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HIGH TEMPERATURE CORROSION OF IRON IN SULFUR CONTAINING ATMOSPHERES

Frank Chin-Tai Yang
(M.S. thesis)

June 1981

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HIGH TEMPERATURE CORROSION OF IRON
IN SULFUR CONTAINING ATMOSPHERES

Frank Chin-Tai Yang
M.S. Thesis

June 1981

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Office of Basic Energy Sciences, Materials Sciences Division of the
To My Dear Parents and Daphne

For Their Love and Assistance over the Years

June 1981
ABSTRACT

The simultaneous oxidation-sulfidation of pure iron in SO_{2}-CO_{2} and SO_{2}-O_{2} atmospheres has been studied at 871°C. Although thermodynamic calculations predict the formation of an oxide layer, complex product layers of oxide and sulfide duplex structure are observed. The outer product layer is an oxide matrix, containing sulfide-rich streaks. The inner layer is porous and also contains sulfides. The rough surface of the oxidized sample is caused by protrusions on the outer scale. The protrusions are thought to grow by the fast transport of iron ions through the sulfide-rich streaks. The existence of sulfide within the scale is due to the depletion of oxygen adjacent to the scale/gas interface shifting the thermodynamic equilibrium to a sulfide stable region. SAM (Scanning Auger Microscopy) and X-ray diffraction show that the form of sulfur in the scale is pure sulfide rather than solid solution within the oxide. Anion inward transport is proposed to account for the formation of the inner porous layer.
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</table>
I. INTRODUCTION

In many industrial applications, alloys are used in gaseous environments that contain oxidizing species in addition to oxygen. For example, virtually all sources of energy and raw materials for the chemical, metallurgical and power generation industries are hydrocarbon fuels - oil, coal, gas - containing sulfur impurities to an extent dependent on the particular supply. Thus, the gaseous atmospheres produced by their combustion can contain mixtures of $O_2$, $N_2$, $H_2$, $H_2O$, $CO$, $CO_2$, $CH_4$, $H_2S$, $SO_2$, $SO_3$, $NH_3$, $C$, $S_2$, etc. in a wide range of concentrations and pressures.

Three general types of complex gaseous environments may be identified:
A. Gas atmospheres contain relatively high concentrations of hydrocarbons, and $CO$, along with possibly $H_2$, $CO_2$ and $H_2O$. These are carburizing but also reducing to the majority of metallic components and thus oxides are not formed as corrosion products. Such atmospheres are generally found in the petrochemical industry, in, for example, ethylene cracking furnaces. Process atmospheres in hydrocarbon reforming may also be similar but more often contain higher oxygen activities allowing simultaneous oxidation. However, irrespective of the bulk gas composition, localized fluctuations in carbon and oxygen potentials can occur.

B. Primary oxygen-rich atmospheres such as are produced by burning a hydrocarbon fuel with excess air. In these the primary corrosion products are oxides. Nevertheless, the small, but significant, concentrations of sulfur and carbon compounds, usually oxides $SO_2$ and $CO_2$, and also $H_2O$ can play a significant role. The introduction of $H_2O$ to an atmosphere has been found to modify kinetics. Primarily addition of $CO_2$ can modify
kinetics and in certain cases introduce the formation of carbides. Addition of \( \text{SO}_2 \) provides for the formation of mixed oxide and sulfide scales, and internal sulfidation.

C. The third type of atmosphere is one that may be carburizing, sulfidizing and oxidizing simultaneously. Such atmospheres are characterized by relatively low oxygen potential and relatively high sulfur and carbon potentials. There is little information on the behavior of alloys under these conditions, although this is an area of increasing significance. Gaseous environments in many of the proposed processes for coal gasification and newer methods of combustion such as fluidized beds, fall into this category. Three basic modes of metal degradation therefore are possible: oxidation, sulfidation and carburization, and while the basic mechanisms of high temperature oxidation and sulfidation of pure metals, binary alloys and more qualitatively of quite complex alloys, are relatively well understood this is perhaps not so with carburization. The problem is even more acute where simultaneous attack by sulfidizing/oxidizing, carburizing/oxidizing, or even sulfidizing/carburizing/oxidizing conditions are involved.

The purpose of this thesis is to establish the basic mechanisms which have been shown to operate as the oxidizing problem is made progressively more complex by simultaneous attack of sulfidation and oxidation.

Generally speaking, metals, and particularly alloys, resist oxidation in pure oxygen by forming a more or less protective oxide scale. When mixed with a second oxidant, such as sulfur, the reaction product may change to include low melting compounds or ionic compounds with higher
ionic conductivities than the oxides normally formed. Both possibilities cause accelerated attack on the metal.

Although a great deal of work has been done concerning the oxidation of alloys in atmospheres containing $\text{SO}_2$, the basic mechanisms still have not been fully understood. Therefore, it is impossible to give engineers well-established guides on the conditions that must be maintained to avoid severe high temperature corrosion attack.

The objective of this research is to present a detailed description of the reaction mechanism of iron in sulfur containing atmospheres.
II. PREVIOUS WORK

Oxidation of iron in atmospheres containing SO₂ has been studied by several workers¹-⁶. The most important findings are summarized in what follows.

A. Equilibrium Phase Diagram

A convenient way of representing the corrosion product which could be formed in some of these cases is to construct Ellingham-Pourbaix-type diagrams. These diagrams map out the ranges of stability of the various condensed phases as a function of the thermodynamic activities of two components of the reactive gas, for example, log oxygen partial pressure and log sulfur partial pressure. An Ellingham-Pourbaix-type diagram for the Fe-S-O system at 871°C (1600°F) is shown in Figure 1, in which the heavy lines denote the boundaries of condensed phases at unit activity. The equivalence of $P_S^2$ to $P_{H_2}/P_{H_2S}$ and $P_{O_2}$ to $P_{SO_2}/P_{SO_3}$ are also indicated on the coordinate. This "Ellingham Plot" is indispensable in the interpretation of product phase formation and morphology in mixed gases.

Figure 2 is the FeS-FeO phase diagram which show the existence of a eutectic at 940°C.

Figure 3 is the liquidus diagram for the Fe-FeS-FeO region of the Fe-S-O system which has been derived by Hilty & Crafts⁷. The system is shown to have a ternary eutectic located at 67% Fe, 24% S, 9% O and approximately 920°C. A liquid miscibility gap extends into the system from the Fe-O side to a sulfur content of 21.5% with a minimum point at approximately 81.5% Fe, 16.5% S, 2% O and 1345°C.
Figure 1. Fe-S-O phase stability diagram at 1144°K (1600°F).
Figure 2. Liquidus curves of systems FeO-FeS, CoO-FeS, CoO-CoS.

Figure 3. Fe-O-S diagram according to Hilty and Crafts.

XBL 815-9916
The solubility of oxygen has been determined at several temperatures in liquid iron containing sulfur. It appears that with increasing sulfur concentrations, the oxygen content of iron first decreases slightly, up to about 0.10% S, and then increases rapidly.

