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IN CARBON-MONOXYDE/CARBON-DIOXYDE GAS MIXTURES.

The Ohio State University, Ph.D., 1979
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OXIDATION AND CARBURIZATION OF Fe-Cr AND Ni-Cr ALLOYS AT 850 AND 950°C IN CO/CO₂ GAS MIXTURES

DISSERTATION

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

By

Jeffery Alan Colwell, B.S.E., M.S.E.

* * * * *

The Ohio State University

1979

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I. INTRODUCTION

Coal gasification is basically the transformation of coal into a final product of synthetic gaseous fuel. Although there are many different commercial processes being tested (both on the laboratory and on pilot plant scale), most of them have similar process steps. The coal is first reacted with steam plus oxygen, or else heat is added, to form synthesis gas with major components carbon monoxide and hydrogen. The synthesis gas may then be catalytically shifted to carbon dioxide and more hydrogen by the reaction

\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \]

so that the \( \text{H}_2 : \text{CO} \) ratio is 3 : 1. Methanation is then effected over a nickel catalyst by the reaction

\[ \text{CO} + 3\text{H}_2 = \text{CH}_4 + \text{H}_2\text{O} \]

The amount of sulfur in the gas (e.g. \( \text{H}_2\text{S}, \text{SO}_2, \text{COS} \)) before the methanation step is very critical because the nickel catalyst becomes poisoned by the adsorption of sulfur. In fact, Rostrup-Nielsen\(^1\) found that the poisoning of a nickel catalyst containing about 10wt.% Ni at 645°C occurred at about \( \frac{P_{\text{H}_2\text{S}}}{P_{\text{H}_2}} = 2 \times 10^{-6} \). Therefore, the synthesis gas is desulfurized before the methanation step. Each commercial coal gasification process has a different scheme for desulfurizing the
synthesis gas. As an example, the gas can be reacted with CaO to form CaS. The resulting CaS can then be disposed of or the CaO regenerated and the sulfur recovered.

A recent conference\(^2\) described various commercial processes for the gasification of coal as well as specific problems associated with the performance of alloys in various environments. Some of these problems include erosion (the mechanical removal of material), gaseous corrosion (the loss of material due to a chemical reaction with the gas) and fused-salt corrosion (attack of an alloy in the presence of a molten salt, e.g. Na\(_2\)CO\(_3\)). Since this investigation is concerned wholly with the gaseous corrosion of alloys in coal gasification-type atmospheres, the other types of alloy degradation, although equally important, will not be considered further.

Gasifier atmospheres are comprised of \(H_2, H_2O, CO, CO_2, CH_4, H_2S, NH_3,\) COS plus virtually any other molecules based on combinations of oxygen, hydrogen, carbon, sulfur or nitrogen. Thus, an alloy intended for coal gasification service will be exposed to gases that are potentially oxidizing, carburizing, sulfidizing or nitriding.

Thermodynamic calculations are useful for predicting whether an element or a compound of that element is in stable equilibrium with a gas. For example, consider a metal, M, in contact with an oxygen containing gas. Let us call the lowest oxide in the M-O system MO\(_y\). We can calculate the required oxygen partial pressure for the conversion of M to MO\(_y\) in the gas. For the reaction

\[
M + \frac{y}{2}O_2 = MO_y,
\]  

(3)
the equilibrium oxygen partial pressure is given by

\[ p_{O_2} = \left( \frac{a_{M_0V}}{a_M} \right)^2 \exp \left( \frac{2\Delta G_{M_0V}^0}{RT} \right) \]  

(4)

where \( a_{M_0V} \) is the activity of the oxide, \( a_M \) is the activity of the metal, \( \Delta G_{M_0V}^0 \) is the Gibbs energy of formation of \( M_0V \), \( R \) is the universal gas constant (8.314 joules/mole \( \cdot \) \( ^\circ \)K), and \( T \) is the absolute temperature (\( ^\circ \)K). For partial pressures lower than this value the metal will be stable in the gas, but for greater pressures, the oxide is the stable phase in that gas. In Eq. (4) if oxygen-saturated metal and metal-saturated oxide are chosen as the standard states, and we consider metal to be in equilibrium with the oxide then the activities of each are unity and, thus, the pre-exponential factor is unity.

In a complex coal gasification atmosphere, there exists a certain equilibrium oxygen partial pressure, sulfur partial pressure and activity of carbon in the gas. These parameters will determine the phase stabilities, i.e., whether the elemental form or a compound is stable, (Equations equivalent to Eq. (4) can be developed for the other oxidants as well). In gases containing more than one oxidant (e.g. C, S\textsubscript{2} and O\textsubscript{2}) there is a competition between C, S\textsubscript{2} and O\textsubscript{2} oxidants with regard to equilibrium phase stabilities. This concept will be discussed later.

In most, if not all, of the high temperature gaseous environments encountered in coal gasification, corrosion of engineering alloys will take place. This corrosion occurs by the chemical reaction between...
elements in the alloy and oxidants in the gas phase. The corrosion rate can be minimized, however, if a slow-growing scale forms rather than a fast-growing phase. Thermodynamic calculations can, in principle, be used to select a gas composition whereby a known slow-growing phase is in equilibrium with the gas, in order to minimize corrosion.

This investigation is based on the thermodynamic calculation of phase stabilities in atmospheres characteristic of coal gasification environments. Not only will we be concerned with phase stabilities in the gas but we shall also consider phase stabilities inside the alloy. Also, the conditions required for the formation of a continuous, compact, slow-growing corrosion product on the surface of the alloy will be described.
II. LITERATURE REVIEW

A. Thermodynamics and Diffusion in the Fe-Cr-C-O System

Very little work has been published regarding phase equilibria in quaternary systems, probably because of the difficulty in representing the four composition variables plus temperature and pressure on a two-dimensional diagram. Several variables can be held constant, however, thus reducing the number of dimensions needed to represent the phase equilibria graphically. But, a large number of such diagrams, and corresponding experiments, would then be needed to adequately describe the entire system. Some selected binary systems (Fe-Cr, Fe-C, Fe-O, Cr-C and Cr-O) and ternary systems (Fe-Cr-O, Fe-Cr-C, Fe-C-O and Cr-C-O) will be discussed here in order to develop reasonable predictions or explanations of phase stabilities in the Fe-Cr-C-O quaternary system.

1. The Fe-Cr System

The Fe-Cr phase diagram is shown in Fig. 1. This plot of temperature versus weight percent Cr shows a γ-loop whose maximum width occurs at about 12.7wt.% Cr. Any Fe-Cr alloy which has more than 12.7wt.% Cr will be ferritic (bcc) at all temperatures. Those solid alloys which have less than 12.7wt.% Cr change from the α-phase (bcc) to the γ-phase with increasing temperature. A change from totally
Figure 1. Fe-Cr phase diagram (from ref. 3).
bcc α-phase to totally fcc γ-phase occurs at a single temperature for only one alloy, a composition of about 7% Cr at 831°C, corresponding to the temperature minimum of the γ-loop. All other alloys with less than 12.7 wt.% Cr undergo a gradual change in equilibrium structure with increasing temperature over a range of temperature with a corresponding two-phase region of α and γ.

Mazandarany and Pehlke have determined the thermodynamic activity of chromium in solid Fe-Cr alloys from 900 to 1200°C. They used a solid electrolyte electrochemical technique which allows the system to be at equilibrium when the measurements are made. Reversible potential measurements were made using the oxygen concentration cell:

\[
\text{Cr, Cr}_2\text{O}_3 |\text{ThO}_2 - 8\text{mol pct } \text{Y}_2\text{O}_3 | \text{Cr(alloy), Cr}_2\text{O}_3
\]

with the net cell reaction,

\[
\text{Cr(oxygen saturated)} = \text{Cr(alloy)}
\]

(5)

With the restrictions of reversibility and constant temperature and pressure, the free energy change for reaction (5) is,

\[
\Delta G_{\text{Cr}} = \bar{G}_{\text{Cr}} - \bar{G}_{\text{Cr}^0} = -3EF = RT \ln a_{\text{Cr}}
\]

(6)

where \(E\) is the open-circuit cell potential in volts, \(F\) is Faraday's constant (96,483 joules/volt-equiv), \(R\) is the gas constant (8.314 joules/ equiv \(\cdot\) K), \(T\) is the absolute temperature (K), and \(a_{\text{Cr}}\) is the activity of Cr in the alloy. Since the anode of cell (I) requires the coexistence of Cr and \(\text{Cr}_2\text{O}_3\) to establish the reference oxygen partial pressure, the activity of chromium is referenced to a standard state.
of oxygen-saturated solid Cr.

The free energy change as a function of temperature for each of the Fe-Cr alloys studied by Mazandarany and Pehlke is reproduced in Table 1. The limiting Raoultian activity coefficients of Cr at high dilution were calculated to be 4.89, 3.99, 3.35 and 2.90 at 900, 1000, 1100 and 1200°C, respectively. The Fe-Cr system exhibits positive deviation from ideality over the entire range of composition for all of the temperatures investigated.

According to Peterson, most of the experimental evidence indicates that self-diffusion in fcc-iron occurs by a vacancy mechanism. At low temperatures single vacancies appear to be operative in bcc-iron, but at higher temperatures, a contribution from divacancies is suspected.

In dilute substitutional solid solutions where iron is the solvent, the diffusion mechanism for solute diffusion should be the same as for self-diffusion in iron. This, of course, could only be true if solutes diffuse independently. With increasing solute content, the diffusion mechanism could change due to solute-solute interactions.

Bowen and Leak have investigated solute diffusion in α and γ-iron using radiotracer techniques. They deposited Cr isotope on pure iron which had a grain size between 2 and 3 mm. The concentration profile was measured by successively sectioning layers and measuring the residual radioactivity of each new surface. The diffusivity of Cr in α-Fe is

\[ D_{\text{Cr}}^{\alpha-\text{Fe}} = 8.52 \exp \left( \frac{-250,622 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec} \] (7)
in the temperature range 797 - 877°C. The diffusivity of Cr in γ-Fe is

$$D_{Cr}^{\gamma-Fe} = 10.80 \exp \left( \frac{-291,625 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec} \quad (8)$$

in the temperature range 960 - 1396°C. They also measured the diffusivity of Cr in γ-Fe by a microprobe analysis technique. The result was close to that obtained by radio-tracers (Eq. 8) and is given by

$$D_{Cr}^{\gamma-Fe} = 4.08 \exp \left( \frac{-286,604 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec} \quad (9)$$

Wulf, McGirr and Wallwork\(^7\) have reviewed the interdiffusion coefficients in the Fe-Cr system at 1250 K as a function of chromium content. They give a plot of the data and an equation derived from a least-squares analysis of the data. This reviewer was unable to use the given equation to calculate the least-squares values and therefore suggests that one use the plotted line rather than the equation. The plot is reproduced as Fig. 2.

2. The Fe-C System

The thermodynamics of the Fe-C system have been studied extensively. The Fe-C system exhibits no equilibrium carbide phase. However, there are several metastable carbides that form upon cooling or upon tempering of alloy steels. The most notable metastable carbide, Fe\(_3\)C, forms upon cooling in binary Fe-C alloys. The kinetics of the transformation of Fe\(_3\)C to iron and graphite are so sluggish that for practical purposes Fe\(_3\)C can be considered a "stable" phase. The Fe-Fe\(_3\)C phase diagram\(^8\), Fig. 3, shows the large solubility of carbon in
Table 1. Partial molar free energy of chromium for various Fe-Cr alloys as a function of temperature (from ref. 4).

<table>
<thead>
<tr>
<th>(N_{\text{Cr}})</th>
<th>(\Delta G_{\text{Cr}}) (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.039</td>
<td>4530-7.94T</td>
</tr>
<tr>
<td>0.069</td>
<td>4020-6.19T</td>
</tr>
<tr>
<td>0.190</td>
<td>4180-5.49T</td>
</tr>
<tr>
<td>0.317</td>
<td>2880-3.62T</td>
</tr>
<tr>
<td>0.478</td>
<td>1820-2.27T</td>
</tr>
</tbody>
</table>
Figure 2. Interdiffusion coefficient in the Fe-Cr system at 1250 K (from ref. 7).
Figure 3. Fe-Fe₃C phase diagram (from ref. 8).
the austenite phase. It also shows that carbon raises the austenite to
delta-ferrite transformation temperature while lowering the temperature
of the ferrite to austenite transformation. Thus, carbon is a potent
austenite stabilizer.

Ban-ya, Elliott and Chipman\(^9\) have studied the thermodynamics of
carbon in austenite in the temperature range 900 - 1400\(^\circ\)C. The activ-
ity of carbon in austenite at various carbon contents was determined
by equilibration in CO/CO\(_2\) gas mixtures. The equilibrium wt.% C in the
alloy was measured at various activities of carbon in the gas. Their
expression for the activity of carbon in austenite relative to graphite
saturation as the standard state is

\[
\log a_C = \frac{3770}{T} + 2.72 \log T - 10.525 + \frac{3860}{T} Y_C + \log Z_C \quad (10)
\]

where \(T\) is the absolute temperature

\[
Y_C = \frac{n_C}{n_{Fe}} \quad (11)
\]

\[
Z = Y / 1 - Y_C \quad (12)
\]

and \(n_c\) and \(n_{Fe}\) are the number of atoms of carbon and iron, respec-
tively. The more conventional definition of atom fraction,

\[
N_C = \frac{n_C}{n_{Fe} + n_C} \quad (13)
\]

can be used instead of \(Y_C\) in Eq. (10) by solving both Eqs. (11) and
(13) for \(n_C\) and then setting them equal. The conversion becomes
The solubility of graphite in austenite can be obtained by substituting \( \log a_C = 0 \) in Eq. (10) and solving for \( Y_C \) or \( N_C \). Likewise, isoactivity curves for carbon in austenite can be calculated. These are reproduced in Fig. 4.

The free energy change for the solution of carbon from its standard state of graphite to a standard state based on an infinitely dilute solution of carbon in \( \gamma \)-Fe is,

\[
C(\text{gr}) = C(\text{in } \gamma \text{-Fe}) ; \\
\Delta G^0 = 72,174 + 52.05 T \log T - 201.46 T \text{ J}
\]  

(15)

Ban-ya, Elliott and Chipman also have combined their data with others to obtain the standard free energy of formation of \( \text{Fe}_3\text{C} \) between 1000 and 1400 K. No attempt was made to fit the non-linear data to an equation, but a plot of \( \Delta G^0 \) versus temperature is given in their paper.

Harvey\(^{10}\) has fit Darken and Gurry's\(^{11}\) tabulated data for the standard free energy of formation of \( \text{Fe}_3\text{C} \) from saturated austenite to an equation. For the reaction

\[
\text{Fe}_3\text{C} + \text{CO}_2 = 3\text{Fe} + 2\text{CO}
\]

(16)

the equation for the logarithm of the equilibrium constant is,

\[
\log \frac{P_{\text{CO}}}{P_{\text{CO}_2}} = \frac{-8328}{T} + 8.272 + 3.06 \times 10^{-4} T
\]  

(17)

in the temperature range 1000 - 1300 K. In the temperature range
Figure 4. Isoactivity curves for carbon in austenite (from ref. 9).
190 - 840°C, Kubaschewski and Evans\textsuperscript{12} give

\[ \Delta G^o = 26,694 - 24.77T \text{ J} \]  \hspace{1cm} (18)

for the reaction

\[ \text{Fe} + 3\text{C(gr)} = \text{Fe}_3\text{C.} \]  \hspace{1cm} (19)

Smith\textsuperscript{14} reported the diffusivity of carbon in bcc-iron as a function of carbon content at 851°C. The diffusivity varied from \(0.41 \times 10^{-7}\) to \(1.04 \times 10^{-7}\) cm\(^2\)/sec for carbon contents ranging from 0.02 to 0.07 g/cm\(^3\), respectively. Beshers\textsuperscript{13} reviewed the diffusivity of carbon in \(\alpha\)-Fe and his Fig. 4 is reproduced here as Fig. 5.

Wells, Batz and Mehl\textsuperscript{15} determined the diffusivity of carbon in austenite as a function of carbon content. The two most dilute carbon contents studied are given here. For 0.5 atomic percent carbon,

\[ D_{C}^{Y-\text{Fe}} = 0.41 \exp \left( \frac{-151,670 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec} \]  \hspace{1cm} (20)

while for 1.0 atomic percent carbon,

\[ D_{C}^{Y-\text{Fe}} = 0.37 \exp \left( \frac{-149,787 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec} \]  \hspace{1cm} (21)

in the temperature range 1100 - 1600 K.

Smith\textsuperscript{14} also determined the diffusivity of carbon in austenite at 1000°C for carbon contents between 0.01 g/cm\(^3\) and 0.10 g/cm\(^3\) in 0.01 g/cm\(^3\) increments. At a carbon content of 0.01 g/cm\(^3\),

\[ D_{C}^{Y-\text{Fe}} = 2.54 \times 10^{-7} \text{ cm}^2/\text{sec}, \]  \hspace{1cm} (22)
Figure 5. Diffusivity of carbon in α-Fe (from ref. 13).
while at 0.10 g/cm$^3$,

$$D_C^{Y-Fe} = 7.65 \times 10^{-7} \text{ cm}^2/\text{sec}.$$ (23)

The diffusion of carbon in iron occurs by an interstitial mechanism with carbon jumping from one octahedral site to another in bcc-iron$^{13}$.

3. The Fe-O System

There are three oxides of iron, Fe$_x$O (wüstite), Fe$_3$O$_4$ (magnetite) and Fe$_2$O$_3$ (hematite). Since all gas compositions in this study are selected so that iron remains noble with respect to oxide formation, the free energy of formation of the lowest oxide of iron, wüstite, will be the only one considered here.

Charette and Flenga$^{16}$ determined the standard free energy of formation of Fe$_x$O by using the cell,

$$\text{M,M}0 | \text{CaO} - \text{ZrO}_2 | \text{Me,MeO} \quad \text{(II)}$$

The reference metal/metal oxide mixture was Ni/NiO. They selected this mixture because their measurement of the free energy of formation of NiO (with pure O$_2$ as a reference) was very close to published literature values. For the reaction,

$$\text{Fe} + \text{NiO} = \text{FeO} + \text{Ni} \quad \text{(24)}$$

the standard Gibbs energy change is

$$\Delta G^0 = -29,740 - 20.04T \text{ J} \quad \text{(25)}$$
in the temperature range 903 - 1540 K. Their expression for the standard Gibbs energy of formation of nickel oxide is,

\[ \Delta G^0 = -233,651 + 84.89T \text{ J/mol NiO} \]  

in the temperature range 911 - 1376 K. Combining Eqs. (25) and (26) one obtains the standard Gibbs energy of formation of \( \text{Fe}_x\text{O} \). For the reaction

\[ x\text{Fe} + \frac{1}{2}\text{O}_2 = \text{Fe}_x\text{O} \]  

\[ \Delta G^0 = -263,391 + 64.81T \text{ J} \]  

where the standard state for iron is oxygen-saturated iron and the standard state for wüstite is iron-saturated wüstite.

The FeO - Fe\(_2\)O\(_3\) phase diagram\(^\text{17}\) is shown in Fig. 6. Oxygen iso-bars are superimposed which show the oxygen partial pressures required for the coexistence of oxygen-saturated iron and wüstite for various temperatures. Figure 3 also shows that wüstite is not a stoichiometric oxide but is highly metal deficient.

