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SOLID-STATE DISPLACEMENT REACTION
BETWEEN IRON AND NICKEL OXIDE AT 1000°C

DISSERTATION

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

By

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1980

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To my late parents and my two brothers, Pravit and Thakon, who provided me the opportunity for receiving conventional education.

To all my teachers who kindly educated me.
ACKNOWLEDGEMENTS

The author would like to express his gratitude to his advisors, Professors John P. Hirth and Robert A. Rapp, for their guidance and encouragement throughout this research program. He also wishes to thank Dr. C.A. Beiser of the National Steel Corporation, Drs. N.L.Peterson and W.K.Chen of the Argonne National Laboratory and Dr. C. Sandberg of the Central Materials Preparation Facility, Purdue University, for their kind provision of the zone-refined pure iron and NiO single crystals, respectively. Gratitude is also expressed to Mr. R. Farrar for his initial guidance in the operation of the scanning electron microscope and to Mr. L. Otenberger (Tiny) for his assistance in the preparation of the Mo holder used in this work. The financial support of the Office of Naval Research under project N00014-75-C-0541 is gratefully acknowledged.

Finally, the firm and consistent support, which gave rise to refreshing spirit, from the author's family, especially from his two brothers, Pravit and Thakon, during his course of study in the Graduate School at Ohio State is deeply appreciated.
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I. INTRODUCTION

Previous studies of solid-state displacement reactions between metals and halides (1), between metals and oxides (2) and between metals and sulfides (3) indicated the existence of several types of reaction product morphologies depending on the thermodynamic and kinetic parameters of the system. These structures were characterized as layered, lamellar and interwoven. The detailed mechanism and the kinetics for the development of layered-type and lamellar-aggregate products have been well-established (1,2,4). However, those for the formation of interwoven-aggregate products have not been well understood.

The objectives of the present studies were to rationalize the development and to determine the kinetics of growth of such an interwoven-aggregate product morphology. The reaction couple between Fe and NiO was chosen for this investigation because it gives rise to an interwoven morphology (2,4). The displacement reaction for this couple was studied at 1000ºC because the thermodynamic and kinetic parameters of the Fe-Ni-O system at such a temperature are relatively well documented.
An understanding of the mechanism and the kinetics of the evolution of the interwoven-aggregate product microstructure may be of engineering importance. A composite material consisting of an interwoven-aggregate of a metal and a compound should be ideal both for transfer of stresses and for resistance to crack propagation. The interlocking microstructure of the interwoven-aggregate should provide an excellent diffusion bonding between a metal and a ceramic, as in the case of enamelling of metals. The selective dissolution of either the metal or the oxide phase of the interwoven morphology should provide a means for the production of a porous oxide or metal screens, respectively. Such porous materials enjoy a range of application, for example, as electrode materials in fuel cells and as catalysts for reactions between gases.
II. LITERATURE REVIEW

Chemical reactions which involve solid reactants and products are called solid-state reactions. These reactions can take place spontaneously if the Gibbs free energy change for the system under isobaric and isothermal conditions is negative. Examples of such reactions are the tarnishing of metals and alloys during dry or wet oxidation, addition reaction between two dissimilar compounds, and displacement reactions. Generally, these reactions are characterized by the diffusion of atoms of type i, or of ions of type i with valence (charge) \( z_i \), in chemical (grad \( \mu_i \)) or electrochemical (grad \( \psi_i \)) potential gradients, respectively, in the products phases. The rate of growth of product phases is generally observed to be inversely proportional to the instantaneous thickness of the product layer. This observation is expressed by Eq. (1) in which \( \xi \) is the instantaneous thickness of the layer, \( t \) is the reaction time, and \( k_p \) is a proportionality constant.

\[
\frac{d \xi}{dt} = \frac{k_p}{\xi} \quad (1)
\]
If the reaction product zones are bounded by time-independent activities (concentrations) of the components, then with the condition that $\xi = 0$ at $t = 0$, Eq. (1) can be simply integrated to yield the thickness of the product layer at time $t$. Thus

$$\xi^2 = 2k_p t$$  \hspace{1cm} (2)

A linear plot of $\xi$ versus $t$ is parabolic. Thus, $k_p$ is often called the parabolic rate constant. In effect, reactions are said to exhibit parabolic behavior when the rate-limiting step is the solid-state diffusion of reacting species through the product phases. In fact, parabolic kinetics cannot be initiated at the very start of the reaction ($t=0$) because the substitution of $\xi = 0$ into Eq. (1) predicts an infinite thickening rate, which is impossible. So at the very start of product formation, some reaction step other than diffusion is rate-limiting.

Previous works on the development of product morphologies and kinetics treatment for the growth of reaction products resulting from some solid-state displacement reactions are reviewed in the following sections.
A. Microstructural Aspects of the Reaction Products

A solid-state displacement reaction, in a possible limiting case, can be represented by that expressed in Eq. (3) as

\[ \text{AX(s)} + \text{BY(s)} = \text{AY(s)} + \text{BX(s)} \]  

(3)

where A, B and X, Y are metal and non-metal species in the system. The mechanism of this double displacement reaction and morphology of the product phases are dictated by the transport and thermodynamic parameters of the system.

Classical treatments for the reaction mechanism have been limited to the cases where all phases involved are ionic conductors (5,6). These theories assumed that all phases involved have limited (negligible) mutual solubility and that the cations A and B are more mobile than the anions X and Y. This is most frequently the case in practice.

According to Jost (5), the reactants AX and BY are separated from one another by the product phases BX and AY. The layer of BX grows adjacent to the reactant AX and a layer of AY grows to cover the reactant BY. This layered product arrangement according to Jost is shown in Fig. 1(a). This morphology requires that there is some solubility of cations A and B in the products BX
Figure 1 - Schematic arrangement of the product phases for the AX/BY displacement reaction as proposed by: (a) Jost (5), and (b) Wagner (1).
and AY, respectively, since these ions must diffuse through both product phases. This type of product arrangement has been observed experimentally for reaction couples between HgCl₂ vs. AgI (8,9), TlCl vs. KI (10), and NaCl vs. KF (11).