B. Microscopic Structure

A typical microstructure of the scale formed on pure iron in atmospheres of low SO₂ content was described by Birks et al. A very thin wustite layer is formed at the metal-scale interface. This layer contains small irregular inlets of FeS. Above it, there is a region of scale consisting of thin FeO and FeS lamellae. Outside this region there is a mixture of magnetite and FeS grains. At the scale/gas interface an Fe₃O₄ layer free of the sulfide is formed.

The formation of sulfides below an oxide scale at the alloy/scale interface is the most common observation. This leads to the obvious conclusion that sulfur can penetrate growing oxide layers: the mechanism is, however, in some doubt. Two possibilities present themselves: dissolution followed by lattice diffusion of sulfur, and transport of gas molecules via physical defects, such as pores and microcracks. These are alternate or parallel mechanisms: both may operate together. The question whether one predominates must remain open at present. For dissolution and ionic transport the solubility of sulfur within the oxide is clearly important. What few data there are, Table 1, indicate these are rather low, 0.1 - 0.01% being fairly common. The exact value will of course depend on the sulfur and oxygen partial pressure: indications are that sulfur solubility increases with sulfur potential (Sievert's law) and for NiO is independent of oxygen potential.
TABLE 1. Solubility of Sulfur in Oxides

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Sulfur Solubility, wt.%</th>
<th>T, °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeO</td>
<td>0.014</td>
<td>1250</td>
</tr>
<tr>
<td></td>
<td>0.03 - 0.4</td>
<td>800</td>
</tr>
<tr>
<td></td>
<td>0.042</td>
<td>1100</td>
</tr>
<tr>
<td></td>
<td>0.011</td>
<td>1050</td>
</tr>
<tr>
<td>Fe$_3$O$_4$</td>
<td>0.03</td>
<td>500</td>
</tr>
</tbody>
</table>

Low sulfur solubilities do not necessarily preclude a lattice transport mechanism since it is the flux, solubility times diffusivity, which is important. Some diffusion data are available, but they are not particularly decisive.

Pre-oxidation of samples prior to exposure to sulfur-bearing gases can delay sulfide-induced attack: it is never completely eliminated. In some experiments, the observed incubation period increased as the thickness of the pre-oxidized scale was increased. However, this result is equally consistent with time-dependent changes in the scale rendering it previous to gaseous transport, or to dissolution of sulfur in the oxide. A conclusion from these experiments, however, appears to be that it would be over optimistic to depend simply on oxide layers for protection from sulfidation under conditions where conjoint attack is possible.

C. Kinetics

It is now necessary to examine what effect the nature of the rate controlling step might have on scale morphology and reaction kinetics.

Effect of Different Rate Determining Steps

The possible rate controlling processes are

a. Reaction at the Fe/scale phase boundary (change over of iron ions and electrons from the metal to the scale)

b. Diffusion in the scale (diffusion of iron ions via vacancies and electrons via positive holes from the inner to the outer phase boundary)

c. Reaction at the scale/gas phase boundary (dissociation and ionization of the oxidizing agent and growth of the lattice of the scale)
d. Diffusion in the gas (transport of the oxidant from the gas stream to the surface of the scale)

In general, addition of sulfur dioxide to the atmosphere was found to increase the corrosion rate. But the effect of sulfur dioxide was greatly reduced if free oxygen was present. Birks et al. found that the reaction kinetics are linear followed by a parabolic period. When the flow rate was increased, the initial constant reaction rate was found to increase and the duration of this stage to decrease (i.e. the change to parabolic kinetics occurred earlier). The effect of both $P_{SO_2}$ and flow rate together suggests that the initial linear reaction is controlled by diffusion of $SO_2$ through a boundary layer in the gas. Eventually, cation diffusion becomes the rate controlling step and parabolic kinetics are observed. The fast corrosion rates are due to sulfide formation particularly in the form of lamellae within the iron oxide.

The higher the oxygen potential of the atmosphere, the sooner a protective oxide layer is formed. For a given $SO_2$ content, this condition is reached sooner as the flow rate of the gas over the specimen surface is increased. The most damaging attack is found with low $SO_2$ concentrations and low flow rates. Such conditions may be found in stagnant pockets of gas, such as in pores or beneath deposits. In these positions, the oxygen potential of the gas will be reduced to very low values whatever the oxygen content of the bulk atmosphere.

Rahmel summarized his mechanistic studies of the reaction of pure Fe in $N_2-O_2-SO_2$ and $CO-CO_2-COS$ mixtures between 700 and 900°C. The $N_2-O_2-SO_2$ gas compositions were chosen such that the more reactive oxidant ($O_2$) was in low concentration (<1%) while the "inert"
species \((N_2)\) was present in relatively high concentrations. In the absence of the second oxidant \((SO_2)\), linear oxidation kinetics resulted as the growth of an \(Fe_xO\) layer was limited by the transport of \(O_2\) through a stagnant gaseous boundary layer. As \(SO_2\) was added to the gas, both \(FeS\) and \(FeO\) formed as an aggregate product (see Fig. 4) with increased linear kinetics so long as the reaction was controlled by transport in the gas phase. On the other hand, when the oxygen content was higher (> 10% \(O_2\)), such that the kinetics were parabolic and controlled by diffusion through an iron oxide scale, the introduction of up to 5% \(SO_2\) did not affect the parabolic kinetics (see Fig. 5), nor was \(FeS\) formed.

In the somewhat analogous reaction of pure \(Fe\) with \(CO-CO_2-COS\) gases, \(CO\) was the diluent, \(CO_2\) the oxidizing agent, and \(COS\) the sulfidizing agent. In these gases, the simple formation of \(FeS\) from \(COS\) or of \(FeO\) from \(CO_2\) is limited by an interfacial reaction step - the breakup of the reactant molecule - and linear kinetics are observed. When the second oxidant is introduced in either case, both the sulfide and oxide are formed in an aggregate scale with increased linear kinetics (see Fig. 6). Again, the parabolic (diffusion controlled) growth of the oxide or sulfide is not influenced by the presence of minor amounts of the second oxidant.

Rahmel\(^2\) rationalized and generalized these observations as follows: 1. when linear kinetics result from rate control at or ahead of the scale/gas interface, then the scale contacting the gas is essentially equilibrated with the base metal and will react with additionally available oxidants; 2. when diffusion control in the scale results in parabolic kinetics, then the scale equilibrates with the reacting gas mixture at the scale/gas interface to exclude
Figure 4. Influence of SO$_2$ on the linear rate constant of the oxidation of iron in N$_2$-O$_2$ mixtures with 0.15 and 1.0\% O$_2$ at 900\°C (linear flow rate of the gas: 5.8 cm/sec).