Swisher and Turkdogan\(^\text{18}\) have reported on the solubility, permeability and diffusivity of oxygen in solid iron. The oxygen solubility was determined by equilibrating samples in \( \text{H}_2/\text{H}_2\text{O} \) gas mixtures. After equilibration, the oxygen content was obtained by vacuum fusion. The permeability of oxygen was obtained by internal oxidation of Fe - 0.1% Al alloys and measurement of the depth of penetration. For the following reaction,
Figure 6. FeO-Fe₂O₃ phase diagram (from ref. 17).
the Gibbs energy change for bcc-iron is

\[ \Delta G^0 = -155,603 + 42.68T \text{ J/g-atom O} \]  

and for fcc-iron

\[ \Delta G^0 = -175,142 + 60.50T \text{ J/g-atom O} \]  

The diffusivity of oxygen in \( \alpha \)-Fe is approximately given by

\[ \log D^{\alpha-Fe}_O \text{ (cm}^2/\text{sec)} = -\frac{5100}{T} - 1.43 \]  

while in \( \gamma \)-Fe it is

\[ \log D^{\gamma-Fe}_O \text{ (cm}^2/\text{sec)} = -\frac{8820}{T} + 0.76 \]  

The solubility and diffusivity of oxygen in \( \alpha \)-Fe are termed approximate by Swisher and Turkdogan. These data for \( \alpha \)-Fe were extrapolated from the data obtained for \( \delta \)-Fe. A single solubility value measured in \( \alpha \)-Fe was close to the extrapolated value. At 950°C the oxygen solubility is about 2 - 3 ppm in \( \gamma \)-Fe and it is about 2 - 3 ppm at 881°C in \( \alpha \)-Fe.

4. The Cr-C System

Three carbides of chromium have been reported as shown by the Cr-C phase diagram\(^3\) in Fig.7. Beginning with the lowest carbide, they are \( \text{Cr}_23\text{C}_6 \) (\( \beta \)), \( \text{Cr}_7\text{C}_3 \) (\( \gamma \)) and \( \text{Cr}_3\text{C}_2 \) (\( \delta \)).
Figure 7. Cr-C phase diagram (from ref. 3).
Kulkarni and Worrell\textsuperscript{19} have measured and reviewed the free energy of formation of the chromium carbides. For the reaction

\[ 23\text{Cr} + 6\text{C} = \text{Cr}_{23}\text{C}_6, \]  

the Gibbs energy change is

\[ \Delta G^\circ = -322,168 - 75.6T \text{ J} \]  

in the temperature range 1150 - 1300 K. For the reaction

\[ 7\text{Cr} + 3\text{C} = \text{Cr}_7\text{C}_3 \]  

the Gibbs energy change is

\[ \Delta G^\circ = -147,277 - 36.4T \text{ J} \]  

in the temperature range 1100 to 1720 K. Finally, for the reaction

\[ 3\text{Cr} + 2\text{C} = \text{Cr}_3\text{C}_2 \]  

the Gibbs energy change is

\[ \Delta G^\circ = -68,618 - 18.4T \text{ J} \]  

in the temperature range 1300 to 1500 K.

In addition, Kulkarni and Worrell\textsuperscript{19} reviewed previous investigations for the Gibbs energy of formation of the carbides. There are large variations as well as large uncertainties (±84 kJ) in some cases. For example, Kubaschewski and Evans\textsuperscript{12} report the standard Gibbs energy of formation of \text{Cr}_{23}\text{C}_6 as
\[ \Delta G^\circ = -41,086 - 38.66 \text{ J/mole Cr}_2\text{C}_6, \]  

(40)

the standard free energy of formation of Cr\textsuperscript{7}C\textsubscript{3} as

\[ \Delta G^\circ = -174,510 - 25.77 \text{ J/mole Cr}_7\text{C}_3 \]  

(41)

and the standard free energy of formation of Cr\textsubscript{3}C\textsubscript{2} as

\[ \Delta G^\circ = -84,354 - 11.63T \text{ J/mole Cr}_3\text{C}_2. \]  

(42)

Recently, Dawson and Sale\textsuperscript{20} used combustion calorimetry to determine the enthalpies of formation of the chromium carbides at 298 K. For Cr\textsubscript{23}C\textsubscript{6}, Kulkarni and Worrell\textsuperscript{13} obtained -342.7 kJ/mole while Dawson and Sale measured -295.0 kJ/mole. The agreement was better for Cr\textsubscript{7}C\textsubscript{3}: -153.6 kJ/mole by Kulkarni and Worrell versus -142.9 kJ/mole by Dawson and Sale. Thus, it is apparent that large differences exist in the values for the standard Gibbs energy of formation of the carbides.

5. The Cr-O System

There is only one reported oxide of chromium, Cr\textsubscript{2}O\textsubscript{3}. Jeannin, Mannerskantz and Richardson\textsuperscript{21} determined the standard Gibbs energy of formation of Cr\textsubscript{2}O\textsubscript{3}. For the reaction

\[ 2\text{Cr} + \frac{2}{3} \text{O}_2 = \text{Cr}_2\text{O}_3, \]  

(43)

the Gibbs energy change is

\[ \Delta G^\circ = -1,115,873 + 251.0T \text{ J} \]  

(44)

in the temperature range 1300 - 1600 K.
Pugliese and Fitterer\textsuperscript{22} also measured the standard Gibbs energy of formation of \( \text{Cr}_2\text{O}_3 \). They averaged their data with those of Tretjakov and Schmalzried\textsuperscript{23} to obtain the equation

\[
\Delta G^\circ = -1,102,860 + 249.4T \text{ J}
\]  

between 800 and 1200°C.

Kubaschewski and Evans\textsuperscript{12} report for reaction (43),

\[
\Delta G^\circ = -1,120,266 + 259.8T \text{ J}
\]  

in the temperature range 298 - 2100 K.

Thus, all of the measurements are close and consistent. The entropy terms are very close but the enthalpy of formation differs slightly with each investigation.

\( \text{Cr}_2\text{O}_3 \) exhibits the corundum-type crystal lattice. The transport properties and defect structure of \( \text{Cr}_2\text{O}_3 \) formed on Fe-Cr alloys during oxidation have been the subject of a review article by Hay, Hicks and Holmes\textsuperscript{24}. They point out that various workers have found that \( \text{Cr}_2\text{O}_3 \) exhibits p-type electrical behavior which indicates a metal-deficient structure. However, experiments in which the oxygen pressure has been varied gave results which cannot be related to any simple defect model. Most workers conclude that Cr vacancies predominate.

Measurements of the tracer diffusion coefficients of chromium, iron and oxygen in \( \text{Cr}_2\text{O}_3 \) are summarized in Fig. 8 as taken from reference 24. Note that the cation is much faster than the anion over the entire temperature range.
Figure 8. Tracer diffusion coefficients in Cr$_2$O$_3$ (from ref. 24).
Caplan and Sproule\textsuperscript{25} have oxidized pure Cr in oxygen between 980 and 1200°C. Some of the results are significant with regard to the transport processes in Cr\textsubscript{2}O\textsubscript{3}. On etched Cr, the oxide layer grows rapidly on some grains and more slowly on others. The thick oxide is fine-grained and develops compressive stress while the thin oxide is monocry stalline and relatively free of stress during growth. Their interpretation is that the single crystal layer grows solely by cation diffusion outward, since no stress develops, with new oxide forming on the outer surface. The polycrystalline scale grows partly by anion transport inward with new oxide forming within the oxide layer causing compressive stresses. Since compressive stresses arise from anion transport and no compressive stress is observed in the cases where oxide grain boundaries do not exist, it follows that the anion transport must occur along oxide grain boundaries. Caplan and Sproule also oxidized an Fe-26Cr alloy and found that the scale that forms is fine-grained and develops compressive stress. Thus, for this alloy, anion transport inward along oxide grain boundaries must occur in conjunction with lattice diffusion of Cr outward through the Cr\textsubscript{2}O\textsubscript{3}.

6. The Fe-Cr-O System

Pelton and Schmalzried\textsuperscript{26} have recently discussed the problems associated with graphically representing phase equilibria in multi-component systems. Different types of diagrams were presented and discussed. One type of diagram uses one generalized thermodynamic potential function and a ratio of conjugate extensive variables as coordinates. In the case of binary alloy/oxygen equilibria, plots of
log $P_{O_2}$ versus the mole fraction of one component are extremely useful. The plot from Pelton and Schmalzried for the Fe-Cr-O system at 1573 K is reproduced as Fig. 9. The phase transformation from $\gamma$ to $\alpha$ occurs at 1573 K over a range of chromium contents which represents a two-phase region. This factor was not taken into account in Pelton and Schmalzried's diagram. They also point out that Birchenall has published a similar diagram which may be more correct because of the use of better activity data. This diagram is reproduced in Fig. 10, which incorporates the $\alpha$ and $\gamma$ alloy modifications, but inverts the ordinate.

Ikeda and Nii studied the thermodynamic stability of oxides formed on Fe-Cr alloys in $H_2/H_2O$ gases at 900°C. The reaction times ranged from 6 minutes to 2 hours. They used a log $P_{O_2}$ versus mole fraction chromium diagram to interpret their experimental electron diffraction results. They concluded that the spinel, $FeCr_2O_4$, forms by the reaction,

$$4Fe + Cr + O_2 = 4FeCr_2O_4 . \quad (47)$$

Ikeda and Nii rejected the mechanism

$$2Fe + 2Cr_2O_3 + O_2 = 2FeCr_2O_4 \quad (48)$$

on the basis of a comparison with their observed experimental results and the phase boundaries calculated from both reactions (47) and (48). Spinel was detected at very much lower oxygen activities than those calculated from reaction (48) but higher than those calculated from reaction (47). The difference in oxygen activities calculated for the
Figure 9. Dissociation pressure diagram for the Fe-Cr-O system at 1573 K (from ref. 26).
Figure 10. Dissociation pressure diagram for the Fe-Cr-O system at 1200°C (from ref. 27).
equilibrium between alloy and spinel, reaction (47), and chromium oxide, iron and spinel, reaction (48), amounts to about three orders of magnitude. They also observed spinel formation once at a slightly lower oxygen partial pressure than that predicted from known thermodynamic data for reaction (47). This led them to conclude that spinel could initially form where it is thermodynamically unstable and then decompose to the stable oxide, Cr₂O₃, with longer oxidation times. It seems more likely that the thermodynamic data used for construction of the equilibrium diagram need to be checked.

Tretjakov and Schmalzried\textsuperscript{23} have measured the free energy of formation of FeCr₂O₄ by using the oxygen concentration cell,

\[
\text{FeO,Cr,FeCr}_2\text{O}_4 \mid \text{ZrO}_2 + \text{CaO} \mid \text{O}_2(\text{air}) \tag{III}
\]

and measuring the open-circuit potential at various temperatures. For the reaction

\[
\text{Fe}_x\text{O} + \text{Cr}_2\text{O}_3 = \text{FeCr}_2\text{O}_4 \tag{49}
\]

the free energy change is

\[
\Delta G^0 = -57,530 + 16.44T \text{ J} \tag{50}
\]

in the temperature range 1000 - 1500 K. Combining Eqs. (28) and (50) one obtains for the reaction

\[
\text{Fe} + \frac{3}{2}\text{O}_2 + \text{Cr}_2\text{O}_3 = \text{FeCr}_2\text{O}_4 \tag{51}
\]

the standard free energy
Kubaschewski and Evans$^{12}$ also report on the standard free energy of formation of iron chromite. For reaction (51),

$$\Delta G^o = -320,921 + 81.25T \ J \ (52)$$

in the temperature range 1173 - 1400 K.

7. The Fe-Cr-C System

Bungardt, Kunze and Horn$^{29}$ have done extensive work on phase stabilities in the Fe-Cr-C system. They summarized their results with several types of diagrams. Three isothermal sections of the ternary system, i.e., chromium content versus carbon content, at 850, 1000 and 1150\degree C, are shown in Fig. 11. They also give pseudobinary diagrams for constant carbon contents (0.05\%, 0.1\%, 0.2\%, 0.4\%, 1.0\% and 2\% C). Finally, plots of temperature vs. carbon content for various chromium contents are given and are reproduced here as Figs. 12 through 17. In all the plots taken from Bungardt, Kunze and Horn, $K_C$ represents Fe$_3$C, $K_1$ represents the carbide based on Cr$_{23}C_6$ and $K_2$ represents the carbide based on Cr$_7C_3$. The lowest carbide of chromium, Cr$_{23}C_6$, in fact, dissolves substantial amounts of iron. Thus, it can be represented by (Fe,Cr)$_{23}C_6$ or, more simply, $M_{23}C_6$. Bungardt, Kunze and Horn$^{29}$ found in their study that the $M_{23}C_6$ compound could be represented by the formula Fe$_8$Cr$_{15}C_6$. Likewise, Cr$_7C_3$ can dissolve an appreciable amount of Fe so that is is often labelled as $M_{7}C_3$. These investigators found that the composition of this carbide varied from Fe$_2$Cr$_5C_3$ to Fe$_4$Cr$_3C_3$. 
Figure 11. Isothermal sections at 850, 1000 and 1150°C for the Fe-Cr-C system. 

\[ K_C = M_2C, \ K_1 = M_{23}C_6 \ \text{and} \ K_2 = M_7C_3 \] (from ref. 29).
Figure 12. Temperature vs. carbon content for the pseudobinary Fe-2\%Cr-carbon system. $K_C = M_3C$, $K_1 = M_{23}C_6$, $K_2 = M_7C_3$ (from ref. 29).

Figure 13. Temperature vs. carbon content for the pseudobinary Fe-5\%Cr-carbon system. $K_C = M_3C$, $K_1 = M_{23}C_6$, $K_2 = M_7C_3$ (from ref. 29).
Figure 14. Temperature vs. carbon content for the pseudobinary Fe-8%Cr-carbon system. $K_C = M_3C$, $K_1 = M_{23}C_6$, $K_2 = M_7C_3$ (from ref. 29).

Figure 15. Temperature vs. carbon content for the pseudobinary Fe-13%Cr-carbon system. $K_C = M_3C$, $K_1 = M_{23}C_6$, $K_2 = M_7C_3$ (from ref. 29).
Figure 16. Temperature vs. carbon content for the pseudobinary Fe-17%Cr - carbon system. \( K_C = M_3C \), \( K_1 = M_{23}C_6 \), \( K_2 = M_7C_3 \) (from ref. 29).

Figure 17. Temperature vs. carbon content for the pseudobinary Fe-25%Cr - carbon system. \( K_C = M_3C \), \( K_1 = M_{23}C_6 \), \( K_2 = M_7C_3 \) (from ref. 29).
More recently, Wada, Wada, Elliott and Chipman\textsuperscript{30} determined the activity of carbon and the solubility of carbides in the Fe-Cr-C system. The iron-rich corner of the ternary section at 1000°C is reproduced in Fig. 18. This diagram predicts the equilibrium carbide phase formed when a particular Fe-Cr alloy is reacted in a gas with a certain activity of carbon. For example, alloys with chromium contents greater than about 15 at.% would be expected to form M\textsubscript{23}C\textsubscript{6} at the lowest carbon activities, while more dilute alloys would be expected to form M\textsubscript{7}C\textsubscript{3} at higher carbon activities. Wada, et al, point out that by extrapolating two of the tie-lines in the $\gamma + M\textsubscript{7}C\textsubscript{3}$ field to the theoretical carbon composition of $M\textsubscript{7}C\textsubscript{3}$, $\gamma_C = 0.43$ ($\gamma_C = n_C/n_{Cr} + n_{Fe}$), one obtains $\gamma_{Cr} = 0.49$ ($\gamma_{Cr} = n_{Cr}/n_{Cr} + n_{Fe}$). This indicates that iron and chromium have approximately equal concentrations in this carbide, which is in the range reported by Bungardt, Kunze and Horn\textsuperscript{29}.

One can define the Raoultian activity coefficient, $\gamma_i$, as the ratio of the activity, $a_i$, to the mole fraction, $N_i$,

$$
\gamma_i = \frac{a_i}{N_i}.
$$

(54)

Then, following Wagner\textsuperscript{31}, by expanding the logarithm of the activity coefficient with a Taylor series and neglecting second and higher order derivatives, one obtains

$$
\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=1}^{n} N_j \left( \frac{\partial \ln \gamma_i}{\partial N_j} \right) N_{\text{solute}+1}
$$

(55)

where the subscript $i$ represents a particular solute in the solvent, $n$ is the number of solutes, $\gamma_i^0$ is the limiting Raoultian activity
Figure 18. Isothermal section at 1000°C for the Fe-Cr-C system (from ref. 30).
coefficient at infinite dilution, and \( N_j \) is the mole fraction of solute \( j \) present. The limiting slopes of \( \ln \gamma_i \) versus \( N_j \) plots (Eq. 55) are termed the activity coefficient interaction parameters and are denoted by the symbol \( \epsilon_j^i \). Thus, Eq. (55) becomes

\[
\ln \gamma_i = \ln \gamma_i^0 + \sum_{j=1}^{N} N_j \epsilon_j^i
\]

Wagner\(^{31}\) has also shown that the following reciprocity relationship exists,

\[
\epsilon_j^i = \epsilon_i^j
\]

Wada, Wada, Elliott and Chipman\(^{30}\) report the activity coefficient of carbon in the ternary Fe-Cr-C system as

\[
\ln \gamma_C = \frac{2300}{T} - 0.92 + \left( \frac{3680}{T} \right) Y_C - \left( \frac{9500}{T} - 3.05 \right) Y_{Cr}
\]

where \( Y \) is defined by

\[
Y = \frac{n_c}{n_{Fe} + n_{Cr}}
\]

and

\[
Y_{Cr} = \frac{n_{Cr}}{n_{Fe} + n_{Cr}}
\]

The range of application of Eq. (58) is 0 to 12wt.% Cr, 0 to 1wt.% carbon and the temperature range 850 - 1200°C. The interaction parameters between 850 and 1200°C were fit to the equation\(^{30},\)
Woodyatt and Krauss\textsuperscript{32} studied the Fe-Cr-C system at 870\textdegree{}C. They, as the others\textsuperscript{29,30}, investigated the iron-rich corner of the ternary section but, in addition, also reported on the high carbon and high chromium regions. They reported a maximum solubility for iron in M\textsubscript{23}C\textsubscript{6} as 42.8wt.\% and the maximum solubility for iron in M\textsubscript{7}C\textsubscript{3} as 58.2wt.\%. Both M\textsubscript{23}C\textsubscript{6} and M\textsubscript{7}C\textsubscript{3} were found to be stoichiometric with respect to carbon, while previous investigations\textsuperscript{33} showed M\textsubscript{3}C and M\textsubscript{7}C\textsubscript{3} forming a pseudobinary system.

\section{The Fe-C-O System}

This section will be devoted entirely to the composition of iron-carbon alloys in carbon monoxide/carbon dioxide gas mixtures. The type of diagram used to represent phase stabilities in metal-carbon-oxygen systems was pioneered by Pourbaix and Rorive-Boute\textsuperscript{34}. In their early work, the Zn-C-O system was represented by a plot of log $P_{O_2}$ vs. \(1/T\). Another way of representing phase stabilities uses the thermodynamic potential of each component in the gas phase as coordinates with the temperature held constant. Several examples of these types of diagrams were presented by Jansson and Gulbransen\textsuperscript{35}.