In certain cases, the solubilities and mobilities of A and B ions in BX and AY, respectively, are too low, and consequently the product layers are formed so slowly that another reaction mechanism may predominate once nucleation has occurred. Thus, an alternative schematic arrangement shown in Fig. 1(b) for the products for the AX versus BY reaction and other displacement reactions could result. Here, Wagner (1) suggested that the product zone could consist of a conglomerate of the products which could be arranged in such a way that an essentially closed circular flow of cations occurs in the product phases such that the cations diffuse only in their own respective compounds. Several reaction couples between metals and halides which exhibit this type of product morphology have been reported (1).

In recent studies (4) on the displacement reactions between metals and oxides, which can be represented by reaction (4),

\[ \nu \text{Me}(s) + M_\delta \text{X}(s) = \text{Me}_\nu \text{X}(s) + \delta \text{M}(s) \]  

(4)
a criterion (4) based on the pertinent transport and
thermodynamic parameters of the reaction system has been
given both for the occurrence of Jost's layered structure
and for the formation of Wagner's conglomerate aggregate.

Essentially, this criterion (4) is analogous to
that of Wagner's theory (12) developed for the stability
of a flat alloy/oxide interface during the oxidation of
an alloy. In the case of displacement reactions, the
stability of a presupposed layered arrangement, as
depicted in Fig. 2, is examined. The assumptions
involved are: (i) local equilibrium is attained at the
phase boundaries; (ii) the rate-limiting step of the
displacement reaction is diffusion in the product phases;
(iii) the rate of cation diffusion in the product
compound is much faster than the rate of anion diffusion;
(iv) there is negligible solubility among the reactants
and products; (v) no additional product forms; and (vi)
the product compound grows at the Me_{x}X/M interface and
the product metal grows at the M/M_{y}X interface.

The stability of the assumed layered morphology
depends on the relative rates of growth of the product
phases. The uneven Me_{x}X/M interface in Fig. 2 would be
unstable with respect to a flat interface if the rate of
growth of the Me_{x}X phase were limited by cation diffusion
in the Me_{x}X. The rate of growth of Me_{x}X at site I (see
Fig. 2) would be greater than at site II, and hence, a
flat interface would eventually form. In this case, a
Figure 2 - Tentatively assumed uneven Me\textsubscript{\nu}X/M interface for a layered product arrangement. After Rapp, et al. (4).
layered product morphology is expected. Alternatively, if the rate of growth of the MeνX is limited by the rate of transport of X atoms through M, then the products at site II would grow faster than at site I. In this case, the MeνX/M interface would be expected to remain uneven and become more exaggerated, that is, the aggregate (two-phase zone) product arrangement would be expected to develop. Surface energy effects could, in principle, affect the stability of a flat interface between the products; however, for all known cases the Gibbs energy for the gross reaction is so large that surface effects are negligible.

The rational rate constants (4) are defined rigorously in more detail in a later section. For the growth of the product compounds in the layered arrangement, k_r(MeνX), describes the rate of arrival of cations, Me^-ν+\textsuperscript{+}, through product, MeνX, to the reaction front, and for the product metal k_r(M) describes the rate of arrival of non-metal atoms through product metal, M, to the reaction front. These rate constants are calculated and compared (4) to decide which diffusion step would be rate-limiting step in the layered arrangement. Accordingly, Rapp et al. (4) predicted a layered arrangement if k_r(MeνX) were less than k_r(M) and an aggregate arrangement if k_r(MeνX) were greater
than $k_r(M)$. Two morphological modifications of the reaction products have been called the lamellar-aggregate and the interwoven-aggregate arrangements (4).

Experimentally (13), this criterion has been found to be very effective in predicting product morphologies for certain reaction couples which fulfill the important assumption that there is negligible solubility among products and reactants. Couples that exhibit layered products are Ni/Cu$_2$O and Co/Cu$_2$O. Those giving rise to lamellar-aggregate are Fe/Cu$_2$O and Mn/Cu$_2$O. Typical morphologies of these two types of microstructure are shown in Fig. 3.

It is important to notice that this criterion is concerned only with the steady-state morphology. During the early stage of the reaction process, the transient morphology may not conform to the structure observed for extended experiments. Specifically, the early stage of the reaction between Fe and Cu$_2$O, which exhibits a lamellar-aggregate product morphology at long reaction times, has been investigated recently by Sonnemann (14). Results indicate that a small region of interwoven iron oxide and copper formed during the early stage of reaction. In this case, the evolution of the steady-state morphology is governed by the "point effect" of diffusion during the transient stage. In other words, tortuosity of structure is associated with local three-
Typical product microstructure of displacement reaction between:

(a) Ni and Cu$_2$O which yields layered type product arrangement;
(b) Fe and Cu$_2$O which yields lamellar-aggregate product arrangement.

After Yurek, et al. (2,18).
dimensional divergence in the diffusion fluxes. Once a sufficiently thick copper layer forms between the two-phase Cu+iron oxide product and Cu2O, one-dimensional diffusion prevails and the parallel rod, or plate structure develops. This is consistent with the previous studies (13).