Figure 5. Influence of SO$_2$ on the parabolic rate constant of the oxidation of iron in oxygen at 900\°C.
Figure 6. Influence of CO\textsubscript{2} on the linear rate constant of the sulfidation of iron in CO-CO\textsubscript{2}-COS mixture with 0.12% COS at 900°C (linear flow rate of the gas: 5.8 cm/sec)

<table>
<thead>
<tr>
<th>Rate determined step of reaction</th>
<th>Rate law</th>
<th>Conc. gradients in the scale and in the convective diffusion boundary layer</th>
<th>Effect of second oxidant on 1 rate of scale</th>
<th>2 composition of scale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reaction at the Fe/Fe\textsubscript{X} phase boundary</td>
<td>complex</td>
<td>Fe</td>
<td>Fe\textsubscript{X}</td>
<td>$C_{eq}$</td>
</tr>
<tr>
<td>Diffusion in Fe\textsubscript{X}</td>
<td>parabolic</td>
<td>$x^2 = k \cdot t$</td>
<td>$C_{eq}$</td>
<td>$C_{X_2}$</td>
</tr>
<tr>
<td>Reaction at the Fe\textsubscript{X}/X\textsubscript{2} phase boundary</td>
<td>linear</td>
<td>$x = k \cdot t$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transport in the gas phase</td>
<td>linear</td>
<td>$x = k \cdot t$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 7. Summary of Rahmel's experimental results. Influence of the second oxidant on the oxidation or sulfidation of iron in dependence of the rate-determining steps of the reaction.
any influence of a less reactive second oxidant. The results are summarized in Fig. 7.

D. Formation of Porous Layer

The other interesting observation is that in many studies of oxidation in sulfur containing atmospheres the scales have been observed not to be compact, but to have a porous inner layer. Inert markers are found at the boundary between the two layers of the scale. Mrowec has proposed a dissociation mechanism for their formation. He suggests that as the scale thickens and become more rigid, it is unable to deform with the contracting metal core, so the scale begins to lose contact with the metal substrate. In addition, the injection of vacancies into the substrate may condense to form pores at the metal-scale interface.

As a result of the formation of this gap, the rate of transport of metal ions to the scale decreases. However, because of the chemical potential gradient and the defect concentration gradient, the oxide or sulfide may begin to decompose. The metal ions migrate out through the scale and the sulfur or oxygen gas diffuses across the gap to oxidize the metal below. Consequently, the inner layer becomes porous.

The alternative explanation which was proposed by Goode et.al. for the formation of a porous inner layer in NiO is that the inner porous layer simply is formed by the inward short circuit transport of oxygen through microcracks incorporating any porosity which has formed at the scale-metal interface, but the details are not available.
III. INTRODUCTION TO PRESENT WORK

In order to investigate the mixed sulfidation and oxidation mechanism of iron in oxygen-rich atmospheres which can be produced by burning fuels, it is necessary to control the experimental conditions so that simultaneous oxidation and sulfidation can occur. According to previous work\textsuperscript{1-6}, the most damaging attack of simultaneous oxidation and sulfidation was found with low SO\textsubscript{2} concentrations and low flow rates. As a consequence, two gas mixtures were used: CO\textsubscript{2}-10\% SO\textsubscript{2} mixture and an air-1\% SO\textsubscript{2} mixture. These gas mixtures equilibrate, at 871°C, to a complex atmosphere containing the species CO\textsubscript{2}, SO\textsubscript{2}, O\textsubscript{2}, S\textsubscript{2}, CO, COS, SO\textsubscript{3}, CS, CS\textsubscript{2}, and S. The partial pressures of these species can be computed from thermodynamic data and are shown in Table 2.

Points A and B of Figure 1 represent the equilibrium gas mixtures of CO\textsubscript{2}-10\% SO\textsubscript{2} (P\textsubscript{O\textsubscript{2}} = 10^{-8.7} atm, P\textsubscript{S\textsubscript{2}} = 10^{-10.1} atm) and air-1\% SO\textsubscript{2} (P\textsubscript{O\textsubscript{2}} = 10^{-0.1} atm, P\textsubscript{S\textsubscript{2}} = 10^{-28.9} atm) respectively. From this diagram, it is obvious that P\textsubscript{S\textsubscript{2}} of CO\textsubscript{2}-10\% SO\textsubscript{2} is below the Fe-FeS equilibrium line (P\textsubscript{S\textsubscript{2}} = 10^{-8.2} atm), i.e., the sulfide is not stable in contact with the gas from a thermodynamic point of view. However, the experimental results show that the sulfur does exist in the scale. The exploration of this phenomenon is one of the main purposes of the present research. The air-1\% SO\textsubscript{2} mixture was used as a comparison for corrosion behavior in high oxygen partial pressure gases.

The experimental temperature is chosen just below the liquid phase formation temperature to avoid the complications due to liquid formation.

In this work, pure iron was exposed to the gas mixtures mentioned above. The scale growth mechanism was proposed by careful examination of the experimental results and confirmed by further experimental evidence.
TABLE 2. Log Partial Pressures of Gas Species After Equilibria in CO₂-10% SO₂ & Air-1% SO₂ at 871°C.

<table>
<thead>
<tr>
<th>Gas</th>
<th>Log Partial Pressure</th>
<th>CO₂-10% SO₂</th>
<th>Air-1% SO₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-4.0</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>-0.0</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>-1.0</td>
<td>-2.0</td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>-8.7</td>
<td>-0.1</td>
<td></td>
</tr>
<tr>
<td>S₂</td>
<td>-10.1</td>
<td>-28.9</td>
<td></td>
</tr>
<tr>
<td>COS</td>
<td>-8.8</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>SO₃</td>
<td>-5.7</td>
<td>-2.2</td>
<td></td>
</tr>
<tr>
<td>CS</td>
<td>-20.7</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>CS₂</td>
<td>-18.5</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>SO</td>
<td>-6.1</td>
<td>-11.6</td>
<td></td>
</tr>
</tbody>
</table>
IV. EXPERIMENTAL

The furnace used was a Lindberg horizontal tube furnace equipped with a 2-1/4" o.d., 2" i.d. mullite tube. The ends of the tube were sealed with compression-type O-ring seals cooled by circulating cooling water. For introduction of the samples into the hot zone, one end of the furnace was equipped with a moveable alumina specimen holder and a Pt/Pt-Rh thermocouple. For introduction of the appropriate gases, the other end was equipped with a safety valve and various gas flow meters. The gases were fed into a mixer at rates which were measured by flow meters. After mixing completely, the gas mixture was fed into the furnace. On the exhaust side, the gases were led through a bubbler containing concentrated NaOH where sulfur compounds were dissolved out before venting the gas.

The samples were made by cutting Golden Metals electrolytic iron containing about 0.09% impurity into 1x1x0.3 cm coupons. Table 3 lists the analysis of the specimen. Specimens were prepared immediately before each run by grinding down to 600 grade carborundum paper followed by degreasing in acetone. Before and after the oxidation test, the furnace was flushed with argon whose oxygen partial pressure is estimated as 1 ppm. The reaction was started by moving the specimen holder from the cold zone to the hot zone. The reactive gas flow rate was about 6 liter/hr. Experimental temperature was 871°C (1600°F).