The stability of iron in CO/CO\textsubscript{2} gases\textsuperscript{36} is shown in Fig. 19. The percent carbon monoxide is plotted vs. temperature. The Boudouard or "sooting" reaction, i.e.,

\begin{equation}
2\text{CO} \rightarrow \text{C(gr)} + \text{CO}_2
\end{equation}
Figure 19. Phase stability diagram for the Fe-C-O system (from ref. 36).
is plotted for both 1 and 100 atmospheres total pressure. At some

temperature, if a gas mixture is selected to the left of the Boudouard
line, carbon monoxide should decompose according to reaction (62) to
form graphite and carbon dioxide. Also, if a gas mixture with 30%
carbon monoxide, \( P_{CO}/(P_{CO} + P_{CO_2}) = 0.3 \), is passed through a furnace
with a temperature gradient, at one atmosphere total pressure, the gas
mixture could be unstable at temperatures below about 600°C. Thus, in
the cooler portions of a furnace, sooting could occur if the kinetics
were favorable. Usually, the Boudouard decomposition of carbon
monoxide requires a catalyst. Also, in Fig. 19, a dashed line is
shown which represents the equilibrium,

\[
3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2
\]

at one atmosphere total pressure. Since this line is to the left of
the Boudouard line, \( \text{Fe}_3\text{C} \) cannot form isothermally in a \( \text{CO}/\text{CO}_2 \) gas
mixture. However, \( \text{Fe}_3\text{C} \) could form upon cooling if the carbon activity
were to become greater than that required for formation at a lower
temperature.

9. The Cr-C-O System

Chromium-carbon-oxygen stability plots calculated by this author
comprise an important part of this dissertation. Different types will
be presented and discussed later. The stability diagram for the pure
chromium-carbon-oxygen system published by Harvey is reproduced as
Fig. 20. Generally, in later sections, the diagrams are presented for
reduced activities of chromium in alloys. In some cases, the reduced
Figure 20. Isothermal phase stability diagram at 1200 K for the Cr-C-O system (from ref. 10).
activity of chromium causes the lowest chromium carbide, \( \text{Cr}_2\text{C}_6 \), to become destabilized in favor of the next lower carbide, \( \text{Cr}_7\text{C}_3 \), or even the highest carbide \( \text{Cr}_3\text{C}_2 \).

**B. Thermodynamics and Diffusion in the Ni-Cr-C-O System**

As in the case of the Fe-Cr-C-O system, this system will be considered as selected binary and ternary systems due to the lack of information on the quaternary system. Some of the possible combinations have been discussed in the previous section and, therefore, will not be repeated here. The Ni-C-O system is of little interest because of the lack of a stable carbide. This reviewer also found no previous work on the Ni-Cr-C system. Possibly, because of the low solubility for Ni in the chromium carbides (compared to iron), an isothermal ternary section would be of little interest.

**1. The Ni-Cr System**

The Ni-Cr phase diagram\(^3\) is shown in Fig. 21. Although it appears that the solubility of Cr in Ni is not well known, all of the alloys studied at 850 and 950\(^\circ\)C in this investigation (less than 21.4 weight percent Cr) should be single-phase austenitic.

Mazandarany and Pehlke\(^4\) published activity data for Cr in solid Ni-Cr alloys. They used cell (I) and Eq. (6) to calculate the activity of chromium from open-circuit cell potentials. The Gibbs energy change as a function of temperature for each of the Ni-Cr alloys studied are reproduced in Table 2. The system exhibits negative
Figure 21. Ni-Cr phase diagram (from ref. 3).
Table 2. Partial molar free energy of chromium for various Ni-Cr alloys as a function of temperature (from ref. 4).

<table>
<thead>
<tr>
<th>N_{Cr}</th>
<th>\Delta G_{Cr} (cal)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.115</td>
<td>1420-6.04T</td>
</tr>
<tr>
<td>0.160</td>
<td>1340-5.04T</td>
</tr>
<tr>
<td>0.210</td>
<td>2200-4.81T</td>
</tr>
<tr>
<td>0.265</td>
<td>3450-4.81T</td>
</tr>
<tr>
<td>0.390</td>
<td>3340-3.22T</td>
</tr>
</tbody>
</table>
deviations from ideality for alloys dilute in chromium and then changes to positive deviation with increasing chromium content. The Raoultian activity coefficients of chromium at infinite dilution in Ni are all 0.47 in the temperature range 1000 – 1300°C.

The tracer diffusion coefficient of Cr in a Ni – 36%Cr alloy in the temperature range 900 – 1250°C is reported to be

\[ D_{Cr} = 3.92 \exp\left(\frac{-220,915 \text{ J/mol}}{RT}\right) \text{ cm}^2/\text{sec} \quad (64) \]

Seltzer and Wilcox also used radioactive tracers to determine the diffusivity of Cr in a Ni – 21.4%Cr alloy in the temperature range 1038 – 1200°C. They report

\[ D_{Cr} = 2.95 \exp\left(\frac{-192,882 \text{ J/mol}}{RT}\right) \text{ cm}^2/\text{sec} \quad (65) \]

They also pointed out that the diffusivity increased as the grain size decreased. Seltzer and Wilcox suspect that some grain boundary contribution to diffusion is included in the above equation since the grain size was about 0.00075 cm.

2. The Ni-O System

According to the Ni-O phase diagram shown in Fig. 22, there is only one oxide of nickel. The Gibbs energy of formation of nickel oxide has already been discussed and is given by Eq. (26). According to Fig. 22, nickel exhibits a retrograde solubility for oxygen. The reported solubility of oxygen in nickel varies from 0.012 wt.% at 1200°C to 0.020 wt.% at 600°C.
Kerr and Rapp\textsuperscript{39} used the cell

\begin{equation}
\text{Co,CoO} \mid \text{ZrO}_2 + \text{Y}_2\text{O}_3 \mid \text{Ni} \mid \text{ZrO}_2 + \text{Y}_2\text{O}_3 \mid \text{Co,CoO}
\end{equation}

(IV)

to determine the solubility and diffusivity of oxygen in nickel between 1000 and 1250\textdegree C. They applied voltages and measured the current as a function of time to arrive at diffusivity values (assumed to be concentration independent) and then the changes in oxygen content with activity changes. They found that the diffusivity of oxygen in solid nickel can be represented by

\begin{equation}
D_{Ni}^{Ni} = 2.06 \exp \left( \frac{-179,912 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec} \quad (66)
\end{equation}

Also, the solubility of oxygen in nickel was fit by the equation

\begin{equation}
N_{0}^{Ni}(\text{Ni-NiO}) = 10.2 \exp \left( \frac{-137,235 \text{ J/mol}}{RT} \right) \quad (67)
\end{equation}

Kerr and Rapp also found experimentally that the solution of oxygen into nickel, as a function of oxygen activity, followed a Langmuir absorption (three-dimensional dissolution) isotherm. A site-blocking model was developed to account for this in which an oxygen atom in solution blocks some of the available sites for other oxygen atoms. This site blocking occurs because of the high strain energy or chemical (electronic) repulsions imposed on the lattice by the oxygen atoms on interstitial sites.

Their measurements for the oxygen solubility differ greatly from those published previously. Alcock and Brown\textsuperscript{40} used a thermogravimetric technique to measure the oxygen solubility in nickel. They
obtained a retrograde solubility of oxygen in nickel. The effect of carbon from the CO/CO$_2$ gas may have influenced their measured solubility. Even if the carbon activity was low enough so that the weight gain due to carbon solution was minimal, carbon may have exerted an influence by a thermodynamic interaction with oxygen. Such an interaction could change the activity coefficient of oxygen in nickel which would change the oxygen content for a constant oxygen activity. Or, for a measured weight gain, i.e., oxygen content, the oxygen activity in the alloy could be different from that in the gas.

3. The Ni-C System

Wada, Wada, Elliott and Chipman$^{41}$ have measured the solubility of graphite in nickel. They found that the solubility, expressed in weight percent, varied non-linearly with respect to temperature from 0.0088 at 500$^\circ$C to 0.396 at 1200$^\circ$C.

The diffusivity of carbon in nickel at 1000$^\circ$C has been reported$^{42}$ as

$$D_{Ni}^{C}(1000^\circ C) = 2.4 \times 10^{-7} \text{ cm}^2/\text{sec}$$

(68)

with an activation energy of 161,084 J/mol. This reviewer used these two values to arrive at the following Arrhenius equation

$$D_{Ni}^{C} = 0.978 \exp \left( \frac{-161,084 \text{ J/mol}}{RT} \right) \text{ cm}^2/\text{sec}$$

(69)

Equation (69) should only be used near 1000$^\circ$C, and with caution, since it is based upon a single datum point.
The Ni-C phase diagram is given as Fig. 23.

4. The Ni-Cr-O System

The Ni-Cr-O system has been studied by Davies and Smeltzer from 900 - 1100°C. They determined the oxygen partial pressures required for equilibrium between various alloys and Cr₂O₃. A summary of their results is given as Fig. 24, in which the logarithm of the equilibrium oxygen pressure is plotted vs. the atom fraction of nickel. Their schematic representation of the equilibrium oxygen pressure diagram for the Ni-Cr-O system and an isothermal ternary section for temperatures between 900 and 1100°C is given in Fig. 25. These authors found that the maximum solubility of nickel in chromium oxide was 0.5 weight percent.

C. Oxidation and Carburization

1. External Scaling

In 1933, Carl Wagner put forth his now-famous theory of the parabolic scaling of a metal. This theory considered the scaling of pure metals, and explained the observed phenomenon that the oxide thickness on the surface of the metal increased parabolically with time, i.e., the scale thickening rate is inversely proportional to the instantaneous scale thickness,

\[
\frac{dx}{dt} = \frac{k}{X}
\]

(70)

where \( X \) is the instantaneous scale thickness, \( k \) is the parabolic rate
Figure 22. Ni-O phase diagram (from ref. 3).

Figure 23. Ni-C phase diagram (from ref. 3).
Figure 24. Dissociation pressures for Cr$_2$O$_3$ coexisting with Ni-Cr alloys at 900, 1000 and 1100°C (from ref. 43).
Figure 25. Schematic representation of ternary sections and dissociation pressure diagrams between 900 and 1100°C (from ref. 43).
constant and \( t \) is the time. For a compact, tightly adherent scale which grows without any contribution from grain boundary diffusion, Wagner developed an equation for the parabolic rate constant in terms of the partial electrical transference numbers for ions and electrons and the Gibbs energy change for reaction. Later, Wagner modified his previous results for the growth of an electronically conducting scale so that the self-diffusion coefficients of the cation and anion, rather than the transference numbers, appear in the expression for the parabolic rate constant,

\[
k = \left. \frac{a_{\text{O}}}{a_{\text{O}}^0} \left( \frac{Z_1}{Z_2^2} \frac{D_1^* + D_2^*}{Z_2} \right) \right|_{\text{dln } a_0} \quad (71)
\]

where \( k \) is defined by Eq. (70), \( a_{\text{O}}^0 \) and \( a_{\text{O}}^0 \) are the activities of oxygen at the metal/oxide and the oxide/gas interfaces, respectively, \( Z_1 \) and \( Z_2 \) are the valences of the cation and anion, respectively, and \( D_1^* \) and \( D_2^* \) are the self-diffusion coefficients of the cation and anion, respectively. The parabolic rate constant has been measured experimentally and compared to the theoretical value defined by Eq. (71) for several metals. For copper, the agreement is excellent for several different oxygen activities in the gas\(^4\). The theory was also tested on the growth of scales in halogen gases and agreement with the theory is excellent\(^4\). Obviously, Eq. (70) can be integrated to give the instantaneous scale thickness at a particular time,

\[
x^2 = 2kt \quad . \quad (72)
\]
Wagner[6] also theoretically analyzed the oxidation rate of alloys. In particular, he considered the oxidation of Ni-Pt alloys. In these alloys, the platinum remains noble while the nickel oxidizes. The same theoretical arguments therefore apply to Fe-Cr alloys when the oxygen activity is low enough so that Fe remains noble but high enough so that \( \text{Cr}_2\text{O}_3 \) is stable. By solving Fick's second law, an expression for the mole fraction of the oxidized component in the alloy as a function of distance and time is obtained

\[
N_A(x,t) = N_A^i + \left( N_A^b - N_A^i \right) \left\{ \frac{\text{erf} \left( \frac{x^2}{4Dt} \right) - \text{erf} \left( \frac{k_p/2D}{2} \right)}{1 - \text{erf} \left( \frac{k_p/2D}{2} \right)} \right\} \tag{73}
\]

where \( N_A^i \) is the mole fraction of the oxidized component at the scale/alloy interface, \( N_A^b \) is the mole fraction in the bulk alloy, \( x \) is the distance, \( t \) is the time, \( D \) is the alloy interdiffusion coefficient and \( k_p \) is the parabolic rate constant describing the recession of the scale/alloy interface. This parabolic rate is related to the scale thickening constant (defined in Eq. 72) by[6]

\[
k_p = k \left( \frac{V_{\text{alloy}}}{V_{\text{oxide}}} \right)^2 \tag{74}
\]

where \( V_{\text{alloy}} \) and \( V_{\text{oxide}} \) are the molar volumes of the alloy and oxide, respectively. Equation (73) is used to calculate the depletion profile of the selectively oxidized component if the parabolic rate constant, diffusivity and interface composition are known. Wagner developed the following equation
to calculate the interface composition. The function $F(u)$ on the right-hand side of Eq. (75) is given by

$$
\frac{N^b_A - N^i_A}{1 - N^i_A} = F \left( \frac{k_p}{2D} \right)^{\frac{1}{2}}
$$

In Wagner's paper, a plot of Eq. (76), $F(u)$ vs. $u$, is given which facilitates the calculation of the interface composition and, hence, the composition profile in the alloy at a particular time.

Bastow, Whittle and Wood recently considered the assumptions involved in Wagner's original treatment of alloy depletion profiles. They compared the theoretical results of Wagner to finite difference analysis and found little difference. Bastow, Whittle and Wood therefore point out that the much simpler analytical solution is preferred over the more cumbersome computer solution. The analyses were tested for an Fe - 27.4%Cr alloy and agreement of theory with experiment was satisfactory. They also developed an expression for the concentration profile when selective oxidation brings about a phase change, as occurs during oxidation of certain Fe-Cr ferritic alloys. Since Cr is selectively oxidized, the depletion of Cr in the surface region brings about a phase change from $\alpha$ to $\gamma$ (see Fig. 1). An earlier theoretical treatment of this phenomenon was in error because no consideration was given to the discontinuity in the concentration profile due to the phase change.
Giggins and Pettit studied the oxidation of Ni-Cr alloys at 900°C in a CO/CO₂ gas which was reducing relative to the Ni-NiO equilibrium. They oxidized a Ni-30Cr alloy and found that a continuous protective Cr₂O₃ layer formed. For alloys more dilute in Cr, internal oxidation of Cr occurred. Internal oxidation will be discussed in the next section.

In a companion paper, Giggins and Pettit investigated the effect of alloy grain size on the oxidation of Ni-Cr alloys in oxygen at 0.1 atm. Fine-grained alloys and alloys with deformed surface layers exhibited the same oxidation behavior. They concluded that the deformed surfaces produced fine grains at the surface by recrystallization of the cold-worked layer when the specimen was heated. Alloys with chromium concentrations between 10 and 30 at.% exhibit a grain-size effect caused by the oxidation of chromium at the grain boundaries.

2. Internal Oxidation

There have been several excellent reviews on the topic of internal oxidation. Internal oxidation may occur when an alloy is exposed to an oxidizing atmosphere. If the solubility of oxygen in the alloy is large enough and the oxygen activity is sufficient to oxidize one component in the alloy but not others, then oxidation of that component may occur inside the alloy. Discrete oxide precipitates can form homogeneously in the alloy grains or along grain boundaries. With time, the internal oxidation front advances into the alloy essentially parallel to the external surface at a parabolic rate. The kinetics of this advancement have been described theoretically by the solution of
the diffusion equation. Although one can rigorously derive the kinetic expression, the same result is obtained by considering the mass balance at the precipitation front. Schematic concentration profiles are shown in Fig. 26 for an A-B alloy where A is noble and B forms BO\textsuperscript{v} inside the alloy. The depth of the precipitation front is denoted as $\xi$. In order that the front advances a distance $d\xi$ in time $dt$, an amount of B must be consumed. This amount of B must react with an equivalent amount of oxygen arriving at the precipitation front. Thus,

$$vN_B^O d\xi = J_O dt$$

(77)

where $N_B^O$ is the mole fraction of B in the bulk alloy and $J_O$ is the flux of oxygen arriving at the precipitation front. Using Fick's first law and assuming a linear oxygen gradient, Eq. (77) becomes

$$vN_B^O d\xi = -D_O^A \frac{\partial N_O^S}{\partial x} dt$$

$$= D_O^A \frac{N_O^S}{\xi} dt$$

(78)

where $D_O^A$ is the diffusivity of oxygen in component A and $N_O^S$ is the mole fraction of oxygen at the gas/alloy interface. Integrating Eq. (78) gives the identical result as does the more formal treatment,

$$\xi^2 = \left(\frac{2D_O^A N_O^S}{vN_B^O}\right) t$$

(79)

Equation (79) describes the kinetics of internal oxidation without accompanying scale formation. Equation (79) also represents the case where the diffusivity of component B is very much less than the
diffusivity of oxygen. For the case where the outward diffusion of
the oxidized element is appreciable, different kinetics are observed:

\[ \xi^2 = \left( \frac{D^A_{O} r_{s1}}{2 D^A_{B} r_{s2}} \right) t \]  

(80)

In this case, an enrichment of solute B occurs in the internal oxidation zone while a corresponding depletion occurs in the unoxidized alloy. The enrichment of B causes an increase in the mole fraction of oxide in the oxidation zone. Figure 27 shows schematic concentration profiles for the enrichment case.

Wagner's theory for the transition from internal oxidation to external scaling assumes that the transition occurs upon the formation of a critical volume fraction of oxide in the matrix. Since the enrichment of solute in the internal oxidation zone increases the volume fraction of oxide, Wagner's theory predicts that enrichment hastens the transition. This has been confirmed experimentally by Rapp. Rapp studied the effect of the partial pressure of oxygen on the transition from internal oxidation to external scaling in Ag-In alloys. As the oxygen activity is lowered (compare Figs. 26 and 27) enrichment occurs, which causes the transition to occur at lower solute contents (indium in Rapp's case).

The theoretical treatment that describes the kinetics of internal oxidation is also valid for many other internal precipitation reactions, e.g., internal carburization, internal nitridation and internal sulfidation.
Figure 26. Concentration profiles for exclusive internal oxidation of alloys without enrichment (from ref. 51).

Figure 27. Concentration profiles for exclusive internal oxidation of alloys with enrichment (from ref. 51).
3. Internal carburization

In 1967 Fujii and Meussner\textsuperscript{55} carburized Fe-Cr alloys beneath an iron oxide scale in pure CO\textsubscript{2}. This somewhat astonishing result occurred even though the atmosphere was considered highly oxidizing. The concentration of chromium varied from 1 to 15wt.% and the temperatures investigated were 700, 900 and 1100°C. In pure CO\textsubscript{2}, the oxide layer that formed on these alloys was duplex, i.e., an outer layer of mostly FeO with a porous inner layer of FeO and FeCr\textsubscript{2}O\textsubscript{4}. They postulated that the CO\textsubscript{2} breaks up on the oxide surface and is transported to the porous inner scale. There, molecules are formed in the pores and the resulting CO\textsubscript{2}-CO mixture, which is now relatively carburizing, equilibrates with the alloy surface. Thus, carbon diffusion into the alloy causes the alloy to become carburized.

The carbide morphology consisted of chromium carbides at grain boundaries, homogeneous precipitates and lamellar precipitates. The lamellar carbides only occurred in the Fe-15Cr alloy. Fujii and Meussner point out that even though their experiments were kinetic in nature, the equilibrium phase diagrams of the Fe-Cr-O and Fe-Cr-C systems were satisfactory in explaining the oxide structures and the carbide precipitation.