Rapp et al. (4) have noticed in the development of their criterion that when the important assumption of the criterion, that is negligible solubility among reactants and products, is not fulfilled, neither a layered type nor a lamellar-aggregate product morphology is observed. Instead, a three dimensional interpenetrating aggregate product morphology, called an interwoven-aggregate is observed. This type of microstructure was found in the couples of Fe/NiO and Co/NiO (13). In the recent studies (15,16) on the displacement reaction between metals and sulfides, almost all reaction couples exhibit the interwoven-aggregate morphology. A well-defined structure of either the layered type or the lamellar-aggregate has not been observed in these studies. The cause is that the reactant compounds usually have some solubility for the reactant metal ions and further some contribution of sulfur vapor in the gas phase may be involved. Consequently, as noted by Shatynski et al., an interwoven-aggregate morphology always develops.
Recently, Metselaar and co-workers (17) have studied the displacement reactions between metals or alloys and oxide powder compacts. Specifically, results for the cases of Ni versus Cu$_2$O and Co versus Cu$_2$O couples are cited here as examples. Their results indicate that two possible product morphologies can result; that is, layered-type and interwoven-aggregate. The first type of structure is consistent with that reported by Yurek (13). Layered product structures were obtained when pre-sintered Cu$_2$O powders were reacted against poly-crystalline Ni. On the other hand, "interwoven-aggregate" product morphologies resulted from reacting compressed Cu$_2$O powders against poly-crystalline Ni. However, compressed powders should contain numerous connected voids (porosity). These voids should be the cause of this peculiar morphology. Critically, it cannot be technically justified to use compacted powders as a reactant material in a fundamental study of solid-state displacement reactions where good contacts of reaction interfaces are of extreme importance. Great caution should be exercised in the interpretation of a peculiar morphology resulting from reactions by powders.

Although most reaction couples in the previous studies (13,15) gave rise to an interwoven-aggregate product, the detailed mechanism for the development
of such a microstructure has not been well understood. Thus, one of the main objectives of this present work is to gain insight into the mechanism that results in the development of such an interwoven morphology. Iron and NiO reaction couples were chosen for this study because the thermodynamic and diffusion parameters at 1000°C for the Fe-Ni-O system are relatively well-established compared with other possible candidate couples.

B. Kinetics of the Displacement Reaction

The quantitative theory for the growth kinetics of the displacement reactions is based essentially on that of Wagner's scaling theory (7), which was developed for the parabolic growth of product layers during the scaling of metals in a gaseous oxidant. Thus, Wagner's Theory is reviewed in this section to provide background for the discussion of a more recent theory (18) proposed for the reaction between metals and compounds.

A solid metal exposed to an oxidizing gas can be oxidized to form an adherent, compact crystalline compound on the surface of the solid reactant if the Gibbs free energy change for the reaction is negative. Such a reaction is represented by Eq. (5)

$$\nu \text{Me}(s) + \frac{1}{2} \text{X}_2(g) = \text{Me}_\nu \text{X}(s)$$

(5)
where Me and X are metal and non-metal species, respectively, and \( \nu \) is the metal to non-metal ratio in the compound.

If the product phase is compact and adherent to the metal substrate, then further reaction requires the diffusion of one or both of the ionic species through the compound. In his classical treatment, Wagner assumed that the cations, anions, and electrons migrate independently across the ionic product layer. Then, the average drift velocity of each charged species in the growth direction is proportional to the electrochemical potential gradient for each species within the scale (all other potential gradients (forces) are assumed to be zero). The equivalent flux (equiv./cm\(^2\).sec) of each species, \( i \), is given by the product of the number of equivalents of \( i \) per cm\(^3\), \( c_i \), and the average drift velocity, \( v_i \) (cm/sec):

\[
j_i = c_i v_i = -B_i c_i \left\{ \frac{1}{N_A} \frac{d\mu_i}{d\xi} + z_i e \frac{d\psi_i}{d\xi} \right\}
\]

In Eq. (6), \( B_i \) is the absolute mobility of species \( i \), and the term in the bracket is the electrochemical potential gradient, which comprises a chemical potential gradient, \( d\mu_i/d\xi \), and an electrical potential gradient, \( d\psi_i/d\xi \). The symbols \( N_A \), \( z_i \) and \( e \) represent Avogadro's
Number, the valence of species $i$ and the electronic charge, respectively.

Because it was derived from electrolysis experiments, the mobility of species $i$ was originally expressed in terms of the electrical transference number for that species and the total electrical conductivity in the compound. Later, upon the advent of tracer self-diffusion measurements, the mobility of species $i$ was related to the diffusivity of that species through the Einstein relation (19),

$$ B_i = \frac{D_i}{kT} $$

which is valid when the activity of species $i$ is proportional to the concentration of $i$.

For oxidation reactions the condition

$$ j_1 = j_2 + j_3 $$

where 1, 2, and 3 represent cations, anions, and electrons, respectively, must be true; otherwise there would be a space-charge accumulation within the scale. A virtual equilibrium is assumed to exist at every point within the scale so that

$$ Me = Me^{z_1+} + z_1e^-; \quad \mu_{Me} = \mu_1 + z_1\mu_3 $$

$$ X = X^{z_2-} + z_2e^-; \quad \mu_X = \mu_2 - z_2\mu_3 $$
In terms of the conditions represented by Eqs. (8), (9) and (10), the flux of ions and electrons in a growing scale is

\[ j = j_1 + j_2 = j_3 \]

where \( j_1 \) and \( j_2 \) are the flux of cations and anions in the compound. The flux could also be obtained as a function of the chemical potential gradient of the metallic component through the use of the Gibb-Duhem relationship and the stoichiometry condition,

\[ \frac{\partial n}{\partial r} = \rho \left( \frac{z}{\partial z} \right) \]

where \( n \) = moles of \( i \).