The surface topography of oxidized samples was examined by scanning electron microscopy after they had been coated by gold sputtering. Scale products were identified by X-ray diffraction and Scanning Auger Microscopy. Polished cross sections were studied by optical microscopy and electron probe microanalysis. The oxidation kinetics were determined from scale thickness measurements on polished cross sections. This has the advantage over a weight change method of avoiding erroneous measure-
TABLE 3. Analysis of the pure iron specimen.

<table>
<thead>
<tr>
<th>Chemical Properties</th>
<th>Specifications</th>
<th>Typical</th>
</tr>
</thead>
<tbody>
<tr>
<td>(4) Iron, Total, %</td>
<td>99.81 min.</td>
<td>99.91</td>
</tr>
<tr>
<td>(3) Aluminum, %</td>
<td>--</td>
<td>0.002</td>
</tr>
<tr>
<td>(6) Arsenic, %</td>
<td>--</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>(5) Carbon, %</td>
<td>0.010 max.</td>
<td>0.003</td>
</tr>
<tr>
<td>(3) Chromium, %</td>
<td>--</td>
<td>0.002</td>
</tr>
<tr>
<td>(3) Cobalt, %</td>
<td>--</td>
<td>0.007</td>
</tr>
<tr>
<td>(3) Copper, %</td>
<td>--</td>
<td>0.004</td>
</tr>
<tr>
<td>(2) Hydrogen, %</td>
<td>--</td>
<td>0.010</td>
</tr>
<tr>
<td>(1) Hydrogen Loss, %</td>
<td>0.08 max.</td>
<td>0.04</td>
</tr>
<tr>
<td>(6) Lead, %</td>
<td>--</td>
<td>&lt;0.001</td>
</tr>
<tr>
<td>(3) Manganese, %</td>
<td>0.005 max.</td>
<td>0.002</td>
</tr>
<tr>
<td>(6) Mercury, %</td>
<td>--</td>
<td>&lt;0.0005</td>
</tr>
<tr>
<td>(3) Molybdenum, %</td>
<td>--</td>
<td>0.007</td>
</tr>
<tr>
<td>(4) Nickel, %</td>
<td>0.050 max.</td>
<td>0.030</td>
</tr>
<tr>
<td>(2) Nitrogen, %</td>
<td>--</td>
<td>0.004</td>
</tr>
<tr>
<td>(2) Oxygen, %</td>
<td>--</td>
<td>0.015</td>
</tr>
<tr>
<td>(4) Phosphorus, %</td>
<td>0.005 max.</td>
<td>0.002</td>
</tr>
<tr>
<td>(3) Silicon, %</td>
<td>--</td>
<td>0.003</td>
</tr>
<tr>
<td>(3) Sodium, %</td>
<td>--</td>
<td>0.002</td>
</tr>
<tr>
<td>(5) Sulfur, %</td>
<td>0.006 max.</td>
<td>0.004</td>
</tr>
<tr>
<td>(3) Tin, %</td>
<td>--</td>
<td>0.002</td>
</tr>
<tr>
<td>(3) Tungsten, %</td>
<td>--</td>
<td>0.001</td>
</tr>
<tr>
<td>(3) Vanadium, %</td>
<td>--</td>
<td>&lt;0.003</td>
</tr>
</tbody>
</table>
TEST METHODS

(1) MPIF Standard 2.43  (2) Vacuum Fusion  (3) Spectrograph
(4) ASTM Analytical Methods  (5) Combustion  (6) Food Chemicals Codex
ments caused by localized variations in the extent of attack.

In some instances, scales were stripped from the metal mechanically by quenching in liquid nitrogen. The detached scales were examined in a scanning microscope fitted with energy dispersive analysis.
V. EXPERIMENTAL RESULTS

A. Microscopic Studies

After exposure of pure iron in CO₂-10% SO₂ atmospheres for three hours, lots of protrusions grow outward from the scale surface as shown in Figure 8. These protrusions are irregular, non-crystalllographic, randomly oriented and with branches and protrusive wrinkles. A closer examination of protrusions is shown in Figure 9. The diameters of some protrusions are over 50 μm. Sulfur rich cores which were detected by SEM or SAM run through the center of the protrusions as shown in the fracture cross-sections in Figure 10. The protrusions were formed by a continuous sulfur rich core which was surrounded by many oxide grains. Oxide grains appear to have grown radially out of the sulfide core.

Sectioned and polished specimens were examined. Typical optical microscopic sections are shown in Figure 11. The oxide/metal interface is relatively uniform, but the outer surface shows protrusions. Near the gas/scale interface, the scale consists of different phases. The white streaks and spots which are rich in sulfur are distributed among the gray oxide matrix. There are sometimes long streaks associated with the protrusions on surface existing in the outer part of the scale. Sometimes there are no sulfide streaks. The existence of sulfide streaks below the protrusion depends on whether the section cuts through a protrusion. In the inner regions of the scale, the sulfide particles are smaller and not as obviously orientated. Finally, close to the metal/scale interface there is an inner layer whose porosity will be shown in later SEM pictures. It is hard to define the two phases in the inner layer because there are no obvious contrasts, but presumably the sulfide phase is intimately mixed with
Figure 8. SEM image of the outer scale surface formed on pure iron oxidized for 3 hours in flowing CO$_2$-10% SO$_2$ at 871°C.

Figure 9. The closer examination of Figure 8.
Figure 10. SEM image of fracture protrusion formed on Fe oxidized for 3 hrs. in CO₂-10% SO₂ at 871°C.
Figure 11. Cross sections of pure iron oxidized in CO$_2$-10% SO$_2$ at 871°C. a) for 3 hrs.; b) for 12 hrs.
the oxide phase in this inner layer rather than the more obvious distribution in the outer layer. Comparing Figures 11-(a), (b), the longer the exposure time, the thicker the outer layer is. But the thickness of the inner layer remains almost unchanged.

A fracture cross section of scale shows that the outer layer is composed of coarse iron oxide grains and small sulfur rich grains as in Figure 12. Some smaller pores exist in the outer layer. The inner layer is porous and with thin sulfide-oxide lamellae as in Figure 13. The pores seem interconnected and some are linearly connected. Some faces of grains are concave in shape. Beneath them, there exists a layer of larger grains at the scale/metal interface as in Figure 14.

From the bottom view of the scale stripped from the metal mechanically by quenching in liquid nitrogen (i.e., at the scale/metal interface), there are many small grains which look like nuclei concentrated in the sulfur rich areas (see Figure 15). This layer is much denser than the porous layer. Figure 16 is the top view of metal surface after the scale was removed. Some scale grains remain attached to it. The metal surface shows the imprint of scale grains. This is an indication of good contact between scale and metal.

