species derived from oxygen, hydrogen, carbon, sulphur and nitrogen at elevated temperatures (400 - 1000 °C). The gas compositions of the five major coal conversion processes, all containing the above molecular species have been reported by MacNab (1).

These chemical species acting alone or together degrade the structural materials, and the oxidation products need not be expected from thermodynamic considerations. Allowances must be made for the fact that although the free energy is the driving force, it bears little or no relation to the rates of reactions. The reactions represent dynamic systems in which metastable phases may form important intermediate reaction products.

The kinetics and mechanism of such a complex system has been studied by considering in sequence, the reaction of one metal, binary alloys and binary based alloys with two oxidants. The technically important reactions listed below are given by Rahmel (2):

1. Simultaneous oxidation and sulphidation.
2. Simultaneous oxidation and carburization or decarburization.
3. Simultaneous oxidation and nitriding.

It is proposed in this study to follow the simultaneous formation of oxide and sulphide on iron and its alloys.

Technical Background

The oxidation of iron and/or nickel and/or chromium has been widely investigated (3,4,5) and is fairly well understood as a result of the studies of C. Wagner (6,7). The corrosion resistance of stainless steels in air or oxygen is held widely to be due to the formation of an adherent compact layer of Cr_2O_3 . Tedman (8) has incorporated the effect of volatilization of Cr_2O_3 at temperatures at or above 1000°C into the corrosion rate equation. The underlying spinels in these oxide scales have been considered also as contributing to the corrosion protection (9).

The high temperature reactions of metals with sulphur and sulphidizing atmospheres such as SO_2 , SO_3 , and H_2 -- H_2S have been studied (2, 10-18). In many cases multilayered scales have been found. In the presence of two oxidants, the sulphide forms as a continuous network under the outer oxide layer, allowing a rapid transport of metal ions through the duplex scales and thus rapid kinetics.

Mechanisms of the simultaneous attack of pure iron with two oxidants have been discussed by Rahmel (2) and Pettit et al. (12). The thermodynamic considerations of Pettit et al. for a metal A in the presence of two oxidants O_2 and X have shown:

For $(a_{\text{O}})_{\text{gas}} > (a_{\text{O}})_{\text{eq}}$ and $(a_{\text{X}})_{\text{gas}} > (a_{\text{X}})_{\text{eq}}$, whether AO or AX appears on the metal surface as the stable phase depends on whether

$$(a_{\text{X}}/a_{\text{O}})_{\text{gas}} \lessgtr (a_{\text{X}}/a_{\text{O}})_{\text{eq}}$$

Furthermore, the second phase which is not stable in contact with the gas may be stable within the external phase or in the metal beneath the external stable phase, provided the second oxidant can penetrate the external scale. Experimental results (12) indicate that N, S, and C can penetrate Cr_2O_3 scales on pure Cr, Ni-20Cr and Fe-25Cr alloys.

In addition, in oxidation reactions with CO_2 or SO_2 in the gas phase, it has been found that rapid oxide formation can apparently increase the activity of the second oxidant to a point where an alloy/second oxidant reaction can take place, even though the activity of this oxidant in the incoming gas is less than that required for the reaction.

Rahmel's work (2) has allowed some correlation to be made between the proposed mechanism and thermodynamic considerations. Birks (15) has pointed out that in addition to the factors important for pure metals, other factors such as, possibility of forming several oxides and sulphides, internal oxidation and sulphidation, the formation of ternary compounds and mixed phases are important for alloys. His work also summarizes the behaviour of those alloys which can be considered as containing low, medium or high chromium contents.

Zelouf (18), Zelouf and Simkovich (19) and Rao and Nelson (16) have studied the behaviour of iron and its alloys in H_2 -- H_2S gas mixtures. Mrowec (17) has summarized the results of studies on binary and ternary alloys in elemental sulphur and H_2 -- H_2S mixtures.

Mrowec has pointed out that whereas Zelouf and Simkovich indicated the influence of hydrogen on the kinetics and mechanism of sulphur corrosion of iron and its alloys, there appears to be no such effect on the rate of sulphur corrosion of Ni-Cr and Co-Cr alloys.

The multilayered scales that do form are composed of an inner porous sulphide layer (the porosity attributed to geometric effects) (17), an intermediate layer of oxy-sulphides and an outer layer of oxide. The outer layer growth appears to be controlled by diffusion of metal ions toward the outer gas/scale interface, whereas the inner layer growth is facilitated by a dissociative mechanism similar to that proposed by Meussner and Birchenall (20). (See also reference 16.) Mrowec (17) has shown also that

inner layer growth is possible without participation of inward diffusion of the oxidant. This growth however is accelerated by the inward diffusion of the oxidant through microfissures formed due to lack of plastic deformation, particularly at corners of samples.

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FIGURE CAPTIONS

- Figure 1 Anodic polarization curves of pure iron, 1018 steel, S.S. 304, S.S. 316, and Ni 200 at 940 °C in ambient air.
- Figure 2 Cathodic polarization curves of pure iron, 1018 steel, S.S. 304, S.S. 316, and Ni 200 at 940 °C in ambient air.
- Figure 3 Anodic and cathodic polarization curves of Ni 200 at 940 °C at three different oxygen pressures.
- Figure 4 Anodic and cathodic polarization curves of Ni 200 at 1000 °C at three different oxygen pressures.
- Figure 5 Resistance of a closed-one-end, 1/2 inch O.D. alumina tube with 1/16 inch wall thickness in a molten sodium carbonate salt at 1000 °C.
- Figure 6 Anodic and cathodic polarization curves of Ni 200 at 1000 °C, using alumina and zirconia tubes as a reference electrode cell compartment.
- Figure 7 Surfaces of constant pressure for carbon dioxide (CO_2). The CO_2 partial pressure (in atmospheres) is labelled under each graph.
- Figure 8 The ratio of the activity of O^{2-} to CO_3^{2-} ($a_{\text{O}^{2-}}/a_{\text{CO}_3^{2-}}$) at different pressures of hydrogen sulfide gas (H_2S). The partial pressure of H_2S is labelled under each graph.
- Figure 9 Regions of dominance for anions in solution calculated from equilibrium of gas environments with molten NaCO_3 at $T = 1300 \text{ K}$, $P_T = 1 \text{ atm}$.

Figure 10a Specimen from run #25, exhibiting non-uniform penetration
(200x).

Figure 10b Specimen from run #19, exhibiting subsurface attack and
spalling (200x).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

SURFACES OF CONSTANT PRESSURE
FOR CARBON DIOXIDE (CO_2).
THE CO_2 PARTIAL PRESSURE
(IN ATMOSPHERES) IS LABELLED
UNDER EACH GRAPH.

Figure 7

THE RATIO OF THE ACTIVITY OF
 O^2 TO CO_3^{2-} ($a_{O^2}/a_{CO_3^{2-}}$) AT
 DIFFERENT PRESSURES OF HYDROGEN
 SULFIDE GAS (H_2S). THE PARTIAL
 PRESSURE OF H_2S IS LABELLED
 UNDER EACH GRAPH.

Figure 8

Figure 9

Figure 10

Figure 10a. Specimen from run #25, exhibiting non-uniform penetration. (200x)

Figure 10b. Specimen from run #19, exhibiting subsurface attack and spalling. (200x)