The quasi-steady-state assumption, i.e., the flux is virtually independent of distance along the diffusion direction, is a good approximation for most solid-state, diffusion-controlled reactions. Then, upon integration, Eq. (11) yields

\[ j = \frac{1}{\xi} \left[ \frac{C_{Me} X}{RT} \int_{\mu_X}^{\bar{\mu}_X} \left( \frac{D_1 z_1}{|z_2|} + D_2 \right) d\mu_X \right] \]

\[ j = \frac{k_r(MeX)}{\xi} \]  

The term in bracket in Eq. (12) is called Wagner's rational rate constant, \( k_r(MeX) \). This constant, which
has units of equiv./cm·sec, indicates the rate of the reaction for a product layer of unit thickness. It is related to the proportionality constant of Eq.(1), which is generally obtained experimentally, by the following expression:

\[ k_r(\text{Me}_\nu \text{X}) = c_{\text{Me}_\nu \text{X}} \cdot k_p(\text{Me}_\nu \text{X}) \]  

(14)

Thus, with the relation of Eq.(14), Eq.(13) can be written in the following forms:

\[ j = \frac{k_p(\text{Me}_\nu \text{X})}{\xi} \cdot \frac{|z_2|}{V_{\text{Me}_\nu \text{X}}} = \frac{k_p(\text{Me}_\nu \text{X}) \cdot z_1 \cdot \nu}{\xi \cdot V_{\text{Me}_\nu \text{X}}} \]  

(15)

where \( V_{\text{Me}_\nu \text{X}} \) is the molar volume of the product compound.

Although the mechanisms of many metal/gas reactions are complex, Wagner's phenomenological equations have been successfully employed to predict reaction rates from transport and thermodynamic data (20,21,22).

This theory has been applied to the case of a layered displacement reaction (Figs. 2 and 3a) between a less noble metal, Me, and a more noble metal compound, \( \text{M}_\gamma \text{X} \), which resulted in the more noble metal, M, and the less noble metal compound, \( \text{Me}_\nu \text{X} \) (4). To be explicit, it was the rational rate constants, as defined by Wagner, that were used to compare the rate of the arrival of \( \text{Me}^{z_1+} \) cations through \( \text{Me}_\nu \text{X} \) and that of \( X \) atoms through \( \text{M} \) to the reaction, front. In this regard,
$k_r(M\nu X)$ was calculated from Eq. (12) as

$$
k_r(M\nu X) = \frac{c_{Me\nu X}}{2} \int_{P_{O_2}}^{P_{02}} \frac{D_1z_1}{z_2} \ d\ln P_{X_2} \tag{16}
$$

where $P'_{X_2}$ is the activity of $X_2$ for the coexistence of $Me$ and $Me\nu X$ and $P''_{X_2}$ is the activity of $X_2$ at $Me\nu X/M$ interface. The diffusivity of the anion $X^{2-}$ was justifiable omitted in Eq. (16) because $D_1$ is always far greater than $D_2$.

Since $X$ atoms diffused through metal $M$, the rational rate constant for the arrival of $X$ atoms at the reaction front, $k_r(M)$, was related to the solubility-diffusivity product of $X$ in $M$ as follows:

$$
k_r(M) = |z_2| D^M_X k^M_s \left[ \frac{1}{2} P''_{X_2} - \frac{1}{2} P''_{X_2} \right] \tag{17}
$$

where $D^M_X$ is the diffusivity of $X$ in $M$, $k^M_s$ is the Sieverts' law constant for dissolution of $X$ in $M$, and $P''_{X_2}$ is the $X_2$ activity for $M/Me\nu X$ coexistence. By comparing the magnitude of these two parameters, the product morphologies for the displacement reactions of certain couples can be predicted, as has been reviewed in the earlier section.

It is interesting to note that in Wagner's classical scaling theory only one product compound, $Me\nu X$,
is formed. However, in certain cases, the dissociation pressure for $M_yX$, $P_{X_2}$ may be so large that a higher compound of metal $Me$, say $Me_\delta X$, can be formed on top of the inner (lower) compound $Me_vX$. This type of reaction can be represented by Eq.(18)

$$(5y+vw)Me + (y+w)M_yX = wMe_vX + yMe_\delta X + (y+w)yM \quad (18)$$

For the cases where products have the lamellar-aggregate arrangement, a quantitative theory (18) has been proposed to describe the growth kinetics of such reaction products. Such a growth model is schematically depicted in Fig.4. Assumptions involved in this theory are based on those described in Wagner's early treatment (7). However, a recent theory takes into account the partitioning of cations at interface between the inner and outer compounds. Then the conventional parabolic constant for the growth of each compound has to be modified.

According to this theory, $Me$ metal is oxidized at the $Me/M_vX$ interface, $M_vX$ grows at the expense of $Me_\delta X$ at the $M_vX/M_\delta X$ interface. The rates of growth of the compound phases, as shown in Fig.4, have been derived to be

$$\frac{d\xi}{dt} = \frac{k_p(M_vX)}{\xi(1+5y/vw)} = \frac{k'_p(M_vX)}{\xi} \quad (19)$$
Figure 4 - A model for the growth of lamellar-aggregate product morphologies. The relative dimensions of the product phases are greatly exaggerated. After Yurek et al. (18).
\[
\frac{d\eta}{dt} = \frac{k_p(Me_\delta X)}{\eta(1+w/y)} = \frac{k_p(Me_\delta X)}{\eta}
\] (20)

and \[
\frac{d\theta}{dt} = \frac{k_p(\text{compounds})}{\theta} = \frac{(1+\eta/\xi)^2}{\theta(1+\delta y/\nu w)} k_p(Me_\nu X)
\] (21)

where the \( k_p \)'s bear the same meaning as those used in the Wagner's derivation; \( \xi, \eta, \theta \) are thicknesses of oxide phases defined in Fig. 4; and \( y \) and \( w \) are the molar partition ratios between \( Me_\nu X \) and \( Me_\delta X \).