B. SAM and X-ray Diffraction Analyses

In order to analyze the oxygen which exists in the scale, SAM (Scanning Auger Microscope) and X-ray diffraction measurements were carried out. Figures 17 (a)-(d) are some of the SAM analyses. Figures 17 (a), and (b) show the elemental distribution in a sulfur rich grain and in an oxide grain respectively. They demonstrate that the sulfur rich particles contain high concentrations of oxygen (at least 10% at.) whilst only small amounts of sulfur are detected in the oxide matrix. Figures 18 (a)-(d) are the Auger electron energy
Figure 12. Outer layer of scales formed on pure iron oxidized for 3 hours in CO₂-10% SO₂ at 871°C a) fracture section; b) sulfur map.
Figure 13. Inner layer of scales formed on iron oxidized for 3 hrs. in CO₂-10% SO₂ at 871°C  a) fracture section; b) lamellae.
Figure 14. Inner layer of scales formed on iron oxidized for 3 hrs in CO₂-10% SO₂ at 871°C a) fracture section; b) S map.
Figure 15. Bottom view of Fe scale (scale-metal interface) oxidized in CO$_2$-10$\%$ SO$_2$ for 3 hrs. at 871$^\circ$C  a) SEM image;  b) S map.
Figure 16. Top view of metal surface after the removal of the scale oxidized in CO$_2$-10% SO$_2$ for 3 hrs. at 871°C.
Figure 17. Concentration profile across the grain of scale fracture section for Fe oxidized in CO$_2$-10% SO$_2$

a) near gas/scale interface;
b) another point near gas/scale interface;
c) near metal/scale interface;
d) another point near metal/scale interface.
Figure 18. Spectra of SAM analyses for Fe oxidized in CO$_2$-10% SO$_2$ for 3 hrs. at XBL 815-9802 871°C. a) before and b) after sputtering the oxide film at point a of Figure 17; c) before and d) after sputtering the oxide film at point b of Figure 17.
diagrams before and after these analyses. There exists a small peak at 150 e.V. position in Figure 18 (d), i.e., small amount of sulfur exists in the oxide. Figures 17 (c), (d) are the other two SAM analyses of the inner layer grains. It is noted that these SAM results are not typical, and are actually very sensitive to position: near the scale/metal interface, the sulfur content increases gradually. However, under a 400 Å/min of argon ion sputtering rate, the Auger electron spectra show that the elements are distributed evenly within the grains. Since SAM only analyses the area of a 1 μm circle where neither pure sulfide nor pure oxide was detected, these sulfur may exist in two forms, either as solid solution or as very fine duplex structure of oxide and sulfide. In order to distinguish, X-ray diffraction was done for further exploration.

Figures 19 (a)-(c) show the results of X-ray diffraction for pure iron specimens exposed in CO$_2$-10% SO$_2$, air, and H$_2$-10% H$_2$S at 871°C separately. (Only significant peaks were drawn down in these figures). The exposures of iron in air and H$_2$-H$_2$S are done to obtain the standard X-ray peaks of FeS, FeO, Fe$_3$O$_4$, Fe$_2$O$_3$ for Fe target. The standard peaks calculated from the Data Card Format are listed in Table 4.

It was found that Figure 19(a) is not a combination of Figure 19(b) and Figure 19(c) as might be expected. Comparing Figure 19(a) and Figure 19(b), the positions of the magnetite and wustite peaks are shifted slightly or split into two peaks. In addition, the peaks for hematite are rarely identified as in Figure 19(a). This is due to the low P$_{02}$ in CO$_2$-SO$_2$ atmosphere. The sulfide peaks in Figure 19(a) broaden a little bit compared with Figure 19(c). (The actual breadth is not drawn down in Figure 19(a)-(d).)
Figure 19. X-ray diffraction for a) Fe exposed to CO₂-10% XBL 815-9803 SO₂; b) Fe exposed to Air; c) Fe exposed to H₂-10% H₂S; d) sintered iron-iron oxide-iron sulfide mixture.
<table>
<thead>
<tr>
<th>Formula</th>
<th>Peak Angle (2θ) (Fe Target)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Peak I</td>
</tr>
<tr>
<td>Iron oxide/wustite</td>
<td>(FeO)8F</td>
<td>53.63</td>
</tr>
<tr>
<td>Iron oxide</td>
<td>(FeO)2R</td>
<td>79.17</td>
</tr>
<tr>
<td>Iron oxide/magnetite</td>
<td>Fe₃O₄</td>
<td>45.02</td>
</tr>
<tr>
<td>Iron oxide/hematite</td>
<td>Fe₂O₃</td>
<td>45.21</td>
</tr>
<tr>
<td>Iron sulfide/pyrrhotite</td>
<td>Fe₀.₉₅S 55.80</td>
<td>55.80</td>
</tr>
<tr>
<td>Iron sulfide/pyrrhotite</td>
<td>Fe₁₋ₓS 55.80</td>
<td>55.80</td>
</tr>
</tbody>
</table>
Since some of the lattice parameters change little, it is therefore believed that the intersolubility of iron oxide and iron sulfide is relatively slight. Other workers' data also tend to confirm this (see Table 1). For further substantiation, the following experiment was carried out. A fine mixture of iron powder, iron oxide powder (obtained by oxidizing iron in air and thus comprising wustite, magnetite and hematite) and iron sulfide powder (obtained by sulfiding iron in $H_2-10\% H_2S$) was pressed and then sintered in a sealed quartz tube, which was filled with low pressure Ar and equilibrated at $871^\circ C$ for two weeks. The iron powder was added to assure the transformation of both the hematite and magnetite into wustite. The X-ray diffraction pattern for the sintered material is shown in Figure 19(d). A comparison with Figure 19(b) and 19(c) indicates, the sulfide and wustite peaks are almost unchanged. The difference between Figure 19(a) and 19(d) is that the magnetite peaks exist only in Figure 19(a) but not in Figure 19(d). This difference is caused by the lower equilibrium $P_{O_2}$ of iron-sulfide-oxide system than that of $CO_2$-$SO_2$ system. As a consequence, it is concluded that the solubilities of oxide in sulfide and of sulfide in oxide must be very small. (Otherwise some significant shifts or new peaks would be observed.)

From the above experiments and analyses, the sulfur rich grain observed in the SAM must indeed be in the form of a fine oxide/sulfide duplex structure.