Grabke, et al\textsuperscript{56,57,58}, have published several papers on the carburization of Fe-Ni-Cr alloys. In the commercial alloys that were studied, internal carburization was promoted by packing in graphite and holding at temperatures between 800 and 1100°C. Experiments were also conducted with CH\textsubscript{4}/H\textsubscript{2} mixtures to fix the carbon activity. The kinetics of internal carburization were parabolic. Morphologies
consisted of $\text{Cr}_7\text{C}_3$ precipitates in a zone beneath the alloy surface with another deeper zone of $\text{Cr}_{23}\text{C}_6$ precipitates. In some cases $\text{Cr}_7\text{C}_3$ scales were observed. Their explanation depends upon an initially present oxide film which is reduced to carbide by reaction with carbon monoxide. They also studied the effect that internal carbide formation has upon mechanical properties. Carburized and non-carburized samples were tested by tensile and notch impact tests. Increasing carburization causes an increase in the tendency for brittle fracture.

Hopkinson and Copson$^{59}$ placed Ni-Cr alloys in pure CO between 721 and 999°C. They found an outer layer of carbon followed by an internal oxidation zone with another zone of underlying carbides. The carbides were not identified, but electron microprobe analysis showed that the chromium content was about 28 wt.% while the nickel content was about 64 wt.%. The oxides were identified by x-ray diffraction of the surface of $\text{Cr}_2\text{O}_3$ and spinel. The reaction time was 7 days and the reaction was measured by the penetration depth. The amount of attack was lower at 721 and 999°C than at the intermediate temperatures. Allying with silicon was found to reduce the attack significantly but not entirely. No reason for this was offered but it may be purely a thermodynamic interaction effect, i.e., silicon is known to have a large effect on the activity of carbon in Fe-base alloys.

Perkins and Goldberg$^{60}$ studied various commercial alloys in $\text{CH}_4/\text{H}_2$ and $\text{CO}/\text{CO}_2$ gas mixtures at temperatures up to 900°C and pressures up to $6.2 \times 10^6$ N/m$^2$ (900 psi). Austenitic stainless steels, Incolloys and Hastelloys were carburized. Generally they found that Fe-Cr-Ni alloys develop three distinct corrosion product zones:
outermost, a Cr$_2$O$_3$ layer, then a layer of oxides or carbides or both, and finally a region of general or grain boundary precipitation of carbides. Preoxidation was found to reduce, but not eliminate, carburization of the alloy. Also, spallation of the scale increased carburization. Perkins and Goldberg also report that carbide penetration increased with increasing surface roughness.

Pettit, Goebel and Goward$^{61}$ analyzed the thermodynamic conditions which define the stable phase in equilibrium with a gas containing more than one oxidant. For example, oxygen plus carbon or oxygen plus sulfur or oxygen plus nitrogen. Oxides are usually more stable on the surface because the Gibbs energy of formation of metal oxides are usually more negative than the corresponding carbides, sulfides and nitrides. However, if the activity of the second oxidant in the gas is greater than that required to form the compound, and, if the second oxidant species can penetrate the oxide scale, then the possibility exists that the second oxidant can form a reaction product inside the alloy beneath the scale. This hypothesis was tested by reacting pure Cr in air (O$_2$ and N$_2$ are the primary oxidants) at 1200°C. The chromium formed a protective oxide, Cr$_2$O$_3$, with Cr$_2$N precipitates in a band beneath the scale/alloy interface. An Fe-25Cr alloy was heated for 20 hours at 900°C in a CO/CO$_2$ gas with a CO/CO$_2$ ratio of 5. An external scale of Cr$_2$O$_3$ formed with a band of Cr$_{23}$C$_6$ precipitates beneath the scale inside the alloy. The same behavior was observed in sulfur-oxygen gases. Thus, it was shown that sulfur, nitrogen and oxygen can somehow penetrate Cr$_2$O$_3$ scales and react with Cr in the alloy to form internal corrosion products. This phenomenon will
deplete the surface region of the chromium needed to maintain a protective $\text{Cr}_2\text{O}_3$ scale.
III. STATEMENT OF PURPOSE

A. Introduction

In coal conversion systems, engineering alloys come into contact with several potentially oxidizing elements at high temperatures. Oxygen, sulfur, carbon and nitrogen are present and, under certain conditions, have the tendency to convert alloying elements into compounds by chemical reaction. Sometimes these reactions can occur on the surface of the alloy thereby depleting the surface region of important alloying elements. Alternatively, reactions can occur internally, e.g., along grain boundaries, by the transport of oxidant into the alloy. In either case, the alloy must be designed to compensate for or minimize these tendencies. Also, process operating ranges, if variable, may be specified whereby alloy degradation is minimized.

For alloys that come into contact with multiple oxidants at high temperatures, any prediction of corrosion morphology or of the kinetics of reaction is difficult. Not only do the number of possible corrosion products increase (compared to a single oxidant), but the thermodynamic stability of various reaction products is difficult to predict due to the interaction of dissolved oxidants on the thermodynamic activity of the alloying elements.

For the case of an alloy "protected" from oxidation by an adherent oxide scale, the maintenance of that scale requires the availability
of the protective component at the alloy/oxide interface. For example, 
$\text{Cr}_2\text{O}_3$ scales on Cr-containing Fe-base alloys are known to be slow 
growing and "protective". Thus, Cr atoms must diffuse in the alloy to 
the alloy/scale interface to replace those Cr atoms lost to oxidation. 
If, however, a second oxidant, such as sulfur or carbon, can diffuse 
into the alloy to form sulfides or carbides of chromium, then the 
availability of chromium for scale growth is decreased and the break­
down of the oxide scale is possible. Obviously, the competition be­
tween sulfur, oxygen, and carbon in the gas phase for reaction with 
chromium in the alloy will have a major effect on the corrosion mor­
phology and kinetics.

In this investigation, rather than studying the corrosion of 
commercial alloys containing many alloying elements in multiple oxi­
dants at high temperatures (complicated by the many combinations of 
possible corrosion products), a more simplified (model) approach was 
undertaken to attempt an understanding of the basic mechanisms in­
volved. In particular, a range of binary alloy compositions were 
selected and reacted in a two-oxidant gas. Iron-chromium and nickel-
chromium alloys were chosen since these two combinations are the bases 
for the bulk of high-temperature alloys. Also, reactive carbon mon­
oxide-carbon dioxide gas mixtures were chosen since equilibrium oxygen 
and carbon activities can be simultaneously established. Alloys 
ranging from dilute to concentrated were tested to determined the 
effect of the second oxidant on the transition from internal oxidation 
to external scaling. Dilute alloys do not have enough chromium to 
form a continuous external scale but form oxide precipitates
internally. An alloy containing more than a critical concentration of chromium in the alloy, which may correspond to the formation of a critical volume fraction of precipitates, will form an external scale. By studying a range of composition in an alloy system where dilute alloys internally oxidize while concentrated alloys form external scales, observations can be made to decide whether an oxide scale is a barrier to carbon penetration, and, therefore, internal carburization.

B. Thermodynamic Considerations

Thermodynamic predictions of phase stabilities are made by using stability plots. In this investigation, all CO/CO$_2$ gas mixtures were set so that iron or nickel remained noble relative to FeO or NiO formation in the gas. Thus, phase stabilities in the Cr-Cr-O system can be considered since Cr is the only component in the binary alloy that will form a binary oxide or carbide. Indeed, some combinations of gas and alloy compositions were suitable to stabilize the ternary spinel FeCr$_2$O$_4$ in the Fe-Cr system. These conditions did not cause an important change from the format just described. The graphical construction of phase stability diagrams is relatively straightforward and will be described briefly.

Figure 28 shows the phase stabilities in the Cr-C-O system plotted as the logarithm of the CO$_2$/CO ratio vs. reciprocal temperature. This diagram was calculated strictly from values for the standard Gibbs energy of formation data for the compound involved. For example, the Cr/Cr$_2$O$_3$ equilibrium line is determined by considering the following
Figure 23. Cr-C-O phase stability plot for pure Cr in CO/CO$_2$ gases.
reaction:

\[ \frac{2}{3}\text{Cr} + \text{CO}_2(g) = \frac{1}{3}\text{Cr}_2\text{O}_3 + \text{CO}(g) \]  

(81)

From the law of mass action and the known standard Gibbs formation energy data,

\[
\frac{a_{\text{Cr}_2\text{O}_3}}{a_{\text{Cr}}^{2/3}} \frac{P_{\text{CO}}}{P_{\text{CO}_2}} = K = \exp \left( \frac{-\Delta G^o_{81}}{RT} \right)
\]

(82)

For \( \text{Cr}_2\text{O}_3 \) and \( \text{Cr} \) in their coexistence standard states, Eq. (82) becomes

\[
\log \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = \frac{1}{2.303} \left( \frac{-\Delta G^o_{81}}{RT} \right)
\]

(83)

which can be plotted on Fig. 28. Other equilibrium lines can be similarly calculated and plotted. For the Boudouard reaction, however, the total pressure must be set in order to plot this reaction on Fig. 28. The equilibrium constant for the Boudouard reaction is given as

\[
K = \frac{a_{\text{C}} P_{\text{CO}_2}}{P_{\text{CO}}^{2/3}}
\]

(84)

but for equilibrium between gas and carbon at unit activity (pure graphite standard state)
\[ K = \frac{P_{CO_2}}{P_{CO}^2}. \]  

(85)

Also, since in the current experimentation

\[ P_{TOTAL} \approx P_{CO} + P_{CO_2} \]  

(86)

Eq. (85) becomes

\[ K = \frac{P_{TOTAL} - P_{CO}}{P_{CO}^2}. \]  

(87)

The partial pressure of carbon monoxide can be found by application of the quadratic formula and setting \( P_{TOTAL} \) equal to 1 atm,

\[ P_{CO} = \frac{-1 \pm \sqrt{1 + 4K}}{2K} \]  

(88)

\( P_{CO_2} \) can be found by substitution of \( P_{CO} \) into Eq. (86). The ratio \( P_{CO_2}/P_{CO} \) can then be calculated at various temperatures using the following Gibbs energy change \( \Delta G \) for reaction (62) to calculate \( K \),

\[ \Delta G_{62} = -166,105 + 169.9T \text{ J} \]  

(89)

Thus, by setting the total pressure, the temperature and the \( CO_2/CO \) ratio, the carbon activity can be uniquely defined. Also, by setting just the temperature and the \( CO_2/CO \) ratio, the oxygen activity is uniquely defined by the following reaction...
\[ \text{CO} + \frac{1}{2}\text{O}_2 = \text{CO}_2 \quad (90) \]

whose standard Gibbs energy change is given by\textsuperscript{62},

\[ \Delta G^o_{90} = -280,118 + 84.5 \text{ J/mole CO}_2 \quad (91) \]

The standard Gibbs energies of formation of the chromium carbides are taken from Kulkarni and Worrell\textsuperscript{19} since pure carbides are assumed in the calculation of Fig. 28. Four zones (I, II, III and IV) are shown on the diagram. These originate by extrapolating lines for metastable equilibria into stable phase fields. Zone I is a region which is bounded by the Cr/Cr\textsubscript{2}O\textsubscript{3} equilibrium and the Cr/Cr\textsubscript{2}C\textsubscript{6} metastable equilibrium. In Zone I, Cr\textsubscript{2}O\textsubscript{3} is the only stable phase. Zone II is bounded by the Cr/Cr\textsubscript{2}C\textsubscript{6} metastable equilibrium, carbide/Cr\textsubscript{2}O\textsubscript{3} equilibrium and the Boudouard reaction. Gas mixtures to the right of the Boudouard reaction are unstable and decompose. In Zone II, although Cr\textsubscript{2}O\textsubscript{3} is the equilibrium phase, Cr\textsubscript{2}C\textsubscript{6} (or another carbide depending upon the gas mixture and temperature) would be stable for the given carbon activity if the Cr\textsubscript{2}O\textsubscript{3} were not more stable than the carbide. Thus, Zone II represents a region where Cr\textsubscript{2}O\textsubscript{3} is stable but Cr\textsubscript{2}C\textsubscript{6} is metastable with respect to the gas. One might then expect (predict) the formation of the carbide in an alloy at a depth not yet reached by the oxygen (Cr\textsubscript{2}O\textsubscript{3}) if the surface can equilibrate to the carbon activity of the gas phase. Likewise, Zone III represents stable equilibrium for the carbide and metastable equilibrium for Cr\textsubscript{2}O\textsubscript{3} in the gas. Obviously, Zone IV corresponds to stable carbide equilibrium only.
Figure 28 was calculated for pure Cr and thus will not apply exactly in the case of an alloy containing chromium at a reduced activity. As chromium is alloyed with iron or nickel, the thermo-dynamic activity of Cr decreases and the stable metal field expands. Then Zone II and Zone III regions decrease, as shown in Fig. 29, where only the lowest carbide of chromium ($\text{Cr}_2\text{C}_6$) is considered for clarity. This stability diagram predicts that in a Zone II gas of give carbon activity, there is a critical chromium activity for which carburization is thermodynamically impossible. For gases of the Boudouard composition, the critical Cr activity is somewhere between 0.1 and 0.5, (these values are plotted on Fig. 29) and represents the intersection of the Zone I/Zone II boundary with the Boudouard line. This boundary does not have the same slope as the Boudouard line so that at all temperatures, the critical chromium activity for carburization in a carbon saturated gas will vary with temperature.

Thus far, phase stability plots for pure chromium (Fig. 28) and for chromium-containing alloys (Fig. 29) in CO/CO$_2$ gases have been presented as a function of temperature. Isothermal phase stability diagrams can also be constructed in which the carbon activity is plotted versus the oxygen activity. This latter type of diagram was useful in explaining corrosion morphologies observed in this study. An isothermal phase stability diagram was constructed for each alloy used and for each temperature of this investigation.

The activity of chromium in each of the alloys is required for the calculations. Activity data are available from Mazandarany and Pehlke. Their data (Tables 1 and 2 in Chapter II) were used to calculate the activity coefficient of chromium as a function of the
Figure 29. Cr-C-O phase stability plot for Cr-containing alloys in CO/CO$_2$ gases. Shows the stable metal field expanding with decreasing chromium activity.
atom percent Cr in both Fe-Cr and Ni-Cr binary alloys at the two reaction temperatures of 850 and 950°C. Figures 30 and 31 show the activity coefficient plots for the Fe-Cr alloys at 950 and 850°C, respectively, while Fig. 32 shows the variation of the activity coefficient in Ni-Cr alloys at these same temperatures. From these figures, the activity coefficient of chromium in each of the alloys used in this investigation could be interpolated and the chromium activity calculated. A summary is given in Table 3.

Figure 33 shows an Fe-Cr-C-O phase stability plot. There are actually seven stability plots superimposed on this figure — one for each Fe-Cr alloy studied. The horizontal lines represent alloy/carbide equilibria while the solid vertical lines represent alloy/oxide equilibria. The same four zones that were defined in Figs. 28 and 29 can also be shown on Fig. 33. For a particular alloy, Zone I is to the right of the alloy/oxide equilibrium boundary (in the stable \( \text{Cr}_2\text{O}_3 \) field) and below the metastable extension of the alloy/carbide boundary. Zone II is still in the stable \( \text{Cr}_2\text{O}_3 \) field but is above the metastable extension of the particular alloy/carbide boundary. The other two zones can be similarly defined. A line of constant total pressure is also shown on Fig. 33. Thus, the oxygen activity and carbon activity cannot be varied independently but must change along that line of constant total pressure. The numbers on the line correspond to experiment numbers. Note that the oxygen partial pressures in all experimental gas mixtures are below the \( \text{Fe}-\text{Fe}_x\text{O} \) equilibrium. Consequently, the iron should have remained noble with respect to wüüstite formation in all experiments. However, the spinel, \( \text{FeCr}_2\text{O}_4 \), was stable for Fe-Cr alloys in all CO/CO\(_2\) gases. It should be emphasized that this is
Figure 30. Activity coefficient of chromium in Fe-Cr binary alloys as a function of the atom percent Cr at 950°C.
Figure 31. Activity coefficient of chromium in Fe-Cr binary alloys as a function of the atom percent Cr at 850°C.
Figure 32. Activity coefficient of chromium in Ni-Cr binary alloys as a function of the atom percent Cr at 850 and 950°C.
Table 3. Chromium activities for the alloys used in this investigation.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$850^\circ C$</th>
<th>$950^\circ C$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe -  2.0 wt.%Cr</td>
<td>0.088</td>
<td>0.078</td>
</tr>
<tr>
<td>&quot; -  4.9 &quot;</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>&quot; -  9.9 &quot;</td>
<td>0.26</td>
<td>0.23</td>
</tr>
<tr>
<td>&quot; - 11.8 &quot;</td>
<td>0.30</td>
<td>0.26</td>
</tr>
<tr>
<td>&quot; - 14.7 &quot;</td>
<td>0.35</td>
<td>0.30</td>
</tr>
<tr>
<td>&quot; - 19.4 &quot;</td>
<td>0.43</td>
<td>0.38</td>
</tr>
<tr>
<td>&quot; - 24.4 &quot;</td>
<td>0.51</td>
<td>0.44</td>
</tr>
<tr>
<td>Ni -  1 &quot;</td>
<td>0.0057</td>
<td>0.0056</td>
</tr>
<tr>
<td>&quot; -  5 &quot;</td>
<td>0.034</td>
<td>0.032</td>
</tr>
<tr>
<td>&quot; -  6.75 &quot;</td>
<td>0.050</td>
<td>0.047</td>
</tr>
<tr>
<td>&quot; - 10 &quot;</td>
<td>0.084</td>
<td>0.079</td>
</tr>
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<td>&quot; - 15 &quot;</td>
<td>0.154</td>
<td>0.143</td>
</tr>
<tr>
<td>&quot; - 21.4 &quot;</td>
<td>0.311</td>
<td>0.282</td>
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</tbody>
</table>
Figure 33. Fe-Cr-C-O stability plot at 950°C.
an equilibrium phase stability diagram in which the lowest carbide is not always in equilibrium with the alloy. In fact, for most of the alloys in this investigation, the lowest carbide becomes metastable and the next carbide, $\text{Cr}_7\text{C}_3$, becomes the stable carbide. In the most dilute alloys, $\text{Cr}_3\text{C}_2$, the highest carbide, can be in equilibrium with the alloy.

From Fig. 33 one can predict which alloys might be carburized according to a metastability criterion, and which ones should not, in a given $\text{CO}/\text{CO}_2$ gas. For example, consider the gas mixture used in experiment number 2 (data point number 2 on the $P_{\text{TOTAL}} = 1$ atm curve). If we extrapolate the carbon activity from point 2 of Fig. 33 horizontally to the left, into the stable carbide fields, we find that this particular carbon activity is in the stable carbide fields for the Fe-9.9, 11.8, 14.7, 19.4 and 24.4 wt.%Cr alloys, but, in the stable alloy fields for the Fe-2.0 and 4.9 wt.%Cr alloys. Consequently, a gas of composition 2 would be expected to carburize all but the Fe-2.0 and 4.9 wt.%Cr alloys by precipitation of $\text{Cr}_7\text{C}_3$. Of course, a carbon gradient in the alloy would modify this condition since the carbon activity in the alloy at the diffusion front would be somewhat lower than that in the bulk gas. For this Zone II gas (defined in Fig. 28), even though $\text{Cr}_2\text{O}_3$ is the stable phase, the carbide is metastable with respect to the $\text{Cr}_2\text{O}_3$. The carbide can be stable in the alloy because the oxygen activity is very low inside the alloy, lower than the equilibrium oxygen activity between the alloy and $\text{Cr}_2\text{O}_3$. Nevertheless, $\text{Cr}_2\text{O}_3$ may be present either as an external scale or as internal oxide precipitates. Other diagrams for Fe-Cr alloys at 850°C and Ni-Cr alloys at 850 and 950°C are shown in Figs. 34 through 36, respectively.
Figure 34. Fe-Cr-C-O stability plot at 850°C.
Figure 35. Ni-Cr-C-O stability plot at 850°C.
Figure 36. Ni-Cr-C-0 stability plot at 950°C.
Similar predictions as to which alloys should carburize (by precipitation of Cr$_7$C$_3$ or Cr$_3$C$_2$, depending upon the alloy) can be developed for all experimental gas compositions.