Thus, the actual parabolic constant for the growth of each oxide, \( k_p' \), is related to its conventional value via (23):

\[
k_p'(Me_\nu X) = (1+\delta \eta V_{Me_\nu X}/\nu \xi V_{Me_\delta X})^{-1} k_p(Me_\nu X)
\] (22)

\[
k_p'(Me_\delta X) = (1+\xi V_{Me_\delta X}/\eta V_{Me_\nu X})^{-1} k_p(Me_\delta X)
\] (23)

Finally, for the total product layer

\[
k_p(\text{compounds}) = \left\{ \left[ k_p'(Me_\nu X) \right]^{\frac{1}{2}} + \left[ k_p'(Me_\delta X) \right]^{\frac{1}{2}} \right\}^2
\] (24)

With the additional assumption that the ionic and atomic fluxes through the reaction products are maximized, this theory has been found to describe
successfully the growth of reaction products from the 
displacement reaction between Fe vs. Cu₂O (18). With 
more recent diffusion and defect data, better agreement 
between the calculated and the observed kinetic 
parameters have been obtained (23).

A quantitative theory describing the growth kinetics 
of displacement reaction products in the interwoven-
aggregate arrangement has not yet been developed because 
of the complications arising from the solubility factors. 
Specifically, consider the displacement reaction between 
Fe and NiO at 1000°C where austenite, wustite and spinel 
are formed as product phases (2). These phases have wide 
ranges of composition across the stability range (24-27). 
A quantitative model must take into account the local 
adjustment in composition between metallic product and 
the oxide phases, the variation of diffusion coefficients 
of the predominant transporting species as a function of 
composition in product compounds, and the defect nature 
in the compounds which can tolerate significant amounts 
of impurities, in Ni-doped wustite and Fe-doped NiO, for 
example. It can be envisioned that such a theory would 
be mathematically very complicated, if not intractible. 

Thus, with regard to the kinetic aspects, the 
purpose of this study was to interpret qualitatively and 
critically the kinetic results as much as possible.
III. EXPERIMENTAL MATERIALS AND PROCEDURE

A. Sample Preparation

(a) Essentially Oxygen-free Iron

A 2-inch diameter and 3-inch long piece of zone-refined pure iron, the total impurities of which were less than 225 ppmw., was provided by Dr. C.A. Beiser of the National Steel Corporation. It was cut into $\frac{1}{2}$" x $\frac{1}{2}$" rectangular bars, ground to have smooth edges and then swaged into 1.1 cm diameter circular rods. Each rod was cut into about 2 mm thick discs with a slow-speed diamond-wafering blade. The discs were preliminarily polished on #240 to #600 emery paper to remove any surface contamination and to make the surface reasonably flat and smooth. All discs were cleaned in ethyl alcohol and acetone and then annealed at 850°C for 2 hours. The annealing was done in a dry H₂ atmosphere to make the iron virtually free of dissolved oxygen. The annealed iron specimens were carefully polished on 120 through 600 grit emery paper to produce discs with very flat and parallel surfaces. The side of the disc that was to be pressed against an oxide sample was polished with one micron diamond paste to produce a mirror-like
finish. These polished metal discs were ultrasonically cleaned and stored in acetone until use.

(b) Ni-Plated Iron Sample

Some of the annealed and metallographically polished iron discs described in the previous section were slightly etched in 2% H₂SO₄, washed with distilled water and then electroplated with a thin layer of Ni on the surfaces. The Watt bath, described in detail by Brown and Knopf (28), was used as the plating solution. A commercially pure Ni sheet which was bent to conform to the contour of the iron discs was used as the anode. A small amount of H₂O₂ was added to the solution as an anti-pitting agent. The plating voltage and the cathodic current density were 1.3 V and 280 mA/cm², respectively. Several discs of iron were plated with Ni of various thicknesses. The side of the plated samples that was to pressed against the NiO sample was repolished with a one micron diamond powder to obtain a shiny and bright surface.

(c) NiO Sample

NiO samples used in this investigation consisted of both single- and poly-crystals. The single crystals of NiO were generously made available by Drs. W. Chen and N. Peterson of the Argonne National Laboratory,
Illinois, and by Dr. Sandberg of the Central Materials Preparation Facility, Purdue University, Indiana. About 1 mm thick discs were cleaved parallel to the cube face of the crystal boules. Each sample was lightly ground on 600 grit emery paper to remove contamination on its edges. The surfaces of the cleaved discs were flat and smooth; and thus no further surface-finish was required.

Poly-crystalline NiO samples used in this study were obtained by oxidizing small pieces of commercially pure Ni, about 1 mm x 10 mm x 10 mm in dimensions. Such pieces of Ni were prepared by rolling a 8 mm diameter Ni rod to approximately a 1 mm thick strip. The strip was then cut into pieces, polished on #240 to #600 grit emery paper to remove contamination and to provide resonably flat and smooth surfaces. Then they were placed on alumina boats containing nickel oxide powder to prevent sticking of the NiO samples to the alumina boats, and were oxidized in air at 1275°C for 45 days and subsequently at 1000°C for 30 days.

After oxidation, the NiO samples were non-destructively tested for completion of oxidation by touching the samples with a strong magnet. Samples that stuck to the magnet implied the presence of residual Ni. These samples were re-oxidized in the furnace until no Ni in metallic form in the oxide samples was detected.
The NiO samples were ground on 240 to 600 grit emery paper in order to produce very flat surfaces. Final polishing was done with one micron diamond paste in order to produce a mirror-like finish. Polishing oil, Buehler Metadi Fluid, was used as a lubricant during polishing. The polished samples were ultrasonically cleaned and stored in acetone.