C. Kinetics

The reaction kinetics of pure iron exposed to $CO_2$-$10\% SO_2$ atmosphere are parabolic during the later stages of growth, the earlier stages (within 1 hr) probably are faster parabolic or linear as shown
in Figure 20. The parabolic kinetics are determined from scale thickness measurements where the thickness of the protrusions has been neglected. (The protrusion height is about 5%-10% of the total thickness.) The parabolic rate is between the rate of pure sulfidation and the rate of pure oxidation. Previous workers found similar results as summarized in Table 5 which includes the partial pressure of $S_2$ & $O_2$ because the sulfidation (oxidation) rate depends on the partial pressure of sulfur (oxygen).

| TABLE 5. Parabolic Rate Data ($g^2 cm^{-4} sec^{-1}$) for the Sulfidation and Oxidation of Pure Iron |
|---------------------------------------------------|---------------------------------------------------|---------------------------------------------------|
| Sulfidation $^{10}(H_2-H_2S)$ | Sulfidation and Oxidation $^{11}(Ar-SO_2)$ | Oxidation $^{11}$(air) |
| $800^\circ C$ | $1.3x10^{-6}$ | $2.48x10^{-7}$ | $5.3x10^{-8}$ |
| ($P_{S_2} = 4x10^{-4}$) | ($5\% \ SO_2$) | |
| $900^\circ C$ | $2.4x10^{-6}$ | $3.76x10^{-7}$ | $2.5x10^{-7}$ |
| ($P_{S_2} = 3.6x10^{-4}$) | ($4\% \ SO_2$) | |
| $1000^\circ C$ | $5.9x10^{-6}$ | --- | $6.5x10^{-7}$ |
| ($P_{S_2} = 2x10^{-2}$) | |

It is very likely that the increase in rates is due to the effect of slight sulfur dissolution in the oxide. Enhanced cation diffusion by sulfur in copper, iron and nickel oxide has been reported by Birks$^{12}$. One possible mechanism for this enhancement is the formation of additional cation vacancies by reaction of the sulfur with the lattice of oxide although the mechanism for this effect is not yet clear. Figure 20 shows the discrepancy between $K_p(H_2-10\% H_2S)$ and
Figure 20. Parabolic plot for growth of scale on Fe exposed to a) \( H_2-10\% H_2S \); b) \( CO_2-10\% SO_2 \); c) Air.

\[ K_p = 8.33 \mu m \ sec^{-\frac{1}{2}} \]

\[ K_p = 3.50 \mu m \ sec^{-\frac{1}{2}} \]

\[ K_p = 3.26 \mu m \ sec^{-\frac{1}{2}} \]
$K_p(CO_2-10\%\ SO_2)$ is quite significant, but $K_p(CO_2-10\%\ SO_2)$ and $K_p(Air)$ are almost the same at later stages. However, the parabolic constants at the earlier stages might be much different because the sulfide fraction is higher in the scale initially.

The reaction kinetics of pure iron exposed to an Air-1% $SO_2$ atmosphere is the same as for pure oxidation.
VI. DISCUSSION

The equilibrium condition of CO$_2$-10% SO$_2$ in this experiment is at point A in Figure 21. According to this thermodynamic equilibrium diagram, sulfide is not a stable phase in contact with the gas nor is the sulfur potential of the gas high enough to form the sulfide of iron. The existence of sulfide in the scale which is detected by EDAX and SAM indicates, however, that the sulfur activity must be increased somehow, probably because oxygen is consumed by the reaction with metal, and as a consequence, the sulfur activity increases. The reaction can be expressed as:

$$\text{SO}_2 + 1/2 \text{S}_2 \rightarrow \text{S} + \text{O}_2$$

In order to interpret this, it is, therefore, important to establish how the composition of the gas mixture, assuming always that it is at equilibrium, and in particular the activities of the oxygen and sulfur reactants, will change when one of the components is removed from the gas by reaction with the metal.

Equilibria in the S-O-C gas system have been calculated by Birks et al. A combination of an Ellingham-Pourbaix-type diagram and a CO$_2$-10% SO$_2$ gas system equilibria diagram is shown in Figure 21. These interdependencies between sulfur and oxygen potentials have a considerable influence on corrosion behavior. For example, a gas mixture equilibrated at the oxide region (point A) might shift into a sulfide stable region (point B) when oxygen is consumed by the reaction with the metal. In other words, during the formation of an oxide phase contiguous to the metal, local equilibria may be set up temporarily at scale/gas interface or internally within the scale which deviate greatly from the bulk gas phase and thereby allow the formation of sulfide.

In the first case, the change of thermodynamic equilibrium to a
Figure 21. Fe-S-O phase stability diagram and partial pressure relationship of oxygen and sulfur for CO$_2$-10% SO$_2$ at 871°C.
sulfide stable region by reaction on the surface, would imply that diffusion of the oxidant through the gas phase to the scale/gas interface is the rate determining step. This implication is in agreement with a linear reaction rate which was observed as discussed in the section on previous work. The formation of sulfide, which causes a depletion of sulfur, can shift the thermodynamic equilibrium back to the oxide stable region, i.e., the gas composition near the scale surface fluctuates between sulfide stable region and oxide stable region. In addition, the reaction rate is so fast that an oxide and sulfide duplex structure, as shown in Figure 13(b), is formed rather than the larger grains of oxide or sulfide. The existence of sulfide is very sensitive to the depletion of oxygen. As the scale thickens, the transport rate of cations is limited, therefore, the depletion of oxygen becomes more difficult and as a consequence there is less tendency for sulfide formation. Figure 22 clearly shows that sulfur concentration decreases from the scale/metal interface to the scale/gas interface.

Figure 21 is a log scale, therefore, the change from point C to point B is much greater than from point A to point B. The amount of oxygen which must be removed in order to reach sulfide stable region (e.g., point B) will be much greater from point C rather than from point A. This accounts for the experimental result that the reaction kinetics of pure iron exposed to Air-1% SO₂ atmosphere (equilibrium at point C) is the same as for pure oxidation since it is impossible to deplete the oxygen locally in this case. As a further consequence, no sulfide was found in the scale.

As an alternative to reaction at the surface of the scale producing an oxygen depletion, there is also the possibility of a change in thermodynamic equilibrium to a sulfide stable region by reaction within the scale, providing gas transport through the scale occurs via physical defects.
Figure 22. Cross section of Fe oxidized in CO$_2$-10% SO$_2$ for 3 hrs. at 871°C a) SEM image b) S map.
(e.g., cracks or pores), rather than via lattice transport. This mechanism may contribute to the existence of sulfide in the scale, but it seems unlikely to be a predominant factor in this experiment since it is difficult to explain the existence of so many protrusions with long sulfide rich cores beneath them, and the sulfide, which was detected by SAM, on the surface of their heads. Sulfide formed by gaseous transport through the scale would be expected to be randomly distributed within the scale, i.e., without continuous streaks and no sulfide on the surface.