Thus, a thermodynamic prediction for simultaneous carburization/oxidation of chromium-containing alloys in carbon-and oxygen-containing gases has been suggested for the first time. For example, if an alloy containing chromium is reacted in Zone II (Fig. 28 or 29), then the stable phase in the gas should be Cr$_2$O$_3$. But, inside the alloy and beyond internal oxidation if it occurs, where the oxygen activity is very low, chromium carbides could be stable. The carbides are then considered stable in the alloy (beneath oxidation) but only metastable at the gas/metal interface since at equilibrium the stable phase must be Cr$_2$O$_3$. Experiments were conducted to test this hypothesis. Individual series of Fe-Cr and Ni-Cr alloys of varying chromium activity (from dilute to concentrated) were selected for reaction in the Zone II region of Fig. 28 or 29. Furthermore, the gas mixtures were always selected so that Fe or Ni remained noble with respect to the formation of a binary oxide. Thus, the transition from internal oxidation of Cr to external scaling in a two-oxidant gas could be studied without the complicating factor of Fe or Ni oxide scales on the alloy surface. (A theoretical kinetic model for the internal dual precipitation for a binary alloy in two-oxidant gases has been developed and is included in the Appendix.) As shown in Figs. 33 through 36, all experimental gas compositions can be in either Zone I (no carburization) or Zone II (possible carburization) depending upon which alloy is considered. All experimental conditions (corresponding to the numbers on Figs. 33 through 36) are summarized in Table 4.
Table 4. Experimental conditions.

<table>
<thead>
<tr>
<th>EXPT.</th>
<th>CO₂/CO</th>
<th>TEMP., °C</th>
<th>a₀</th>
<th>P₀₂</th>
<th>TIME, hr.</th>
</tr>
</thead>
<tbody>
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<td>2</td>
<td>0.11</td>
<td>950</td>
<td>0.136</td>
<td>9.62 x 10⁻¹⁸</td>
<td>12</td>
</tr>
<tr>
<td>3</td>
<td>0.17</td>
<td>950</td>
<td>0.084</td>
<td>2.30 x 10⁻¹⁷</td>
<td>12</td>
</tr>
<tr>
<td>4</td>
<td>0.25</td>
<td>950</td>
<td>0.053</td>
<td>4.97 x 10⁻¹⁷</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>0.35</td>
<td>950</td>
<td>0.035</td>
<td>9.74 x 10⁻¹⁷</td>
<td>12</td>
</tr>
<tr>
<td>6</td>
<td>0.31</td>
<td>850</td>
<td>0.175</td>
<td>5.65 x 10⁻¹⁹</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>0.48</td>
<td>850</td>
<td>0.100</td>
<td>1.35 x 10⁻¹⁸</td>
<td>12</td>
</tr>
<tr>
<td>8</td>
<td>0.70</td>
<td>850</td>
<td>0.060</td>
<td>2.88 x 10⁻¹⁸</td>
<td>12</td>
</tr>
<tr>
<td>9</td>
<td>0.31</td>
<td>850</td>
<td>0.175</td>
<td>5.65 x 10⁻¹⁹</td>
<td>12</td>
</tr>
<tr>
<td>10</td>
<td>0.08</td>
<td>950</td>
<td>0.193</td>
<td>5.09 x 10⁻¹⁸</td>
<td>12</td>
</tr>
<tr>
<td>11</td>
<td>0.15</td>
<td>950</td>
<td>0.096</td>
<td>1.79 x 10⁻¹⁷</td>
<td>12</td>
</tr>
</tbody>
</table>
IV. EXPERIMENTAL PROCEDURE

The compositions, in weight percent, of the Fe-Cr and Ni-Cr alloys reacted in CO/CO₂ gases are as follows: Fe – 2.0, 4.9, 9.9, 11.8, 14.7, 19.4 and 24.4Cr and Ni – 1, 5, 6.75, 10, 15 and 21.4Cr. The Fe-Cr alloys were cast from high purity components specifically for this investigation by Lockheed Palo Alto Research Labs. Plates were received in the hot-rolled condition. The Ni-Cr alloys were donated by Pratt and Whitney Aircraft and Battelle-Columbus Labs. The Ni-21.4 was received as cold-rolled sheet and the rest were received in the as-cast (chill block) condition.

Carbon monoxide of commercial purity grade (99.5%) was further purified by passing over copper turnings at about 400°C, then over Ascarite to remove CO₂ and finally magnesium perchlorate to remove water vapor. The copper turnings served a dual purpose: one to remove oxygen and the other to act as a hot surface where iron carbonyl could decompose. Prior to using copper turnings at this temperature, the gas was passed through them at about 200°C. Excessive sooting in the gas inlet tube (also the exit line) caused plugging and changes in the preset flowmeter settings due to the increase in back-pressure. We believe that a reaction between the steel cylinder and the gas formed iron carbonyl which later decomposed in the gas inlet tube into Fe and CO. The Fe then catalyzed the Boudouard reaction which caused sooting.
Also, orange deposits were present on the inside of the reaction tube which were probably iron oxide. Passing carbon monoxide over the hot copper turnings minimized the sooting problem. Carbon dioxide was purified to the extent of water vapor removal by passing over magnesium perchlorate. The two gases were mixed in a chamber containing glass beads after passing through separate capillary flowmeters. The flowmeters were calibrated by the soap film technique in which the time taken for a soap film to travel through a known volume is used to calculate the volumetric flowrate. The ratio of the flowrates gives the partial pressure ratio.

Flowmeter calibration was not the only method used to determine the CO₂/CO ratio. A solid electrolyte oxygen gauge was also used. The gauge is a ZrO₂ (in this case the ZrO₂ was fully stabilized with 8wt.% Y₂O₃) tube which is an oxygen ion conductor when used in the temperature and oxygen activity ranges of this study. If ZrO₂ is placed between two isolated chambers having different oxygen activities then a voltage across the ZrO₂ is established which is given by

\[ E = \frac{-RT}{4F} \ln \left( \frac{P'O_2}{P''O_2} \right) \]  

(92)

where \( E \) is in volts, \( R \) is the gas constant, \( T \) is in °K, \( F \) is Faraday's constant and \( P'O_2 \) and \( P''O_2 \) are the oxygen partial pressures on either side of the ZrO₂.

A schematic diagram of the experimental set-up is shown in Fig. 37. A mullite reaction tube (2x2½x18") was fitted with a brass
Figure 37. Schematic representation of the experimental set-up.
flange which was epoxied to the tube. The top part of the flange contained CAJON o-ring fittings which were used as gas-tight pass-throughs for the various tubes. The flange halves were bolted together with an o-ring between to ensure a gas-tight seal. A pyrex chamber was also epoxied to the top half of the flange. This chamber contained a gas-tight winch at the top that was used to raise and lower samples from the furnace hot zone. In this way gas mixtures could be adjusted before starting a run. The samples (slabs about 5x10x2 mm) were tied to a quartz sample holder rod with pure platinum wire. The temperature was measured with a calibrated Pt/Pt-10Rh thermocouple (referenced to the ice point) which was placed in a closed-end Al₂O₃ protection tube. The thermocouple output as well as the voltage from the ZrO₂ oxygen gauge was measured with a Leeds and Northrup potentiometer. The ZrO₂ oxygen gauge was made from a yttria-doped fully stabilized tube (¼"OD x 18", from Zircoa Corp. nuclear grade zirconia). The bottom 2 cm of the tube was platinized by applying Engelhard platinum paste (diluted with toluene) on the outside and inside and then sintering for a few hours at 800°C. This procedure produces a platinum electrode on the two surfaces of the electrolyte. A Pt lead wire from the outside electrode was attached to the outside of the tube by wrapping it around the tube and tying it on with Pt wire; the other end was routed through a brass flange in a single bore Al₂O₃ tube which was epoxied at the top to make a gas-tight seal. The Pt lead wire from the inside electrode was attached by putting a Pt wire through a 1/8" x 22" single bore Al₂O₃ tube and letting the weight of the tube maintain electrical contact at the bottom of the ZrO₂ tube. The inside of the tube was
used as the reference with the oxygen partial pressure of air (0.21 atm). An open-circuit voltage measurement gives the oxygen partial pressure (using Eq. 92) in the gas flowing through the system. The measured oxygen partial pressure can be used to calculate the $P_{\text{CO}_2}/P_{\text{CO}}$ ratio which can then be used to calculate the carbon activity for a given total pressure. The total pressure was always 1 atm in this investigation. Temperature control was always within ±1°C by using a Barber-Colman proportional controller. Photographs of the experimental set-up are shown in Figs. 38 and 39. Figure 39 shows a close-up of the flange assembly.

Samples were prepared by successively grinding on 240, 320, 400 and 600 grit SiC papers. They were then rinsed in acetone and dried by an air blast. All samples received a 2 hour anneal prior to reaction in the CO/CO$_2$ gas. Samples for run number 2 were annealed in argon which had been purified by passing over titanium sponge at about 800°C. But, the oxygen activity was not low enough to stop some superficial oxidation of chromium in the alloy, so, the samples were removed from the apparatus and lightly re-abraded on 600 grit SiC paper. In all subsequent experiments samples were annealed in flowing hydrogen which caused no observable oxidation of chromium. After the two hour anneal the samples were raised from the furnace hot zone into the pyrex chamber above the brass flange. This area was relatively cool because a fan was used to cool the brass. The samples remained in the apparatus overnight in flowing argon to allow outgassing of the hydrogen before the experiment.
Figure 38. Photograph of the experimental set-up.
Figure 39. Close-up of the flange assembly of Fig. 38.
For a particular experiment, the gas mixture was set by adjusting the flowmeters to give the desired reading from the zirconia oxygen gauge. After the mixture was fairly stable, the samples were lowered into the furnace hot zone for 12 hours. However, the voltage reading from the oxygen gauge was not constant throughout the experiment. The voltage drifted upward (in the more reducing direction) with time. This may have been due to the finite time required to flush residual oxygen from the system. In any case, the flowmeters were adjusted throughout the experiment to maintain the desired voltage reading from the zirconia cell (always equal to or better than ±1 mV). After 12 hours the samples were raised from the hot zone while allowing the CO/CO₂ gas mixture to continue flowing. After the samples were cool (a few minutes) the CO/CO₂ gas flow was stopped, the system flushed with argon and the samples removed.

Post-reaction examination began with x-ray diffraction of the exterior surface of the sample to aid in the identification of phases. Chromium radiation was used without a filter. Scanning electron microscopy was then employed to examine the surface oxide morphology on selected specimens. Next, the samples were mounted in epoxy and polished with 1 micron diamond paste on a Syntron vibratory polisher for optical metallography of the cross-sections. Electron probe microanalysis was also used to determine the chromium concentration profile in selected samples. The polished cross-sections were carbon-coated to minimize beam drift during the microprobe trace.
V. RESULTS AND DISCUSSION

The exterior surfaces of some samples were examined by X-ray diffraction after reaction in the CO/CO$_2$ gases. Chromium radiation was used without a filter to maximize the intensity of oxide peaks. The oxide phases that were positively identified (in some cases positive identification could not be made) are given in Table 5. This was used to detect the presence of spinel in some cases and also to find out whether the objective of reacting the samples in a gas mixture where wüstite was unstable was met. In some of the more dilute alloys that internally oxidized, the volume fraction of the oxide phase may not have been great enough to detect Cr$_2$O$_3$ or FeCr$_2$O$_4$ by X-ray diffraction. Visual inspection of the color of the exterior surface after reaction was correlated to the X-ray diffraction results; green scales were identified as Cr$_2$O$_3$, brown scales were found to be FeCr$_2$O$_4$ and black scales were Fe$_x$O.

A photomicrograph of the polished cross-section of the Fe-2.0 wt.% Cr alloy used in experiment number 2 (950°C, $P_{CO_2}/P_{CO} = 0.11$) is shown in Fig. 40. The internal oxidation zone is clearly visible beneath the alloy/gas interface. The X-ray diffraction results indicate that FeCr$_2$O$_4$ is present. This phase may also be present in the near surface region because it is stable in the gas, but, Cr$_2$O$_3$ should be the phase in equilibrium with the alloy. Near the surface...
Table 5. X-ray diffraction results.

<table>
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<th>EXPT.</th>
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<th>Diffraction Product</th>
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<tbody>
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<td>FeCr$_2$O$_4$</td>
</tr>
<tr>
<td></td>
<td>Fe-4.9Cr</td>
<td>FeCr$_2$O$_4$</td>
</tr>
<tr>
<td></td>
<td>Fe-14.7Cr</td>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>Fe-19.4Cr</td>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>Fe-24.4Cr</td>
<td>Cr$_2$O$_3$</td>
</tr>
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</tr>
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<td>Fe-4.9Cr</td>
<td>FeCr$_2$O$_4$</td>
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</tr>
<tr>
<td></td>
<td>Fe-11.8Cr</td>
<td>FeCr$_2$O$_4$, Cr$_2$O$_3$</td>
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<td>EXPT.</td>
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<td>-------</td>
<td>----------------</td>
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<tr>
<td>11</td>
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<td>Cr$_2$O$_3$</td>
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Figure 40. Optical micrograph of the cross-section of an Fe-2.0wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 400x.
Fe and Cr$_2$O$_3$ can react with available dissolved oxygen to form the spinel, which is stable in the gas. Figure 41 shows a photomicrograph of the cross-section of the Fe-4.9wt.% Cr alloy used in the same experiment. Note that the volume fraction of the oxide has increased but in both this and the Fe-2.0wt.% Cr alloy no carburization has occurred.

In Fig. 42, the cross-section of the Fe-9.9wt.% Cr sample is shown at 100X. Even at this low magnification the internal oxidation zone can be seen. More important, however, is the presence of the grain-boundary carbides. These carbides extend throughout the entire cross-section. Upon reconsideration of Fig. 36, we see that this result fits the prediction: Fe-4.9wt.% Cr should not carburize while Fe-9.9wt.% Cr should. But, the diagram predicts the carbide phase to be the equilibrium Cr$_7$C$_3$. A selective etching technique described by Woodyatt and Krauss$^{32}$ was used to identify carbides. A potassium permanganate etch (4g KMnO$_4$ + 4g NaOH + 100ml H$_2$O) will stain M$_{23}$C$_6$ carbides tan while leaving M$_7$C$_3$ carbides unattacked. Since the carbides in Fig. 42 were stained tan by this etch we conclude that they are M$_{23}$C$_6$. Also, from another experiment which produced the same carbides that etched tan, the alloy was dissolved in a methanol-10% Br solution for about 2 days. The residue was filtered and then examined by X-ray diffraction and compared with the known patterns$^{32}$ for the alloy carbides. The only carbide present was M$_{23}$C$_6$, which corroborates the etching technique. Thus, the use of the equilibrium stability plots is not justified since M$_{23}$C$_6$ is present rather than M$_7$C$_3$. Figure 43 shows a higher magnification view of the same sample.
Figure 41. Optical micrograph of the cross-section of an Fe-4.9wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.11$ for 12h. 400X.
Figure 42. Optical micrograph of the cross-section of an Fe-9.9wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 100X.
Figure 43. Optical micrograph of the cross-section of an Fe-9.9wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 400X.
The internal oxidation zone is more clearly visible along with a denuded zone between the end of the internal oxidation zone and the beginning of the grain boundary M$_{23}$C$_6$ precipitation. The carbides are also visible by using polarized light but the staining etch gives better contrast. An explanation for the denuded zone will be offered later. Figure 44 shows the cross-section of the Fe-11.8wt.% Cr alloy also used in experiment 2. The volume fraction of oxide is larger than that in the Fe-9.9wt.% Cr alloy but the transition from internal oxidation to external scaling had not yet occurred.

Figure 45 shows the cross-section of the Fe-14.7wt.% Cr alloy used in experiment 2 at 100X. The left-hand edge of the micrograph coincides with the alloy/gas interface. Figure 45 shows a single-phase region at the surface with a two-phase region deeper in the alloy. This alloy is originally ferritic but at the high carbon activity of this experiment, carbon diffusion into the alloy stabilizes the austenite phase at the surface with a two-phase region of austenite and ferrite further inside the alloy where the carbon activity is lower. This can be explained by considering Figs. 15 and 16. One must visualize the Fe-15% Cr phase diagram by considering the available Fe-13% Cr and Fe-17% Cr phase diagrams. We can see that at high carbon contents (at the surface), austenite ($\gamma$) is stable, while at lower carbon contents (inside the alloy) austenite and ferrite ($\alpha+\gamma$) are stable. With higher carbon contents, $\gamma + M_{23}C_6$ can even be stable at the surface. This is actually the case in experiment 2 as shown by Fig. 46, in which the etchant shows the $M_{23}C_6$ carbides at the surface. A higher magnification view of this sample is shown in
Figure 44. Optical micrograph of the cross-section of an Fe-11.8wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 400X.
Figure 45. Optical micrograph of the cross-section of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.11$ for 12h. Unetched. 100X.
Figure 46. Optical micrograph of the cross-section of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. Etched for carbides. 100X.
The internal oxidation zone is visible with some internal film formation and intermittent external scaling. Again, a denuded zone between the internal oxidation zone and the carbide precipitation is present. The carbide morphology is somewhat different in this alloy compared with the more dilute alloys discussed before. The lamellar colonies appear to originate at alloy grain boundaries. This carbide precipitation extends into the alloy only as far as the austenite phase as shown in Fig. 46. A photomicrograph of one of these carbide colonies is shown at 1250X in Fig. 48. There must be an orientation relationship (habit plane) between the carbide phase and the matrix because the carbides appear to precipitate along specific crystallographic planes. The structure of both the matrix and the carbide is cubic.

Figure 49 shows a cross-section of the Fe-19.4wt.% Cr alloy used in experiment 2. This alloy has an external scale of Cr₂O₃, a denuded zone, and then a band of grain-boundary $M_{23}C_6$ carbides. These carbides can also be seen to precipitate at oxide inclusions. Figure 50 shows a cross-section of the Fe-24.4wt.% Cr alloy from the same experiment. This alloy also scaled and formed $M_{23}C_6$ precipitates in a band beneath the scale with an intervening denuded zone. In this alloy, in addition to the grain-boundary carbides, general carbide precipitation occurred within the alloy grains.

In all of the alloys that carburized in experiment 2 (and in all subsequent experiments as well), the carbide present was not the equilibrium $M_7C_3$ or $M_3C_2$, but the metastable $M_{23}C_6$. Consequently, the equilibrium phase stability diagrams (Figs. 33-36) are not of any
Figure 47. Optical micrograph of the cross-section of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 400X.
Figure 48. Optical micrograph of a carbide colony in the Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 1250X.
Figure 49. Optical micrograph of the cross-section of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. 400X.
Figure 50. Optical micrograph of the cross-section of an Fe-24.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO}$ = 0.11 for 12h. 400X.
further use for predicting carburization during these experiments. Since metastable $M_{23}C_6$ was observed in all cases of carburization, metastability plots have been developed to explain and, therefore, predict carburization in these alloys. These diagrams are constructed like the equilibrium diagrams except that metastable carbide equilibria are shown (see Figs. 51 through 54). Predictions from extrapolations of the carbon activity of a certain experiment into the carbide or alloy field for a particular alloy are the same as the equilibrium diagrams in principle. Naturally, for a given alloy, the carburization prediction from a metastability diagram differs (occurs at a lower carbon activity) compared with the same stability diagram since the solubility of a metastable phase in the alloy is greater than that of a stable one.