For short time experiments, some of both the single- and poly-crystalline NiO samples were annealed in an atmosphere which had an oxygen potential fixed thermodynamically at $P_{O_2} = P_{O_2}^*(Ni/NiO)$ by the presence of a boat containing a mixture of 3:1 weight ratio Ni + NiO powders. Ar gas was used as the diluent. The annealing was done at 1125°C for 30 days and subsequently at 1000°C for 2 days. This was done to established a Ni-rich skin on the NiO samples. These samples were called, for the purpose of our discussion, Ni-rich NiO.

Some of the other NiO single crystals were annealed in air at 1000°C for 15 days. These samples were called O-rich NiO.

B. Reaction of the Samples

The surface finished Fe and NiO were held in excellent contact with a Mo holder and accessories, the assembly of which is depicted in Fig. 5. The
Figure 5- Assembly of the reaction system in the Mo holder.
contacting surfaces of all the components involved were so carefully prepared that the variation in the parallelism across two surfaces of each component, as measured by a precision height gauge that can detect the variation in height in the order of \( \pm 0.000005 \) inch, was within \( \pm 0.0005 \) inch.

The coefficient of linear thermal expansion of Ni is about three times as large as that of Mo; therefore, even neglecting all other minor expansions from other components in the system, upon heating, the reaction couple was forced together. Thermal strain, defined as the constraint in the total thermal expansions along the cylindrical axis of all components inside the Mo holder against the expansion along the same direction of the Mo wall, was estimated from the pertinent linear coefficients of thermal expansion \((29,30)\) and the pertinent thicknesses of all components. This was found to be about 0.3% axial strain.

As reaction products are formed, the strain resulting from phase transformation must be taken into account. Estimation of such strain is based on the law of conservation of mass, that is, products form at the expense of reactants. If it is assumed that the average molar partition between austenite and wustite, austenite and spinel, and austenite and Fe-doped NiO in the pertinent two-phase aggregate are constant, then the
volume change caused by the phase transformation is calculated as follows.

First of all, the volume fractions of \( \gamma \), in the \( \gamma \)-wustite, \( \gamma \)-spinel and \( \gamma \)-NiO aggregate for one particular reaction time, say 4 hours, were estimated from the area fractions of \( \gamma \) in the representative photomicrograph of the products. Such estimation was done by super-posing small square grids on the metallograph and counting the fraction of the total number of the grids points that lay on the austenite phase. Then, with the knowledge of the molar volume of each phase involved (31), the moles of each product phase could be calculated. Consequently, the moles of \( 0 \) which must come from reduced NiO can be deduced. By approximating the Fe content in the \( \gamma \) phases, the moles of reactant Fe could be estimated. With the numbers of moles of products formed and of reactants consumed, the volume change of the whole system caused by phase transformation can be calculated. The volume strain is calculated from the ratio of the volume change to the total volume of reactant phases. This volume strain was estimated to be 6\%. If a purely dilatational volume strain is assumed, although radial expansion was more favorable than expansion along axis of the reaction couple, then a maximum strain of \( (6/2) = 2 \) (%) should result. This is superimposed on the thermal
strain estimated earlier to yield a total of 2.3% axial strain. Such a strain exceeds the elastic limit of all materials involved in the system. Hence, plastic deformation and creep should take place in the soft materials (the metallic phases) to relax the build-up of stress. This was likely to take place in the readily deformable iron reactant phase because the known yield strengths of metals (29) are less than those known for oxide materials (30). The austenite product phase at a homologous temperature of about 0.7 should also be very soft; however, as examined from the product microstructure this phase does not appear to be compressed, in any manner, from the constraint in expansion as a result of phase transformation. This is because it was supported by its oxide conjugate in the interwoven arrangement. Thus, although the Mo holder did result in constraint of expansion along the major growth direction, it did not have any detrimental effect on the reaction process. Instead, constraint in expansion should be beneficial in the healing of voids associated with reaction process.

The reaction couples in the Mo holder were placed in the hot zone of a resistance-heated tube furnace. The temperature of the hot zone, which was about 70 mm long, was maintained at the desired reaction temperature to within ±4°C with the aid of a Wheelco on-off
temperature controller which was modified to provide a high-to-low power cycle instead of a complete on-off cycle.

The control thermocouple was placed adjacent to the furnace windings. However, the actual temperature of the reaction couple was monitored with the aid of a Pt vs. 10% Rh-Pt thermocouple placed near the sample holder adjacent to the reaction couple. The setup is schematically depicted in Fig. 6.

For short-time experiments at 1000°C, the furnace was superheated to approximately 1120°C before the reaction couples were inserted into the hot zone. This superheating enabled the temperature of the couple to be raised up to 1000°C within approximately 80 seconds. However, for long-time experiments, the furnace was superheated to about 1055°C so as to be able to bring the temperature of the reaction couples to 1000 ± 4°C within about three and a half minutes. As the specimens were inserted, the power supply to the furnace was turned off to allow the furnace to cool down to desired temperature, 1000 ± 4°C. These superheating and cooling exercises were carefully arranged to avoid overheating the samples and to allow the reaction couples in the kinetic study to be subjected to the same transient time.
Figure 6- Setup in the hot-zone region of the furnace:

A. The Mo holder
B. Alumina boat containing Ni+NiO powder mixture
C. Pt-10% Rh-Pt thermocouple
D. 28 mm O.D. quartz tube
E. 2\1/2 in. I.D. mullite tube
F. Pieces of 15 mm O.D. mullite tube
Purified Ar was slowly flowed over the reaction system in order to minimize interactions of the reactants with the furnace atmosphere. The Ar was passed through a cleaning train which consisted of (i) BTS catalyst, from BASF corporation, New Jersey, which was held at 160°C to remove oxygen and to convert hydrogen to water vapor and carbon monoxide to carbon dioxide; (ii) anhydrous Mg(ClO₄)₂ to remove water vapor; and (iii) Ascarite to remove hydrocarbons and carbon dioxide.