As mentioned earlier, after exposure of pure iron to CO₂-10% SO₂ atmospheres, there are two kinds of irregularities in the microstructure of the scale (see Figure 8). The larger irregularities are the protrusions which are irregular, not crystallographically facetted, randomly oriented, with branches and sulfide-rich core. The smaller ones are the protrusive wrinkles formed on the surface of the scale and on the protrusions (see Figure 9). These phenomena are not observed in either pure sulfidation or pure oxidation, where the scale surface usually forms some type of crystallographic facetting. As a consequence, they must be related to the specific growth mechanism of these duplex scales. The formation of protrusions on the scale is explained by the following mechanism (see Figure 23):

Step 1

As discussed earlier, during oxidation of pure iron in CO₂-10% SO₂, the gas layer adjacent to the metal becomes enriched in sulfur vapor due to the depletion of oxygen consumed by oxidation, and consequently there is a local change of the gaseous equilibrium into a sulfide stable region leading to the formation of sulfide. In this case, the reaction rate is limited by diffusion in gas phase and a linear rate is observed.
Figure 23. Mechanism for the formation of protrusion.
Step 2

The existence of sulfide is very sensitive to the depletion of oxygen. Removal of oxygen can be easily obtained by a high iron activity. There are two possible ways in which a high iron activity can occur. The first is over a pre-existing sulfide-rich area, through which the cations transport is faster than in the oxide, and as a consequence, a high iron activity might be expected to exist in the sulfide-rich area (i.e., a surplus of iron ions waiting for the possibility of reaction) so as to consume more gases and grow faster than the surrounding oxide. This phenomenon insures that once the sulfide exists, the depleted atmosphere always surrounds it, and any available oxidant, either sulfur or oxygen, can react with the iron ions to form sulfide or oxide causing the protrusion to continue to grow into the undepleted atmosphere rather than spread laterally. In other words, the scale/gas equilibrium has not been achieved at the surface of sulfide-rich areas, as mentioned earlier, and the gas composition locally fluctuates between sulfide and oxide stable regions. This leads to the continuous formation of sulfide and oxide lamellar type structure at the original sulfide-rich area on the surface of the scale.

The other possibility for the formation of a high iron activity center is a short circuit path in the predominantly oxide scale. An indication that this can also be a contributory factor is demonstrated by an experiment in which a sample was oxidized initially in sulfur-free atmosphere. Pure iron was preoxidized for three hours in air then exposed to the CO\textsubscript{2}-10% SO\textsubscript{2} atmosphere for one hour. In this case, no sulfide rich areas exist when the SO\textsubscript{2}-containing environment was introduced. The existence of protrusions with sulfide-rich cores indicates that depletion of oxygen again happened over some areas. The most probable explanation is that
the depletion can be caused by fast transport of iron ions through some type of short circuit path, such as grain boundaries. Figure 24 shows that the protrusions exist evenly over the surface with a relatively uniform oxide layer beneath them. However, the decrease in number and size of the protrusions suggests that the oxide layer provides a barrier to the formation of the protrusions.

Step 3

It should be remembered, however, that sulfide is not the thermodynamically stable phase in equilibrium with the bulk gas, and that eventually oxide can be formed when the atmosphere approaches that of the bulk gas by transport of oxidants such as CO₂ or SO₂ to the surface. If oxide is formed as illustrated in Step A, branches in the protrusions will be produced due to the blockage by oxide. If oxide is formed as illustrated in Step B, however, the sulfide-rich streak will continue to grow. If the oxide covers the sulfide-rich core as illustrated in Step C, the protrusion will be buried as the surrounding oxide grows around it.

Step 4

As a result of the surrounding oxide growing with the protrusions, the long streaks of sulfide and oxide lamellar structure are formed. Also, some sulfide-rich streaks buried are inside the scale, and some isolated sulfide-rich grains are formed by short circuit path and are randomly distributed within the scale as shown earlier in Figure 11.

The mechanism proposed is consistent with the following facts:

a. No protrusions are ever formed in pure sulfidation or oxidation for neither local fluctuation in surface gas composition between sulfide and oxide stable regions, nor local diffusion rate differences caused by sulfide within the scale can occur.

b. No protrusions are found in sulfur containing atmospheres
Figure 24. Top view of Fe preoxidized in air for 3 hrs. at 871°C and subsequently exposed to CO₂-10% SO₂ for 1 hr. a) SEM image; b) S map.
with over 10% free oxygen since depletion of oxygen is hardly achieved.  

c. As the exposure time increases, the number of protrusions decreases because the outward transport rate of cations is limited by the scale thickness, i.e., differences between sulfide-rich and oxide-rich areas diminish.

In order to confirm this mechanism, it is important to identify these sulfide-rich active centers. No sulfur was detected by SEM or SAM on the heads of the protrusions. It is believed that these active centers are covered with oxide during the cooling stage following the experiment, by oxygen impurities within argon gas used for flushing the reaction chamber. Consequently, a specimen was cooled in the sulfur containing atmosphere (CO₂-10% SO₂) instead of the argon atmosphere. This time, the SEM and EDAX pictures (see Figure 25) showed the existence of sulfides at the head of the protrusions. They developed a flower-like appearance (see Fig. 26) indicating that the protrusions grow at a rapid rate at their heads. This experiment tends to confirm that the protrusions are formed by rapid ionic transport through the sulfide-rich areas.

Figure 10, shown previously, portrays fracture sections through a protrusion with a sulfide-rich core which is surrounded by oxide grains formed during the Ar flushing stage. The surface of the sulfide/oxide duplex protrusion, where it penetrates into the gas which would be closer to the bulk gas composition (CO₂-10% SO₂ or flushing argon) tends to be converted to oxide. As a consequence, these oxide grains grow in a columnar orientation normal to the surface of the protrusion. This orientation also indicates that the transport through the sulfide-rich core is faster than through the oxide grains. Otherwise, the oxide would grow parallel rather than perpendicular, to the sulfide-rich core, and it
Figure 25. Top view of Fe oxidized in CO₂-10% SO₂ for 3 hrs. at 871°C
a) SEM image  b) S map.
(cooled down in sulfur containing atmosphere)
Figure 26. A closer examination of Figure 25
a) SEM image; b) S map.
would be impossible for so many oxide grains to form and cover the sulfide-rich core.

The protrusive wrinkles formed on the scale surface and on the surface of the protrusions, as shown in Figure 9, are probably caused by grain boundary diffusion which is enhanced by the sulfide. Figure 27 shows that those wrinkles grow along the scale grain boundaries.

Wrinkles are not found in either pure sulfidation or pure oxidation although the grain boundary exists in both cases. Therefore, it is believed that sulfur plays an important role in grain boundary diffusion. Many evidences\textsuperscript{14} show that the sulfur can penetrate through oxides. The existence of sulfide in the grain boundaries of oxides might enhance the transport rate of cations probably because bonding for sulfide is much weaker than oxide.