The presence of $M_{23}C_6$ in the alloy represents a double metastability in the gas since carbides are not stable in the gas in the first place. If the equilibrium carbides had formed, then these would be considered stable in the alloy (because the oxygen activity is low) but metastable in the gas because $\text{Cr}_2\text{O}_3$ is the more stable phase. This represents a single metastability with respect to the gas. But, since metastable $M_{23}C_6$ is precipitated in the alloy (rather than the equilibrium carbide) the precipitation of this carbide represents a double metastability condition with respect to the gas. The reason for the formation of a metastable carbide may be due to a nucleation effect. The metastable carbide, $M_{23}C_6$, is cubic (as is the alloy matrix) but the equilibrium carbide $M_7C_3$ is trigonal.
Figure 51. Fe-Cr-C-O metastability plot at 950°C.
Figure 52. Fe-Cr-C-O metastability plot at 850°C.
Figure 53. Ni-Cr-C-O metastability plot at 850°C.
Figure 54. Ni-Cr-C-O metastability plot at 950°C.
In the discussion of the results of experiment 2, a denude zone between the internal oxidation zone (or external scale) and the internal carbides was described. This was found in all experiments where carburization occurred except one. In experiment 5 (950°C, $P_{CO_2}/P_{CO} = 0.35$), carburization of the Fe-19.4wt.% Cr alloy occurred with the lamellar carbide structure as shown in the photomicrograph of the cross-section in Fig. 55. X-ray diffraction of the exterior surface showed that Fe$_x$O, FeCr$_2$O$_4$ and Cr$_2$O$_3$ were present (see Table 5). Note that a denuded zone does not appear to be present in this figure.

To examine this further, the polished cross-section of this sample was deeply etched for 5 minutes in a solution of methanol-10% Br and then examined by scanning electron microscopy (SEM). Figures 56 and 57 clearly show that the carbides are directly oxidized to the more stable oxide phase. For comparison, the Fe-14.7 and 19.4wt.% Cr alloys of experiment 2 (denuded zone present) were etched in the same way and examined by SEM. This is shown in Figs. 58 and 59. In this case, the denuded zone is clearly present which indicates carbides dissolve in favor of the more stable oxide. The presence of Fe$_x$O on the surface is somewhat puzzling at first since the oxygen activity of the gas mixture was selected to be below the iron/wüstit equilibrium. If we refer to Fig. 9 we can see that the stable wüstit field exists at lower oxygen activities as the chromium content is increased slightly. Consequently, the Fe-19.4wt.% Cr alloy could have been in the stable wüstit + spinel field since the oxygen activity was very close to that of the Fe/Fe$_x$O equilibrium. Other experiments at lower oxygen activities were probably low enough so that alloys were in the
Figure 55. Optical micrograph of the cross-section of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.35$ for 12h. 300X.
Figure 56. Scanning electron micrograph of the cross-section of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.35$ for 12h. Etched in methanol-10% Br for 5 min. 1200X.
Figure 57. Scanning electron micrograph of the cross-section of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.35$ for 12h. Etched in methanol-10% Br for 5 min. 1600X.
Figure 58. Scanning electron micrograph of the cross-section of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h. Etched in methanol-10% Br for 5 min. 1000X.
Figure 59. Scanning electron micrograph of the cross-section of an Fe-24.4wt.% Cr alloy reacted at 950°C with $\frac{P_{CO_2}}{P_{CO}} = 0.11$ for 12h. Etched in methanol-10% Br for 5 min. 1000X.
alloy + spinel field.

None of the Ni-Cr alloys studied were found to carburize in the selected gas mixtures. Figure 60 shows the cross-section of the Ni-1wt.% Cr alloy after experiment 8 (850°C, $P_{CO_2}/P_{CO} = 0.70$). Very fine precipitates are present along alloy grain boundaries only. This is in contrast to the mode of precipitation in the Fe-Cr alloys where oxide precipitates were present inside the alloy grains as well as at the grain boundaries. The cross-section of the Ni-5wt.% Cr alloy is shown in Fig. 61. The alloy is internally oxidized with more oxides present along the grain boundaries than the Ni-1wt.% Cr alloy. Figure 62 shows the cross-section of the Ni-6.75wt.% Cr alloy with extensive grain boundary oxidation while Fig. 63 shows the Ni-10wt.% Cr alloy with a lesser amount. The Ni-15wt.% Cr alloy has fewer oxide precipitates still, as shown in Fig. 64. Thus, the transition from internal oxidation to external scaling is beginning to occur but still more Cr is needed in the alloy to exclude grain-boundary scales. Figure 65 shows the cross-section of the Ni-21.4wt.% Cr alloy. This material had many oxide inclusions in the as-received condition as seen in the interior regions away from the surface. This alloy appears to have an external scale in some regions but also has ingrown $Cr_2O_3$ that is attached to the scale. This is better shown in Fig. 66 which shows the same alloy after experiment 9 (850°C, $P_{CO_2}/P_{CO} = 0.31$). The external scale is clearly visible along with regions of ingrown oxide. Figure 67 shows the Ni-21.4wt.% Cr alloy after experiment 10 (950°C, $P_{CO_2}/P_{CO} = 0.08$). This gas mixture had the lowest oxygen activity (and, therefore, the highest carbon activity) of any experiment and
Figure 60. Optical micrograph of the cross-section of a Ni-1wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.70$ for 12h. 400X.
Figure 61. Optical micrograph of the cross-section of a Ni-5wt.% Cr alloy reacted at 850°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.70$ for 12h. 400X.
Figure 62. Optical micrograph of the cross-section of a Ni-6.75wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.70$ for 12h. 400X.
Figure 63. Optical micrograph of the cross-section of a Ni-10wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.70$ for 12h. 400X.
Figure 64. Optical micrograph of the cross-section of a Ni-15wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.70$ for 12h. 400x.
Figure 65. Optical micrograph of the cross-section of a Ni-21.4wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.70$ for 12h. 400X.
Figure 66. Optical micrograph of the cross-section of a Ni-21.4wt.% Cr alloy reacted at 850°C with \( \frac{P_{CO_2}}{P_{CO}} = 0.31 \) for 12h. 400X.
Figure 67. Optical micrograph of the cross-section of a Ni-21.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 400X.
produced an external scale with very small regions of ingrown oxide. Figure 68 shows the Ni-21.4wt.% Cr alloy after experiment 11 (950°C, $P_{CO_2}/P_CO = 0.15$) with an external scale and some regions of ingrown oxide. So, either low oxygen activity or high carbon activity, or both, appear to promote scale formation in Ni-Cr alloys with very little ingrown oxide. Whether the ingrown oxide is beneficial or not is not known, but, it seems likely that the ingrown oxide might offer some resistance to scale spallation during cyclic oxidation.

Photomicrographs have not been presented for every experiment but representative microstructures have been shown. Table 6 summarizes the optical metallography results and the carburization predictions from the metastability plots (Figs. 51 through 54). This table shows where the transition from internal oxidation to external scaling occurred for each experiment. For example, in experiment 2 it occurred between Fe-14.7 and 19.4wt.% Cr and in experiment 8 between Ni-15 and 21.4wt.% Cr. From Table 6 one can see that the predictions for carburization by $M_{23}C_6$ formation are remarkably close to the experimental data. For example, in experiment 2, carburization also occurred in the two alloys more dilute than the predicted one. In experiment 3, the prediction for carburization changes, but again the difference between the prediction and experiment is two alloys from the prediction. However, in this experiment the two most concentrated alloys that should have carburized did not, presumably because the presence of external oxide scales hindered carbon penetration. Carburization in experiment 4 occurred in the alloy that was one alloy more dilute than the prediction while in experiment 6 it
Figure 68. Optical micrograph of the cross-section of a Ni-21.4 wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.15$ for 12h. 400X.
Table 6. Optical metallography results and predictions from stability plots.

<table>
<thead>
<tr>
<th>EXPT.</th>
<th>Alloy</th>
<th>Oxide Morphology</th>
<th>Carbide Morphology</th>
<th>Carburization Prediction from Metastability Diagram</th>
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</thead>
<tbody>
<tr>
<td>2</td>
<td>Fe-2.0Cr</td>
<td>internal ppts.</td>
<td>-</td>
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</tr>
<tr>
<td></td>
<td>Fe-4.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td>950°C</td>
<td>Fe-9.9Cr</td>
<td>internal ppts.</td>
<td>grain boundary $M_{23}C_6$ throughout alloy</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-11.8Cr</td>
<td>internal ppts.</td>
<td>grain boundary $M_{23}C_6$ throughout alloy</td>
<td>no</td>
</tr>
<tr>
<td>$P_{CO_2}/P_{CO} = 0.11$</td>
<td>Fe-14.7Cr</td>
<td>internal ppts./external scale</td>
<td>lamellar $M_{23}C_6$ in $\gamma$; none in $\alpha+\gamma$</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>Fe-19.4Cr</td>
<td>external scale</td>
<td>band of grain boundary $M_{23}C_6$</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>Fe-24.4Cr</td>
<td>external scale</td>
<td>band of grain boundary and homogeneous $M_{23}C_6$</td>
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Table 6. (continued)

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<td>internal ppts.</td>
<td>-</td>
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<tr>
<td>950°C</td>
<td>Fe-4.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-9.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-11.8Cr</td>
<td>internal ppts.</td>
<td>grain boundary $M_{23}C_6$ throughout alloy</td>
<td>no</td>
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<td>$P_{CO_2}/P_{CO}=0.17$</td>
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<td>internal ppts./external scale</td>
<td>lamellar $M_{23}C_6$ in $\gamma$ beneath internal ppts.; none in $\alpha+\gamma$</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-19.4Cr</td>
<td>external scale</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>Fe-24.4Cr</td>
<td>external scale</td>
<td>-</td>
<td>yes</td>
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Table 6. (continued)

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<th>Carburization Prediction from Metastability Diagram</th>
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<tr>
<td>950°C</td>
<td>Fe-4.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-9.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-11.8Cr</td>
<td>internal ppts.</td>
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<td>no</td>
</tr>
<tr>
<td>$\frac{P_{CO_2}}{P_{CO}} = 0.25$</td>
<td>Fe-14.7Cr</td>
<td>internal ppts./external scale</td>
<td>lamellar $M_{23}C_6$ in $\gamma$ beneath internal ppts.; none in $\alpha + \gamma$</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-19.4Cr</td>
<td>external scale</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>Fe-24.4Cr</td>
<td>external scale</td>
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Table 6. (continued)

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<th>Carburation Prediction from Metastability Diagram</th>
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<td>Fe-4.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
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<tr>
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<td>Fe-9.9Cr</td>
<td>internal ppts.</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-11.8Cr</td>
<td>internal ppts.</td>
<td>-</td>
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</tr>
<tr>
<td>950°C</td>
<td>Fe-14.7Cr</td>
<td>internal ppts.</td>
<td>small amount of lamellar $\text{M}_{23}\text{C}_6$</td>
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</tr>
<tr>
<td></td>
<td>Fe-24.4Cr</td>
<td>external scale</td>
<td>-</td>
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Table 6. (continued)

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<th>Carburization Prediction from Metastability Diagram</th>
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<tr>
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Table 6. (continued)

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<td>Oxide Morphology</td>
<td>Carbide Morphology</td>
<td>Carburization Prediction from Metastability Diagram</td>
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<td>internal ppts.</td>
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<th>Carburization Prediction from Metastability Diagram</th>
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<td>internal ppts.</td>
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<td>Ni-15Cr</td>
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<td>external scale</td>
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<td>external scale</td>
<td>-</td>
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<tr>
<td></td>
<td>Fe-14.7Cr</td>
<td>internal ppts./</td>
<td>-</td>
<td>yes</td>
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<td></td>
<td>external scale</td>
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<th>Carbide Morphology</th>
<th>Carburization Prediction from Metastability Diagram</th>
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<td>internal ppts.</td>
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<td>no</td>
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<td>950°C</td>
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<td>Ni-15Cr</td>
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<td>no</td>
</tr>
<tr>
<td></td>
<td>Ni-21.4Cr</td>
<td>ingrown external scale</td>
<td>-</td>
<td>no</td>
</tr>
<tr>
<td>P_{CO}/P_{CO} = 0.15</td>
<td>Fe-14.7Cr</td>
<td>internal ppts./external scale</td>
<td>lamellar $M_{23}C_6$ beneath internal oxides</td>
<td>no</td>
</tr>
<tr>
<td></td>
<td>Fe-19.4Cr</td>
<td>external scale</td>
<td>-</td>
<td>yes</td>
</tr>
<tr>
<td></td>
<td>Fe-24.4Cr</td>
<td>external scale</td>
<td>-</td>
<td>yes</td>
</tr>
</tbody>
</table>
only occurred in the alloy that was two alloys more concentrated than the prediction. In most experiments the difference between the prediction and experiment amounts to only a few weight percent Cr. However, in the case of the Ni-Cr alloys the predictions cannot be adequately evaluated because carburization was never observed in these alloys. For alloys that formed external scales carburization was often absent because Cr$_2$O$_3$ scales probably act as a barrier to carbon penetration.

This remarkably close prediction for carburization occurs even though the alloy/carbide equilibria lines on the metastable diagrams were based on the assumption that pure Cr$_{23}C_6$ was present. However, as discussed in Chapter II, these carbides dissolve substantial amounts of iron so that the Gibbs free energy of formation of an alloy carbide can be somewhat lower than that of the pure carbide. This, in turn, lowers the carbon activity for the alloy/carbide equilibrium. This shift is in the proper direction to explain the small disparity between the predictions and experiments. Another factor can cause a shift in these boundary positions. The interaction parameter of carbon upon chromium is about -11 at 950°C which will cause the activity of chromium to decrease in the presence of carbon (the magnitude depends upon the amount of carbon). Thus, dissolution of carbon from the gas into the alloy causes the stable alloy field to expand which is opposite the shift due to the consideration of alloy carbides rather than pure carbides. There is probably a complex interplay between these two factors which will establish the true position of the alloy/carbide boundaries. Unfortunately, no free
energy data are available for these alloy carbides. Also, since carbon concentration profiles change with time due to diffusion, the carbon activity for equilibrium between the alloy and the carbide will vary with position in the alloy.

Upon comparing experiments 2 and 10, an interesting fact is observed - even though experiment 10 had a higher carbon activity than experiment 2, no carburization was observed in experiment 10. In experiment 10, only the three most concentrated alloys were selected so that both Ni-Cr and Fe-Cr alloys could be studied in one experiment. The Fe-14.7wt.% Cr alloy formed both an external scale and internal precipitates while the Fe-19.4 and 24.4wt.% Cr alloys formed exclusive external scales. Remember that in experiment 2 carburization was observed beneath the oxide scales. The important difference between the two experiments is that the scales in experiment 10 spalled almost completely upon cooling leaving a shiny surface while the scales in experiment 2 were more adherent. Two SEM photographs of the surface of the Fe-24.4wt.% Cr after experiment 10 are shown in Figs. 69 and 70. Figure 69 shows one of the very few areas where the scale remained on the alloy. Note the large voids at the scale/alloy interface and the small areas where the scale is actually in contact with the alloy. This sample was tilted to reveal these voids as well as the oxide whiskers growing out from the surface of the oxide. Figure 70 shows a more representative area (untilted) where the scale had spalled completely. Again note the small contact area between the scale and the alloy. If carbon can diffuse into the alloy only through areas where the scale is in contact with the alloy (no gas
Figure 69. Scanning electron micrograph of the surface of an Fe-24.4wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.08$ for 12h. 900X.
Figure 70. Scanning electron micrograph of the surface of an Fe-24.4wt. % Cr alloy reacted at 950°C with \( P_{\text{CO}_2}/P_{\text{CO}} = 0.08 \) for 12h. 1000X.
phase transport) then a larger fraction of voids at the scale/alloy interface would hinder carburization. Since the scales in experiment 2 did not spall we believe that the fraction of voids was small which permitted better scale adhesion. Consequently, carbon could diffuse into the alloy and cause carbide precipitation. The reason for the difference in the fraction of voids at the alloy/scale interface in the two experiments is probably due to a differing preparation of the specimen prior to reaction. Before experiment 2, the samples were annealed for 2 hours in argon which had been purified by passing over titanium sponge at about 800°C. After the anneal, the samples were raised from the furnace hot zone and some superficial oxidation of chromium was discovered. The samples were removed from the apparatus and lightly re-abraded on 600 grit SiC paper to remove the oxide. The samples were then replaced and the experiment started. In all subsequent work (including experiment 10) the samples were annealed in flowing hydrogen which produced no visible oxide. Thus, the samples were not removed and re-abraded. The extra amount of cold work in experiment 2 could cause better scale adhesion since dislocations near the scale/alloy interface could act as condensation sites for the vacancies produced by the diffusion of chromium atoms outward to form the scale. Recrystallization at the surface probably took place in experiment 2. Thus, a higher grain boundary area due to the fine grain size at the surface was present and these grain boundaries could act as vacancy sinks also. Consequently, the existence of extra cold work at the alloy surface could cause better scale adhesion because the vacancies produced by chromium diffusion would not
nucleate voids if sinks were available to absorb them. Alternatively, the H₂-anneal may have introduced dissolved H into the alloy, which upon oxidation could lead to H₂O(vapor) at the metal/scale interface. But, between each anneal and experiment, the samples were cooled above the furnace and held for about 16 hours in flowing argon to allow hydrogen to diffuse out of each sample before reaction in the CO/CO₂ gas. Therefore, the effect of water vapor was probably minimal. This scale-adhesion argument naturally applies for only those alloys that scale. The Fe-14.7wt.% Cr alloy also did not carburize even though a continuous external scale was not present. It did have areas of intermittent scale formation which can act as barriers to carbon penetration into the alloy. Therefore, the flux of carbon into the alloy occurs essentially in the internal oxidation zone regions and thus, the total amount of carbon in the alloy is too low to cause carbide precipitation.