With the presence of the Mo holder, the partial pressure of oxygen in the furnace atmosphere was thermodynamically limited to \( P_{O_2}(Mo/MoO_2) = 1.36 \times 10^{-15} \) atm \( (32,33) \), which is almost identical to \( P_{O_2}(Fe/FeO) \) which is \( 1.31 \times 10^{-15} \) atm \( (32,34) \) at 1000 °C. This oxygen partial pressure was less than the dissociation pressure for NiO, \( 4.4 \times 10^{-11} \) atm \( (34) \). Thus, under this circumstance, the free surface of NiO sample would be reduced substantially. To minimize the reduction of the NiO sample near its free surface region, the Mo container and the Mo plug were intentionally oxidized in air at about 400°C so that all fresh surface of the Mo holder and the plug were covered with a thin molybdenum dioxide film. A relatively low temperature was chosen to oxidize the Mo so as to minimize the MoO₃ fume which would be
generated otherwise. Then an alumina boat containing a mixture of Ni+NiO powder was placed upstream relative to the reaction couple near the hot zone of the furnace. This was to establish the oxygen partial pressure in the furnace at $P_{O_2} = P_{O_2}^{(Ni/NiO)}$. This potential of oxygen was discerned from the examination of specimens after reaction and the alumina boat was pulled out from the furnace, allowed to cool rapidly in fast flowing Ar gas. The presence of the coexistent Ni and NiO on the surface of the sintered powder in the alumina boat could be detected by examining the color of the mixture under a light microscope.

A reaction was terminated by the rapid removal of the reaction couple to the cool-zone of the furnace, the temperature of which was about 150°C, allowing its temperature to rapidly decrease to about 200°C in fast flowing purified Ar in about 3 minutes. Then the sample holder was withdrawn from the furnace and air quenched to room temperature.

C. Examination of Reaction Couples

The reacted couples were removed from the Mo holder and mounted in vertical position, with the aid of a sample clip, in a plastic resin that hardens upon the addition of a catalyst, Buehler Epoxide resin and hardener. The mounted samples were sectioned by a
slow-speed diamond-wafering wheel in a direction parallel to the major growth direction of the reaction products. Each section was ground on 400 to 600 grit emery paper and final polished with one micron diamond paste using polishing oil as lubricant.

All the metallography was performed with the aid of an Olympus PME light microscope. Selective etching was the most effective way to identify the reactant and product phases in this reaction system. Nital 4% was used to etch selectively the iron and wustite phases, while 50% HCl in alcohol was used to dissolve iron, wustite and spinel phases. The Ni-alloy, Fe-doped NiO, and NiO were virtually unattacked by these etchants.

Representative examples of product microstructure and thickness were taken from the region near the middle section of the product zone.

Product thicknesses were measured with a filar eye-piece which was calibrated against a stage micrometer. The thicknesses were measured to three significant figures. Seven measurements of all thicknesses were obtained and an average value was calculated.

A JEOL JXA-35 scanning electron microscope was also employed to examine the product morphologies. A thin layer of gold was evaporated onto the surfaces of the couples in order to minimize charge build-up in
the oxides and to make the surface of the mounted samples electronically conductive. For the same reason, a thin layer of carbon was evaporated onto those samples which were analyzed qualitatively for the presence of various elements in the reactant and product phases. The analysis was done in an energy dispersive X-ray spectrometer, EDAX, which was so equipped that it worked synchronously with the scanning electron microscope.
IV. DEVELOPMENT OF THE INTERWOVEN-AGGREGATE PRODUCT MORPHOLOGY

A. Review of Thermodynamic Data

The pertinent physical and thermodynamic properties of all the components involved are reviewed in this section so as to form a basis for the discussion of the development of the interwoven-aggregate product morphology resulting from the reaction between Fe and NiO.

Iron and nickel are completely miscible at 1000°C (35). Magnetite, Fe$_3$O$_4$, and nickel ferrite, NiFe$_2$O$_4$, which have the inverse spinel structure (36,37,38,39,40), form an isomorphous solid solution at 1000°C (24,25,26,27). The octahedral sites of the oxygen ion sublattice are shared by divalent ions, Ni$^{2+}$ and Fe$^{2+}$ and some of the trivalent Fe$^{3+}$, with the remaining Fe$^{3+}$ ions situating in the tetrahedral sites of the oxygen ion sublattice.

Wustite and NiO both have the NaCl-type crystal structure. The ionic radii of the divalent Fe and Ni ions in these oxides are 0.77 and 0.68 Å, respectively (41).
Equilibrium compositions of wustite, spinel, Fe-doped NiO and austenite at phase boundaries have been determined by several workers using various methods of investigation. The recent data are summarized in Table 1.

The trend of recent results (26,27) indicates that the solubility of Ni in wustite is higher than that in coexisting spinel; that NiO can tolerate a higher solubility of Fe; and that \( \gamma \) coexisting with spinel and NiO has a larger Fe content. The concise thermodynamic data of the Fe-Ni-O system at 1000°C has been presented in the form of a \( P_{O_2} \) vs. \( X_{Ni} \) plot by Davies and Smeltzer (25), as reproduced in Fig. 7. Over the wustite-alloy phase field, the oxygen pressure increases with increasing nickel content, from \( 1.31 \times 10^{-15} \) atm, corresponding to iron-wustite equilibrium, to \( 5.5 \times 10^{-14} \) atm, which is the invariant oxygen pressure associated with the wustite-spinel-alloy phase field. The nickel contents of the phases in this field vary from 0.5 to 2 a/o for wustite, 0.6 to 1.4 a/o for spinel and 79.5 a/o to 80 a/o for the austenite alloy. Over the spinel-alloy phase field, the oxygen pressure increases to the invariant value of \( 2.5 \times 10^{-11} \) atm for the spinel-nickel alloy equilibrium. The spinel and nickel oxide are
Table 1. Compositions at Invariant Oxygen Pressures in the Fe-Ni-O system at 1000°C