As described in the experimental results (see Figure 14(a)), a porous layer exists beneath the outer layer which contains the sulfide-rich streaks and grains. Currently, two theories are proposed to explain the formation of this porous layer: a dissociation mechanism and inward diffusion of anions. Both were described in the section on previous work. Inward diffusion of oxygen and sulfur seems to be a better explanation for the present results, although the dissociation mechanism is an alternative. The details are described as following:

**Step 1**

The growth of the scale depends mainly on the outward diffusion of cations but oxygen or sulfur diffusion inward may also be a contributing factor. Figure 28 shows that scale pegs penetrate into the metal matrix. These probably grow via a short circuit path. Some of the pegs are connected with each other. These pegs are an indication of inward transport of oxygen or sulfur.
Figure 27. SEM images of fracture protrusion formed on Fe oxidized in CO$_2$-10% SO$_2$ for 3 hrs. at 871°C.
Figure 28. Microstructure of metal/scale interface on Fe exposed to CO$_2$-10% SO$_2$ for 3 hrs. at 871°C.
Step 2

Since the rate of outward transport of cations is much faster than the inward transport of anions, pores might be expected to form at the scale/metal interface due to the volume difference of outward diffusion of cations and inward diffusion of anions. Of course, other factors are also involved and some deviations from this simple mechanism may be caused by plastic deformation of the scale or by the gaseous transport through the scale.

Step 3

Once the pores have been nucleated, then during continued scale thickening, the pores can gradually move away from the scale/metal interface into the bulk of the scale by a dissociation mechanism as illustrated in Figure 29.

The combination of sulfur or oxygen with metal ions at the scale/metal interface can either form new nuclei, or continue to extend the grains already existing there. Figure 15 indicates that lots of nuclei are found at the scale/metal interface. These nuclei are formed by the inward transport of anions. It is clear that these nuclei concentrate on the sulfide-rich areas. This also confirms that the anion transport rate is enhanced by sulfur. Figure 14 shows that a layer of dense, larger grains exists at the scale/metal interface. Both Figures 14 and 15 are evidence for the existence of inward transport of oxygen or sulfur.

It is difficult to explain two of the observed facts by a dissociation mechanism: Firstly, the good contact of scale/metal interface that is indicated by grain imprint on metal surface as shown in Figure 16, and secondly, the nuclei which are formed on the scale side of the interface and not on metal side as indicated when the scale is mechanically removed from the substrate.
Figure 29. Mechanism for the formation of porous layer.
The mechanism of formation of the inner porous layer is completely different from that of the outer layer. As a consequence, the streaks which exist in the outer layer cannot be observed in the inner layer as shown in Figure 11. The inner porous layer is formed mainly because of the presence of sulfide. However, the supply of sulfur is greatly reduced as the scale thickness increases. And, as a consequence, the growth of the inner layer is eventually limited because of the decreased supply of sulfur. Thus, as shown in Figure 11 (a) and (b), the inner layer does not grow significantly as the outer layer does. Small pores were also found in the outer layer (See Figure 12). These pores can probably be formed either by dissociation of the oxide or an imperfect outward growth of scale involving so many irregular protrusion which will probably join together.

The differences in porosity between the inner and outer layers are also believed to be due to the relatively fast transport in wustite (the major component for the inner layer) rather than in magnetite (the major component for the outer layer). The dissociation rate is limited in the outer layer and thus, fewer and smaller pores were observed.

This mechanism was further confirmed by the following experiment. A sample of pure iron was exposed in a sulfur containing atmosphere for three hours followed by another three hours air exposure. Since the transport is faster in the sulfide-rich areas than in the oxide, the outer oxide layer which formed during the air exposure could not supply enough anions for the transport inwards along the sulfide-rich channel. This created a deficiency of mass, resulting in the protrusions becoming porous (see Figure 30), as illustrated in Figure 31.

The following experiment was performed in order to further substantiate whether, during the scale growth process, inward diffusion of oxygen
Figure 30. SEM images of fracture protrusion formed on Fe oxidized in \( \text{CO}_2 - 10\% \text{ SO}_2 \) for 3 hrs. and subsequently exposed to air for 3 hrs. at \( 871^\circ \text{C} \).
Step 1

After exposed pure iron in 10% SO₂, 90% CO₂ atmosphere for three hours, the protrusion on the scale is dense as shown in Figure 10, since the sulfur and oxygen can be easily obtained through the fast transport of sulfide-rich channel.

Step 2

Following three hours air exposure, sulfur rich channel is blocked by oxide layer, the anion transports faster in sulfur rich area than in outer oxide layer. Therefore, small pores begin to form due to the unbalanced anion inward transport.

Figure 32(a) shows a baby protrusion with fewer pores. Less sulfur content in the protrusion is probably the reason for its small size and less pores.

Step 3

After a period of time, porous core is produced as in Figure 30. Figure 32(b) shows that the porous core extends into the scale. It is noted that the wrinkles do not appear on the surface of these protrusions, (Compare Figure 30 with Figure 10). Since sulfur transports inward, the sulfur enhanced grain boundary diffusion is no longer available.

Figure 31. Mechanism for the formation of porous protrusion.
Figure 32. SEM images of fracture cross section of scale formed on Fe oxidized in CO₂-10% SO₂ for 3 hrs. and subsequently exposed to air for 3 hrs. at 871° C.

a) a baby protrusion
b) a porous streak beneath protrusion.
or sulfur really occurs and, if so, by what mechanism. A pure iron sample was sulfidized first and then subsequently oxidized. Figure 33 demonstrates three ideal sulfur distribution through the scale for different dominant transport processes. Figure 34 shows the SAM analysis for a sample of pure iron presulphidized for 10 minutes then oxidized for 20 minutes at 300°C. Comparing with Figure 33, it clearly shows that oxygen or sulfur inward transport occurs. Figure 34 also shows that sulfur and oxygen penetrate into the metal matrix (for iron is over 50 atomic % in the inner part). This also indicates that sulfur and oxygen transport inwards. The temperature 300°C was chosen rather than 871°C in order to produce a scale thin enough to be amenable to analysis by SAM. However, results were similar to an Fe-25% Cr specimen carried out in a similar way but at 871°C.15
Figure 33. Ideal sulfur distributions over scale for different dominant processes.

a) oxygen or sulfur vacancy diffusion
b) dissociation mechanism or pure cation vacancy diffusion
c) oxygen or sulfur short circuit diffusion.

Figure 34. The SAM analysis for a sample of pure iron presulfidized for 10 minutes and subsequently exposed to air for 20 minutes at 871°C.
VII. CONCLUSION

1. The increased corrosion rate of iron exposed to oxygen-rich but sulfur-containing atmospheres and the formation of protrusions at the surface of the scale is due to the rapid transport of iron ions through sulfide-rich channels.

2. Wrinkles which are formed by sulfur-enhanced grain boundary diffusion are found on the scale.

3. The scale is composed of grains of different sulfur content which is in the form of sulfide and oxide lamellar structure.

4. The existence of sulfide in the scale is due to the depletion of oxygen contiguous to the scale/gas interface. This phenomenon shifts the thermodynamic equilibrium in the gas from one in which oxide is stable to one in which sulfide is the stable phase.

5. The unbalanced diffusion of inward transport of anion is the cause of the formation of pores in the scale.
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