Let us now consider reasons for the denuded zone between the internal oxidation zone (or external scale) and internal carbides. Since Cr₂O₃ is a corrosion product (most stable phase in the gas) at the surface of the alloy, chromium atoms must diffuse from the interior of the alloy to replenish those lost to oxidation. Also, since a certain minimum amount of chromium is required to precipitate a carbide (based upon a solubility product argument), the presence of chromium depletion near the alloy surface might explain the denuded zone. The chromium concentration in the denuded zone may be just too low to form carbides. Chromium concentration profiles were therefore determined by electron probe microanalysis (EPMA) in all of the alloys used in
experiment 2. The ratio of the intensity of chromium radiation given off at a point in the alloy to the intensity of a pure chromium standard (the k-ratio) was used to determine the concentration of chromium in the alloy. A commercially available computer program (FRAME) was used to correct the k-ratio for atomic number, absorption and fluorescence effects (ZAF correction) to arrive at the weight percent Cr at various postitions in the alloy. Generally, concentrations were determined in 5 to 10 micron intervals. The microprobe traces are given in Figs. 71 through 77. A sketch of the morphology is shown above each trace. In Figs. 71 and 72 only internal oxidation occurs with little chromium depletion in advance of the internal oxidation front. For the Fe-9.9wt.% Cr alloy shown in Fig. 73, significant chromium depletion in the denuded zone is observed near carbide precipitates. In Figure 74 a large amount of depletion in the region near carbides is seen but, in the denuded zone very little depletion apparently occurred. Figure 75 shows the Fe-14.7wt.% Cr trace which clearly shows the composition difference between the α and γ phases. In this case, there is some depletion in the γ layer near the surface. This area was selected for analysis because no carbides were observed beneath this small section of external scale. Figures 76 and 77 show the concentration profiles for the alloys that scales: Fe-19.4 and 24.4wt.% Cr. The depletion of chromium in the denuded zone is shown for both alloys. The chromium concentration of the alloy in equilibrium with its carbide is about 18wt.% for the 19.4% alloy (Fig. 76) while it is about 23% for the 24.4% alloy (Fig. 77). Figure 78 shows a schematic isothermal section of the Fe-Cr-C ternary diagram
Figure 71. Chromium concentration profile in the Fe-2.0 wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.11$ for 12h.
Figure 72. Chromium concentration profile in the Fe-4.9 wt.% Cr alloy reacted at 950°C with \( \frac{P_{CO_2}}{P_{CO}} = 0.11 \) for 12h.
Figure 73. Chromium concentration profile in the Fe-9.9wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h.
Figure 74. Chromium concentration profile in the Fe-11.8wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h.
Figure 75. Chromium concentration profile in the Fe-14.7 wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.11$ for 12h.
Figure 76. Chromium concentration profile in the Fe-19.4\% Cr alloy reacted at 950°C with $P_{CO_2}/P_CO = 0.11$ for 12h.
Figure 77. Chromium concentration profile in the Fe-24.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_CO = 0.11$ for 12h.
Figure 78. Schematic isothermal ternary section of the Fe-Cr-C system.
in which the $\gamma/M_{23}C_6$ equilibrium is considered. On this diagram the $M_{23}C_6$ carbide is considered to be stoichiometric with respect to carbon. Also, the approximate compositions from EPMA for the $\gamma/M_{23}C_6$ equilibrium are shown for the Fe-19.4 and 24.4wt.% Cr alloys, 18 and 23wt.% Cr, respectively. The figure shows that because these chromium contents are different for the two alloys that the carbon activities must also be different, i.e., the alloy/carbide equilibria lie on different tie-lines. Thus, if chromium depletion is to explain the absence of carburization, then the carbon activity at the scale/alloy interface must be lower for the Fe-24.4wt.% Cr alloy than that for the Fe-19.4wt.% Cr alloy. It is certainly possible that the scale found on each alloy was slightly different (either chemically or physically). Consequently, the carbon transport through the scale, e.g., through microcracks or by lattice diffusion, could have been greater (establishing a higher carbon activity at the scale/alloy interface) in the case of the Fe-19.4wt.% Cr alloy. This would explain the different chromium contents for the alloy/carbide equilibrium for the two different alloys even though they were reacted in the same gas. But, in the case of the internally oxidized alloys that carburized, the chromium content for the alloy/carbide equilibrium in the Fe-9.9wt.% Cr alloy is lower than that for the Fe-11.8wt.% Cr alloy. Therefore, the carbon activity must again be different for these two alloys. In both of these alloys, however, there is no physical barrier which could account for different carbon activities in the two alloys.
We can also develop another explanation for the denuded zones based upon thermodynamic interaction effects (mentioned briefly already). The presence of carbon lowers the activity of chromium, i.e., the interaction parameter, $e_{Cr}^C$, is negative. Thus, a carbon gradient in the alloy also implies an opposite chromium gradient even if there is no chromium depletion. When chromium depletion due to scale growth is also present, the effect is more pronounced. Figure 79 shows the two generally observed corrosion morphologies: A, internal oxidation with carburization and B, external scaling with carburization. In Fig. 79 a schematic isothermal phase stability diagram is shown. On this diagram, reaction path information is presented schematically. Since the presence of carbon decreases the chromium activity, near the surface of the alloy where the carbon activity is high, the chromium activity is lower than inside the alloy where the carbon activity is low. On the diagram $a'_C$ represents the carbon activity at the gas/alloy interface (internal oxidation) or the scale/alloy interface (external scaling) and $a''_C$ represents the carbon activity inside the alloy where it has little, if any, effect on the chromium activity. Since a carbon gradient is established from the alloy surface to the alloy interior for relatively short reaction times, there will be a corresponding chromium activity gradient. Thus, the alloy/carbide equilibrium will exist at various carbon activities based upon the changing chromium activities. This implies a curved alloy/carbide boundary. Schematic reaction paths are shown for both the case of carburization beneath internal oxidation (A) and carburization beneath an external scale (B). These
Figure 79. Schematic reaction paths plotted on a metastability diagram for both external scale formation and internal oxidation. The interaction of carbon on chromium activity is considered to explain denuded zones.
reaction paths have been constructed to show how denuded zones can be present depending upon the carbon gradient in the alloy. At equilibrium, however, when diffusion has eliminated the carbon gradient, then the more conventional stability diagram applies and denuded zones should not be present.

We have given two possible reasons for the denuded zone between oxidation and carburization zones in Fe-Cr alloys upon reaction in CO/CO$_2$ gas mixtures. The first was based upon chromium depletion only, in which it was pointed out that the carbon activity must be lower for a given alloy compared to a more dilute alloy. The second involved the ternary interaction effect of carbon on the chromium activity. The chromium activity was shown to be reduced at the alloy surface (where the carbon activity is high) compared to the bulk alloy (where the carbon activity is low) due to thermodynamic interaction effects. But, a more accurate explanation probably involves both factors. Just as the presence of carbon lowers the chromium activity, chromium also lowers the carbon activity. So, for a constant carbon content in an alloy, a chromium gradient will cause an opposite carbon activity gradient. This effect is in the right direction to explain how the carbon activity could be lower at the alloy/carbide boundary for a concentrated alloy compared to a more dilute one.

Metallographic Observations

The remainder of this chapter contains selected scanning electron micrographs of the exterior surfaces of alloys after reaction in various gas mixtures. Figure 80 shows an area which formed an external scale on the Fe-14.7wt.% Cr alloy in experiment 4 (950°C,
Figure 80. Scanning electron micrograph of the surface of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.25$ for 12h. 2000X.
PCO2/PCO = 0.25). The lower right corner of the micrograph shows a region where the scale is still attached while the rest shows the underlying alloy where the scale spalled. In the area where the scale spalled, the voids at the scale/alloy interface are readily seen. Figure 81 shows the surface the Fe-19.4wt.% Cr alloy used in the same experiment. In this micrograph, the lower portion shows the scale still attached but in the upper portion the scale has spalled. The voids at the scale/alloy interface are again visible. X-ray maps for Cr and Fe, which correspond to the secondary electron image of Fig. 81, are shown in Figs. 82 and 83, respectively. The high concentration of Cr and low concentration of Fe in the lower region (a higher density of spots means a higher concentration) is an indication that the lower region is Cr2O3. Also, the X-ray diffraction results of Table 5 show that Cr2O3 is present. Figure 84 shows another area of the same sample with the scale on the left side of the micrograph. The corresponding X-ray maps are given in Figs. 85 and 86. Note the difference between Figs. 81 and 84. In Fig. 81 the scale appears to have spalled very near the scale/alloy interface since the voids are clearly visible, while in Fig. 84, the scale has fractured somewhere within its cross-section. Figure 87 shows a higher magnification view of Fig. 84. Thus, a Cr2O3 scale formed under these experimental conditions can spall by scale fracture within the scale or by fracture near the scale/alloy interface.

Figure 88 shows the surface of the Fe-2.0wt.% Cr alloy used in experiment 5 (950°C, PCO2/PCO = 0.35). X-ray diffraction showed that Fe3O was present on the surface (see Table 5). Figure 89 shows the
Figure 81. Scanning electron micrograph of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.25$ for 12h. 1000X.
Figure 82. Cr-Kα X-ray map of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with \( P_{\text{CO}_2}/P_{\text{CO}} = 0.25 \) for 12h. 1000X.
(corresponds to previous secondary electron image)
Figure 83. Fe-K$_\alpha$ X-ray map of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.25$ for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 84. Scanning electron micrograph of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.25$ for 12h. 1000X.
Figure 85. Cr-K$_\alpha$ X-ray map of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with P$_{CO_2}$/P$_{CO}$ = 0.25 for 12h. 1000X.
(corresponds to previous secondary electron image)
Figure 86. Fe-Kα X-ray map of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.25$ for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 87. Scanning electron micrograph of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.25$ for 12h. 2000X.
Figure 88. Scanning electron micrograph of the surface of an Fe-2.0wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.35$ for 12h. 1000X.
Figure 89. Scanning electron micrograph of the surface of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.35$ for 12h. 1500X.
Fe-14.7wt.% Cr alloy used in the same experiment. Fe\textsubscript{x}O and FeCr\textsubscript{2}O\textsubscript{4} were found by X-ray diffraction as shown in Table 5. The discrete round phase on the top is probably Fe\textsubscript{x}O while the underlying phase is probably FeCr\textsubscript{2}O\textsubscript{4}. The underlying phase appears to be continuous in some areas but in others it appears as channels. These channels may have formed on pre-existing polishing scratches from the sample preparation technique. Figure 90 shows the surface of the Fe-19.4wt.% Cr alloy from the same experiment. X-ray maps are also shown for Cr and Fe in Figs. 91 and 92, respectively. Considering all three figures, the large-grained phase at the bottom of Fig. 90 is wüstite, the fine-grained phase in the middle is spinel and, at the top of the micrograph, a Cr\textsubscript{2}O\textsubscript{3} scale is shown. X-ray diffraction substantiated the presence of all three phases (Table 5).

Figure 93 shows the surface of the Fe-4.9wt.% Cr alloy exposed in experiment 6 (850°C, P\textsubscript{CO\textsubscript{2}}/P\textsubscript{CO} = 0.31). The channels again probably result from the pre-reaction specimen preparation. Although no X-ray diffraction data are available for positive identification, the small islands are probably Cr\textsubscript{2}O\textsubscript{3} because the small amount of chromium in this alloy is not enough to form a continuous scale. Discrete precipitates of Cr\textsubscript{2}O\textsubscript{3} are formed inside the alloy and they should also be present on the surface. Corresponding to the precipitation of Cr\textsubscript{2}O\textsubscript{3}, iron must diffuse away from the precipitates; therefore, iron crystals may also be present on the surface since iron is stable in the gas. The surface of the Fe-9.9wt.% Cr alloy after the same experiment is shown in Fig. 94. A higher magnification view is given in Fig. 95 with corresponding X-ray maps for Cr and Fe in Figs. 96 and 97,
Figure 90. Scanning electron micrograph of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with \( \frac{P_{CO_2}}{P_{CO}} = 0.35 \) for 12h. 1000X.
Figure 91. Cr-K$_\alpha$ X-ray map of the surface of an Fe-19.4 wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO}$ = 0.35 for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 92. Fe-Kα X-ray map of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with P_{CO_2}/P_{CO} = 0.35 for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 93. Scanning electron micrograph of the surface of an Fe-4.9wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1000X.
Figure 94. Scanning electron micrograph of the surface of an Fe-9.9wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1000X.
Figure 95. Scanning electron micrograph of the surface of an Fe-9.9wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1800X.
Figure 96. Cr-\(K\alpha\) X-ray map of the surface of an Fe-9.9wt.% Cr alloy reacted at 850°C with \(P_{\text{CO}_2}/P_{\text{CO}} = 0.31\) for 12h. 1800X. (corresponds to previous secondary electron image)
Figure 97. Fe-K$_\alpha$ X-ray map of the surface of an Fe-9.9wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1800X. (corresponds to previous secondary electron image)
respectively. Because Fig. 96 shows essentially no chromium above background levels in the regions of the large crystals, the crystals on the surface are concluded to be pure iron. Figure 98 shows the surface of the Fe-11.8wt.% Cr alloy after the same experiment. Figures 99 and 100 give the corresponding X-ray maps for Cr and Fe, respectively. The lower left and upper right corners of the micrograph shows discrete islands which resemble those of Figs. 94 and 95. Consequently, these are identified as pure Fe. Bounding the areas which contain the islands, a somewhat rumpled area is seen and then further still a smoother area. These are more easily seen by comparing both the secondary electron image (Fig. 98) and the X-ray maps (Figs. 99 and 100). The rumpled area (particularly noticeable at the center bottom of Fig. 98) is probably FeCr₂O₄ while the smoother areas are probably Cr₂O₃. Figure 101 shows the external scale formed on the Fe-24.4wt.% Cr alloy during the same experiment. It does not appear to be as continuous and protective as the scales formed at 950°C. The oxide grains seem to have just began to grow together in some regions while the alloy grain boundaries are still visible in others. The X-ray maps that correspond to Fig. 101 are shown in Figs. 102 and 103. Notice that in the regions where the oxide grains have begun to grow together, the iron concentration is lower than in the other region. This is an indication of the porous nature of this scale.

Figure 104 shows the surface of the Fe-9.9wt.% Cr alloy after experiment 7 (850°C, \( \frac{P_{CO_2}}{P_{CO}} = 0.48 \)). This sample has been tilted and shows wüsite growing from the surface (X-ray diffraction shows that wüsite is present). Figure 105 shows a low magnification view
Figure 98. Scanning electron micrograph of the surface of an Fe-11.8wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 550X.
Figure 99. Cr-Kα X-ray map of the surface of an Fe-11.8wt.% Cr alloy reacted at 850°C with P_{CO_2}/P_{CO} = 0.31 for 12h. 550X. (corresponds to previous secondary electron image)
Figure 100. Fe-Kα X-ray map of the surface of an Fe-11.8wt.% Cr alloy reacted at 850°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.31$ for 12h. 550X. (corresponds to previous secondary electron image)
Figure 101. Scanning electron micrograph of the surface of an Fe-24.4wt.% Cr alloy reacted at 850°C with $\frac{P_{CO_2}}{P_{CO}} = 0.31$ for 12h. 1000X.
Figure 102. Cr-K$_\alpha$ X-ray map of the surface of an Fe-24.4wt.% Cr alloy reacted at 850°C with P$_{CO}$/P$_{CO}$ = 0.31 for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 103. Fe-Kα X-ray map of the surface of an Fe-24.4wt.% Cr alloy reacted at 850°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.31$ for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 104. Scanning electron micrograph of the surface of an Fe-9.9wt.% Cr alloy reacted at 850°C with $\frac{P_{CO_2}}{P_{CO}} = 0.48$ for 12h. 1200X.
of the surface of the Fe-11.8wt.% Cr alloy used in the same experiment. Figures 106 and 107 give the corresponding X-ray maps for Cr and Fe, respectively. The regions of high chromium intensity (Fig. 106) are probably spinel regions because the iron intensity (Fig. 107) is slightly lower in the same region. If these regions of high chromium intensity were Cr$_2$O$_3$, we would expect much lower iron intensities. Figure 108 shows a higher magnification view of the same sample. The crystals that are growing from the surface are probably wustite.

Figure 109 shows the surface of the Fe-24.4wt.% Cr alloy after the same experiment. The corresponding X-ray maps are shown in Figs. 110 and 111. Again the scale formed at this temperature appears very porous. The center area of Fig. 109 may be spinel since there is a slight chromium depletion and iron enrichment in that region (Cr$_2$O$_3$ has 68.4% Cr, FeCr$_2$O$_4$ has 46.5% Cr with 25.0% Fe).

Figure 112 shows the Ni-5wt.% Cr alloy surface after experiment 9 ($850^\circ$C, P$_{CO2}$/P$_{CO} = 0.31$). The corresponding X-ray images for Cr and Ni are shown in Figs. 113 and 114. By considering the X-ray maps we can see that in Fig. 112 Cr$_2$O$_3$ grows outward at the alloy grain boundaries and discrete crystals of pure nickel are present (NiO is unstable in the gas). Thus, the diffusion of chromium outward along alloy grain boundaries is much faster than the transport of oxygen into the alloy. This is in contrast to Fe-Cr alloys where grain boundary oxidation was not observed but, instead, discrete oxide precipitates were formed inside the alloy. Figure 115 shows the surface of the Ni-6.75wt.% Cr alloy after the same experiment. Regions of pure nickel crystals are shown as well as grain boundary oxidation.
Figure 105. Scanning electron micrograph of the surface of an Fe-11.8wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.48$ for 12h. 100X.
Figure 106. Cr-Kα X-ray map of the surface of an Fe-11.8wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO}$ = 0.48 for 12h. 100X. (corresponds to previous secondary electron image)
Figure 107. Fe-K_x X-ray map of the surface of an Fe-11.9wt.% Cr alloy reacted at 850°C with P_{CO2}/P_{CO} = 0.48 for 12h. 100X. (corresponds to previous secondary electron image)
Figure 108. Scanning electron micrograph of the surface of an Fe-11.8wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.48$ for 12h. 1000X.
Figure 109. Scanning electron micrograph of the surface of an Fe-24.4wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.48$ for 12h. 1300X.
Figure 110. Cr-Kα X-ray map of the surface of an Fe-24.4wt.% Cr alloy reacted at 850°C with P_{CO2}/P_{CO} = 0.48 for 12h. 1300X. (corresponds to previous secondary electron image)
Figure 111. Fe-Kα X-ray map of the surface of an Fe-24.4wt.% Cr alloy reacted at 850°C with P_{CO}/P_{CO} = 0.48 for 12h. 1300x. (corresponds to previous secondary electron image)
Figure 112. Scanning electron micrograph of the surface of a Ni-5wt.% Cr alloy reacted at 850°C with \( P_{CO_2}/P_{CO} = 0.31 \) for 12h. 1000X.
Figure 113. Cr-Kα X-ray map of the surface of a Ni-5wt.% Cr alloy reacted at 850°C with $P_{CO}/P_{CO}_2 = 0.31$ for 12h. 1000X. (corresponds to previous Secondary electron image)
Figure 114. Ni-Kα X-ray map of the surface of a Ni-5wt.% Cr alloy reacted at 850°C with \( \frac{P_{\text{CO}_2}}{P_{\text{CO}}} = 0.31 \) for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 115. Scanning electron micrograph of the surface of a Ni-6.75wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1000X.
of chromium. Whiskers of oxide are also visible on the grain boundary oxides. This implies that the scale grows at the gas/scale interface by chromium diffusion outward through the scale. The surface of the Ni-10wt.% Cr alloy is shown in Fig. 116. The volume fraction of oxide has increased with oxide grains growing together. Pure nickel crystals are also present in Fig. 116 as shown by the corresponding X-ray maps of Figs. 117 and 118. Figure 119 shows the surface of the Ni-15wt.% Cr alloy reacted in the same experiment (9). The specimen has been tilted to reveal the oxide whiskers growing outward from the surface of the oxide. The scale appears to be somewhat porous and, therefore, might not be very protective. Figure 120 shows the surface of the Ni-21.4wt.% Cr alloy after the same experiment. Whiskers are again present on the oxide surface. In some areas oxide grains have grown together to form an apparently protective scale while in other areas oxide grains are visible. An X-ray scan for Ni showed that no Ni was present in the area of Fig. 120. Another view of the same sample is shown in Fig. 121. By looking at the corner of the sample the length of the oxide whiskers is very clearly seen. Perhaps the low oxygen activity in these gases promotes whisker formation. If a local instability occurs then a whisker may form and grow into the gas to react with available oxygen. An oxygen activity gradient in the gas would result and, therefore, promote further growth.

Figures 122 and 123 show a region on the surface of the Fe-14.7 wt.% Cr sample after experiment 10 (950°C, P_{CO_2}/P_{CO} = 0.08). This is a view of an area that formed an external scale. The scale does not appear very protective and optical metallography did show internal
Figure 116. Scanning electron micrograph of the surface of a Ni-10wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1000X.
Figure 117. Cr-K\alpha X-ray map of the surface of a Ni-10wt.% Cr alloy reacted at 850°C with P_{CO2}/P_{CO} = 0.31 for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 118. Ni-K\(_\alpha\) X-ray map of the surface of a Ni-10wt.% Cr alloy reacted at 850°C with \(P_{\text{CO}_2}/P_{\text{CO}} = 0.31\) for 12h. 1000X. (corresponds to previous secondary electron image)
Figure 119. Scanning electron micrograph of the surface of a Ni-15wt.% Cr alloy reacted at 850°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.31$ for 12h. 2000X.
Figure 120. Scanning electron micrograph of the surface of a Ni-21.4wt.% Cr alloy reacted at 850°C with P_{CO_2}/P_{CO} = 0.31 for 12h. 1800X. (Note: EDAX shows no Ni peak)
Figure 121. Scanning electron micrograph of the surface of a Ni-21.4wt.% Cr alloy reacted at 850°C with $P_{CO_2}/P_{CO} = 0.31$ for 12h. 1800X. (sample tilted to observe whiskers)
Figure 122. Scanning electron micrograph of the surface of an Fe-14.7wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 300X.
Figure 123. Scanning electron micrograph of the surface of an Fe-14.7wt.% Cr alloy reacted at 950°C with $\frac{P_{CO_2}}{P_{CO}} = 0.08$ for 12h. 1500X. (higher magnification view of spalled area on previous figure)
precipitates as well as the scale (see Table 6). The center region of Fig. 122 shows an area where the oxide has spalled. This area is shown at higher magnification in Fig. 123. The surface of the alloy beneath the scale shows steps which may have formed by the vaporization of chromium from preferred crystallographic planes. The chromium must be transported via the gas phase; from the alloy surface through the voids formed by oxidation and finally to the underside of the oxide layer. Figure 124 shows the surface of the Fe-19.4wt.% Cr alloy after experiment 10. Whiskers are also present here and the scale does not appear to be protective in some areas since depressions between oxide grains are visible. The surface of the Fe-24.4wt.% Cr alloy has already been shown in Figs. 69 and 70. Even on this alloy (where the scale did not spall) there are regions where the oxide grains have not grown completely together to form a coherent scale (see lower right corner of Fig. 69). Figure 125 shows the Ni-5wt.% Cr alloy after experiment 10. Figures 126 and 127 give the corresponding X-ray maps for Cr and Ni, respectively. From these we see that chromium oxide is present at the alloy grain boundaries and is growing outward. Presumably this is due to the outward diffusion of chromium along the alloy grain boundaries. A higher magnification view of Fig. 125 is given in Fig. 128. This figure shows the $\text{Cr}_2\text{O}_3$ at the grain boundaries to be more compact than that further away from the grain boundaries where individual oxide grains are seen. Figure 129 shows the increased volume fraction of $\text{Cr}_2\text{O}_3$ on the surface of the Ni-15wt.% Cr alloy. Small regions where a smooth, compact scale formed are visible along with areas where oxide islands are present.
Figure 124. Scanning electron micrograph of the surface of an Fe-19.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 1000X.
Figure 125. Scanning electron micrograph of the surface of a Ni-5wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 500X.
Figure 126. Cr-Kα X-ray map of the surface of a Ni-5wt.% Cr alloy reacted at 950°C with $P_{\text{CO}_2}/P_{\text{CO}} = 0.08$ for 12h. 500X. (corresponds to previous secondary electron image)
Figure 127. Ni-K$_\alpha$ X-ray map of the surface of a Ni-5wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 500X. (corresponds to previous secondary electron image)
Figure 128. Scanning electron micrograph of the surface of a Ni-5wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 1800X.
Figure 129. Scanning electron micrograph of the surface of a Ni-15wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 500X.
The external scale formed on the Ni-21.4wt.% Cr alloy is shown in Fig. 130. This scale appears porous in some areas and compact in others as did the other scales formed on this alloy at different temperatures and gas mixtures. But, in this case optical metallography showed a compact scale with very little ingrown oxide.

In summary, the scanning electron microscopy results showed the surface morphology of selected samples. X-ray mapping and X-ray diffraction were used as an aid to identify, wherever possible, surface oxides and pure metal phases. These results can be compared with the available optical metallography results (Table 6) to determine if the appearance of various types of scales can be correlated with protective or non-protective behavior. Some scales were not compact and smooth but had small channels or pores between oxide grains. One would not normally classify these as protective but perhaps these channels do not continue completely inward to the alloy surface. The absence of carburization in alloys with this type of scale tends to support this idea. Also, in some cases these channels may disappear with longer oxidation times because some areas appear compact and smooth. This was particularly noted in the oxidation of the dilute Ni-Cr alloys where the oxide formed at the alloy grain boundaries was not as porous as that formed away from the boundaries. This probably occurs because the flux of chromium outward must pass through the previously formed oxide at the grain boundaries. It can react with oxygen in the channels to form new oxide, which reduces the size of the pores. Thus, a finite amount of chromium arriving at the surface goes to "channel filling" while the rest diffuses further
Figure 130. Scanning electron micrograph of the surface of a Ni-21.4wt.% Cr alloy reacted at 950°C with $P_{CO_2}/P_{CO} = 0.08$ for 12h. 1000X.
out along the surface to form new oxide grains away from the boundary.
VI. SUMMARY AND CONCLUSIONS

The combined oxidation and carburization of Fe-Cr and Ni-Cr alloys in CO/CO₂ gas mixtures has been investigated. This two-component gas mixture was selected to simplify a complex coal gasification atmosphere containing many oxidants. Previous work on Ag-In alloys indicated that the critical In content needed for an alloy to passivate (form a compact, adherent external scale) decreases as the oxygen activity in the gas is lowered. This was not observed with the Fe-Cr and Ni-Cr alloys reacted in CO/CO₂ gases. Generally, 20-25wt.% Cr is needed in an alloy to ensure formation of an external Cr₂O₃ scale in air (P₀₂ = 0.21 atm). In the CO/CO₂ gases of this investigation (P₀₂ ~ 10⁻¹⁸ atm), we have found that 20-25wt.% Cr is also needed to avoid internal oxidation of chromium. Perhaps the presence of a second oxidant in the gas (carbon) negates the effect of low oxygen activity on the transition from internal oxidation to external scaling. Furthermore, on the basis of this research, alloy design for oxidation resistance in coal gasification atmospheres can, therefore, follow the well-established guidelines for service in air.

A method for predicting the onset of carburization based upon thermodynamic metastability diagrams has been developed for the first time. The predictions are remarkably close to the experimental observations. However, more accurate thermodynamic data are necessary to
develop a more quantitative model. The amount of carburization in the alloys that formed external oxide scales was less than that found in alloys that internally oxidized. Thus, we conclude that Cr₂O₃ acts as a barrier to carbon penetration. The mechanism for the transport of carbon through the scale, e.g. by lattice diffusion or by transport through microcracks, is not known. Since alloys are designed to form external oxide scales for oxidation resistance, the presence of these scales will increase carburization resistance.

The presence of a hard grain-boundary phase in an alloy is known to degrade the mechanical properties. Thus, the influence of grain-boundary carbides on the mechanical properties of these alloys should be studied in the future to determine the magnitude of this effect. Also, the precipitation of chromium-based carbides causes a depletion of chromium in the alloy matrix. Thus, the amount of chromium available to maintain the external scale is decreased and the possibility of scale break-down exists. Long-term testing of the alloys being considered for coal gasification service is needed to determine if more chromium is needed in certain alloys to compensate for this effect.

More research on the Gibbs energy of formation of alloy carbides is also needed. The thermodynamic predictions in this investigation were based upon calculations using the Gibbs free energy of formation of pure chromium carbides. But these carbides can dissolve substantial amounts of iron (as well as other elements) so that the free energy of formation of a particular alloy carbide can be quite different from that of the pure carbide. Thus, the predictions for carburization
could be modified if more accurate data were available.

Carburization and oxidation of Fe-Cr and Ni-Cr binary alloys only have been considered thus far. A logical extension of this research would be to study the combined oxidation and carburization of ternary Fe-Ni-Cr alloys. The activity of chromium in these alloys is already available so that predictions based upon the same principles can be applied. Again, it would be very useful to have free energy data for the alloy carbides in this system so that accurate predictions could be made.

In all of the experiments of this study, CO/CO$_2$ gases were used to establish the oxygen activity and carbon activity of the gas. With this mixture, the oxygen activity and carbon activity cannot be varied independently. Instead, all gas mixtures exist along a line of constant total pressure. Also, for Fe-Cr alloys in CO/CO$_2$ gases, the gas cannot be made reducing enough (the carbon activity would have to be greater than one) to make the spinel, FeCr$_2$O$_4$, unstable. However, if the oxygen activity could be varied independently of the carbon activity, then one could do experiments in a gas mixture where spinel is unstable and Cr$_2$O$_3$ is the only stable oxide. There may be a difference in oxide morphology, or even the composition where the transition from internal precipitation to external scaling occurs, depending upon whether the spinel can form. In the case of Ni-Cr alloys all experiments were done with NiCr$_2$O$_4$ unstable. The difference in oxide morphology between the Fe-Cr and Ni-Cr alloys may be due to this effect. In order to achieve independence between the oxygen activity and carbon activity a more complex gas could be used. A CH$_4$/H$_2$O/H$_2$ gas
is suggested for this. The carbon activity is set by the CH$_4$/H$_2$ ratio while the oxygen activity is set by the H$_2$O/H$_2$ ratio. Of course, CO and CO$_2$ would also be formed in a gas with methane, hydrogen and water vapor as the initial components. Consequently, the approach toward internal equilibrium in the gas may be sluggish. Nevertheless, the gas could be passed over a platinum catalyst at the reaction temperature to ensure that equilibrium is reached before reaction with the alloy samples.

A theoretical model for dual internal precipitation in alloys reacted in two-oxidant gases was developed before the experimentation. The model postulates two adjacent zones of internal precipitation. Since the experiments show a denuded zone between both regions of precipitation it is of little use in this alloy system. However, it may be valid in other alloy systems or other gases. Consequently, the model is presented in the Appendix.
ON THE KINETICS OF INTERNAL PRECIPITATION IN GASES CONTAINING TWO OXIDANTS

INTRODUCTION

In various stages and components of the different processes encountered in coal gasification and other processes involving fossil fuels, multi-component alloys come into contact at elevated temperatures with gases containing multiple oxidants: oxygen, sulfur, carbon, etc. Often these gases will exist at low oxygen activities. Previous studies\(^1\) in low oxygen activity mixed environments have shown, for example, that carbides and sulfides of chromium precipitate beneath a \(\text{Cr}_2\text{O}_3\) scale on a Ni-Cr or Fe-Cr alloy. Obviously the internal precipitation of chromium carbides and sulfides would be detrimental in the maintenance of a protective \(\text{Cr}_2\text{O}_3\) scale, because of the depletion of Cr in the alloy.

While many studies have been reported on the singular internal oxidation, carburization, nitrification and sulfidation of alloys, the competition between these processes when an alloy is exposed to an environment of mixed reactants has not been examined. In gaseous reactions with mixed environments, e.g., gases with the mutual presence of oxygen and sulfur or of oxygen and carbon, the expectations for corrosion morphologies and kinetics need to be examined.

In this paper we consider theoretically a mixed gas of two potential oxidizing components, e.g., a \(\text{CO}/\text{CO}_2\) mixture, which
exhibits a low equilibrium oxygen activity. The gas mixture is assumed to react with a binary alloy in which one component is noble in the gas phase. To be specific, we consider Cr to be the reactive component since Cr is frequently present in high-temperature alloys and also forms a stable oxide, nitride, sulfide and carbide. To study specifically the competition in the internal precipitation reactions without the complicating formation of an external scale, the reactive Cr component in the bulk alloy is assumed to be dilute. The simpler, analogous problem of internal oxidation in oxygen of a dilute noble metal-base alloy has received considerable theoretical and experimental attention.$^{51,54}$

**Notation**

- $J_X, J_O$: flux of component $X$ and oxygen, respectively. $X$ could be carbon, for example.
- $D_X, D_O$: diffusivities of component $X$ and oxygen, respectively
- $N_X, N_O$: mole fractions of component $X$ and oxygen, respectively
- $N^S_X, N^S_O$: mole fractions at the gas/metal interface
- $N^O_{Cr}$: original mole fraction of Cr in the alloy
- $V_M$: molar volume of the alloy
- $I, II$: superscripts denoting Zone I and Zone II, respectively
- $\xi$: position of precipitation front for Zone I in the alloy
- $\chi$: position of precipitation front for Zone II in the alloy
MATHEMATICAL FORMULATION

In order to obtain an analytical solution we shall assume that the diffusivity of each component in the alloy is independent of its composition and the gradients in concentration of the other components, the internal precipitates are assumed to have no effect on the diffusion of the solutes in the alloy. We shall also assume that the molar volume of the alloy is independent of composition. The equations developed in this paper are described by the schematic model shown in Figure 131. The formulation of the presumed model is based on the following assumptions:

(1) The mixed gas environment is such that Cr₂O₃ is the thermodynamically most stable compound in the gas phase, but the compound CrXₙ is stable at the activity of X in the gas phase if the oxygen activity were less than P₀₂ (Cr-Cr₂O₃). These conditions are met in gas compositions within regime II of Fig. 28.

(2) The alloy is dilute in Cr so that an external scale does not form. Hence, internal precipitates of Cr₂O₃ are expected.

(3) Because the X components (carbon or sulfur) exhibit significant solubilities and diffusivities in the base metal, metastable carbides or sulfides would be expected to form in advance of the Cr₂O₃ precipitation front.

(4) The metastable compound CrXₙ (carbide or sulfide) is converted within the alloy to Cr₂O₃ via a displacement reaction between solute oxygen and CrXₙ precipitates.
Figure 131. Assumed concentration profiles for dual internal precipitation in two-oxidant gases.
(5) Both of the compounds \( \text{CrX}_\gamma \) and \( \text{Cr}_2\text{O}_3 \) are relatively quite stable so that negligible solute Cr remains in solution in the presence of the solutes \( X \) or \( O \), respectively.

We may now proceed by considering the flux balance at the internal oxidation (displacement reaction) front, \( \xi \).

The flux of \( X \) in Zone II is given by

\[
J^{II}_X = J^I_X + \Delta J_X
\]  

(93)

where \( \Delta J_X \) is the increase in the flux of \( X \) due to the displacement reaction

\[
\Delta J_X = \frac{2\gamma}{3} J^I_O
\]  

(94)

Fick's first law may be written in conjunction with the reaction zone interface velocities

\[
J^{II}_X = \frac{D_X N_X^\xi}{V_M (X-\xi)} = \frac{\gamma N^O}{V_M} \cdot \frac{dX}{dt}
\]  

(95)

\[
J^I_X = \frac{D_X (N_X^S - N_X^\xi)}{V_M \xi}
\]  

(96)

\[
J^I_O = \frac{D_O N_O^S}{V_M \xi} = \frac{3N^O}{2V_M} \cdot \frac{d\xi}{dt}
\]  

(97)

Substituting Eqs. (95) - (97) into Eq. (93), one obtains,

Rearranging Eq. (97),
\[
\frac{1}{\xi} = \frac{3N^0_{Cr}}{2D_{O^N_0}} \cdot \frac{d\xi}{dt}
\]
which may be substituted into Eq. (98) to yield,
\[
\frac{\gamma^N_{Cr}}{V_M} \cdot \frac{d\chi}{dt} = \frac{D_X (N_X^S - N_X^F)}{V_M} \cdot \frac{d\xi}{dt} + \frac{2\gamma}{3} \left( \frac{3N^0_{Cr}}{2V_M} \cdot \frac{d\xi}{dt} \right) + \frac{2\gamma}{3} \left( \frac{3N^0_{Cr}}{2V_M} \cdot \frac{d\xi}{dt} \right)
\]

Let us define parabolic rate constants \( k_I \) and \( k_{II} \),
\[
\frac{d\xi}{dt} = \frac{k_I}{\xi}
\]

and
\[
\frac{d\chi}{dt} = \frac{k_{II}}{\chi}
\]

Substitution of Eqs. (100) and (101) into Eq. (99) and rearrangement gives
\[
\frac{k_{II}}{\chi} \cdot \frac{\xi}{k_I} = \frac{3D_X (N_X^S - N_X^F)}{2\gamma D_{O^N_0}^S} + 1
\]

Substitution for \( \chi \) and \( \xi \) by Eqs. (100) and (101) yields
Rearranging,

\[ \frac{k_{II}}{k_I} \left( \frac{2k_{II}}{k_{II}^t} \right)^{1/4} = \frac{3D_X(N_X^S - N_X^F)}{2D_O^S N_O^S} + 1 \]  \hspace{1cm} (103)

We may evaluate \( N_X^F \) in Eq. (104) by the use of Eq. (95),

\[ \frac{\frac{D_X}{V_M}(X-X^\xi)}{V_M} = \frac{\gamma N_{Cr}^O}{V_M} \cdot \frac{dX}{dt} = \frac{\gamma N_{Cr}^O}{V_M} \cdot \frac{k_{II}}{X} \]  \hspace{1cm} (105)

Solving Eq. (105) for \( N_X^F \) gives

\[ N_X^F = \left( k_{II} - k_{II}^I k_{II}^I \right) \frac{N_{Cr}^O}{D_X} \]  \hspace{1cm} (106)

Substituting Eq. (106) into Eq. (104) yields

\[ \frac{3N_{Cr}^O}{2N_O D_O} k_{II} + \left( \frac{1}{k_I^4} \right) = \frac{3N_{Cr}^O k_{II}^4}{2N_O D_O} k_{II} = \frac{3D_X N_X^S}{2D_O N_O^S} + 1 \]  \hspace{1cm} (107)

By inspection of Eq. (97),

\[ k_I = \frac{2D_X N_X^S}{3N_{Cr}^O} \]  \hspace{1cm} (108)
Substitution of Eq. (108) into Eq. (107) causes the second term in
the left-hand-side to go to zero. Thus, the rate of growth of
Zone II is described by

\[
k_{II} = \frac{D_X^{\text{S}} N_X^S}{Y_{NO}^{\text{Cr}}} + \frac{2P_{\text{NO}}^{\text{S}}}{3N_{\text{Cr}}^O}
\]

(109)

This value for \(k_{II}\) is obviously the sum of \(k_I\) of Eq. (108) plus the
parabolic rate constant expected for the exclusive precipitation of
\(\text{CrX}_\gamma\) in absence of \(\text{Cr}_2\text{O}_3\) precipitation. It is remarkable that the
derivation of Eq. (109) does not utilize any assumptions that the
component \(X\) is either more soluble than oxygen, or that \(X\) diffuses
faster than oxygen. Therefore, when the thermodynamic assumptions
of the theory are met, an internal precipitation of \(\text{CrX}_\gamma\) preceeding
internal oxidation must be generally expected. The values of \(k_I\)
and \(k_{II}\) can now be substituted into Eq. (106) to determine \(N_{X}^S\).

Some comments regarding the expected validity of the assumptions
are in order. Firstly, the model assumes that a displacement
reaction is brought to completion at a specific location in the alloy
where the compound \(\text{CrX}_\gamma\) is converted to \(\text{Cr}_2\text{O}_3\). The realization of
this occurrence implies zero solubility for oxygen in the phase
field alloy plus \(\text{CrX}_\gamma\). Furthermore, the complete localized conver­
sion reaction would require the complete dissolution of \(\text{CrX}_\gamma\)
precipitates and the complete formation of the \(\text{Cr}_2\text{O}_3\) precipitates
over a very limited range of distance. The alternate extreme to
this assumed model is the conversion of the \(\text{CrX}_\gamma\) precipitates by
the growth of a Cr$_2$O$_3$ layer on each precipitate. Such a reaction would spread the conversion out over a large distance and an analytic analysis would require a knowledge of the details of the conversion kinetics. This alternate model (scaling oxidation of individual CrX$_y$ precipitates) would necessitate a mutual presence of solute oxygen and X in the conversion zone, and concentration profiles would require non-zero curvature. In view of these analytic complications, the description of future experiments may best be made in terms of deviations from the initially assumed model of Fig. 131.
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