<table>
<thead>
<tr>
<th>( P_0 = 5.5 \times 10^{-14} \text{ atm} ) (25)</th>
<th>Wustite ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>Austenite ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>Spinel ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>NiO ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.51 53.0*</td>
<td>79.5 20.5</td>
<td>0.55 42.0</td>
<td>- -</td>
<td>(24)</td>
<td></td>
</tr>
<tr>
<td>Coexisting Phases:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.81 -</td>
<td>80.3 19.7</td>
<td>0.47 -</td>
<td>- -</td>
<td>(26)</td>
<td></td>
</tr>
<tr>
<td>( \gamma )-wustite-spinel</td>
<td>2.1 44.7</td>
<td>80.0 20.0</td>
<td>1.4 41.4</td>
<td>- -</td>
<td>(27)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>( P_0 = 2.5 \times 10^{-11} \text{ atm} ) (25)</th>
<th>Wustite ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>Austenite ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>Spinel ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>NiO ( \text{a/oNi} ) ( \text{a/oFe} )</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>- -</td>
<td>99.5 0.5</td>
<td>14.3 28.4</td>
<td>43.5 6.5</td>
<td>(24)</td>
<td></td>
</tr>
<tr>
<td>Coexisting Phases:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>- -</td>
<td>99.6 0.4</td>
<td>13.1 29.7</td>
<td>42.5 7.5</td>
<td>(25)</td>
<td></td>
</tr>
<tr>
<td>( \gamma )-spinel-NiO</td>
<td>- -</td>
<td>97.4 2.6</td>
<td>9.5 -</td>
<td>35.5 14.5</td>
<td>(26)</td>
</tr>
<tr>
<td>- -</td>
<td>94.0 6.0</td>
<td>11.6 31.3</td>
<td>40.0 10.0</td>
<td>(27)</td>
<td></td>
</tr>
</tbody>
</table>

* This is a suspicious value because Fe in wustite under no circumstance can exceed 50 a/o.
Figure 7 - Equilibrium oxygen activity-composition diagram for the Fe-Ni-O system at 1000°C. After Davies and Smeltzer (25).
represented, in Fig. 7, as Ni$_{0.8}$Fe$_{2.04}$ and Ni$_{0.85}$Fe$_{0.15}$, respectively. But the compositional determinations of spinel, as shown in Table 1, vary from Ni$_{0.65}$Fe$_{2.35}$O$_4$ to NiFe$_2$O$_4$ and compositions of nickel oxide from Ni$_{0.74}$Fe$_{0.26}$O$_4$ to Ni$_{0.87}$Fe$_{0.13}$O$_2$. The nickel-rich alloy, in Fig. 7, contains 99.6 a/o Ni. Nickel oxide subsequently exists in equilibrium with metal up to the dissociation pressure of pure nickel oxide, $4.4 \times 10^{-11}$ atm (34).

B. Development of Reaction Products at the Early Stage of Reaction.

NiO in contact with pure iron is unstable because the dissociation pressure of NiO (34) is respectively 4 and 2 orders of magnitude greater than those of wustite (34) and magnetite (25). In effect, Fe would be oxidized while NiO would be reduced.

Since NiO has some solubility for Fe ions, the Fe atoms in contact with NiO are oxidized and then dissolve into the NiO. The possible interaction between Fe and NiO can be represented by:

$$Fe + V_{Ni}^{\prime \prime} + 3h = Fe_{Ni}$$  \hspace{1cm} (25)

and

$$2Fe + 3Ni_{Ni}^{X} = 2Fe_{Ni}^{*} + V_{Ni}^{\prime \prime} + 3Ni$$  \hspace{1cm} (26)

where the defect notation of Kroger and Vink (45) has
been used.

For an O-rich NiO, the intrinsic concentrations of cation vacancies and holes are $2.5 \times 10^{-4}$ and $5 \times 10^{-4}$ mole fractions, respectively, whereas the corresponding concentrations for a Ni-rich NiO are $7 \times 10^{-6}$ and $14 \times 10^{-6}$ mole fractions, respectively (46). Thus, the excess positive holes in the O-rich NiO are annihilated according to Eq.(25), until the limiting concentration corresponding to that of the Ni-saturated NiO is reached.

Since the amount of positive holes consumed in Eq.(25) is three times as many as that of the cation vacancies, the excess positive holes should be reduced down to the limiting value first. If all these excess positive holes were reduced, they could only result in about $1.6 \times 10^{-4}$ mole fraction of Fe in the NiO. However, the solubility of Fe in NiO at the invariant $P_{O_2}$ corresponding to the coexisting $\gamma$-spinel-NiO phases is about 0.1 mole fraction (27). Therefore, dissolution of Fe ions into NiO according to Eq.(25) should be very small. Alternatively, a process like that described by Eq.(26) should be dominant. The interaction between the Ni cations and the Fe atoms gives rise to the increase in the cation vacancies in the NiO. This is consistent with the localized electroneutrality condition, ENC, for a Fe-doped NiO, that is
The Ni atoms resulting from Eq. (26) should migrate into the Fe phase in order to dissipate the activity gradient. These Ni atoms can dissolve into the Fe phase, as depicted in part (b) of Fig. 8, because the Fe-Ni system is isomorphous at 1000°C.

For a metal deficient NiO crystal, the intrinsic defect equilibrium is given by

$$
\frac{1}{2} O_2(g) = V''_{Ni} + O_0^x + 2h
$$

(28)

The equilibrium constant of Eq. (28) is

$$
K_I = \frac{[V''_{Ni}] [h]^2}{P_{O_2}^{1/2}}
$$

or

$$
[h] = \frac{K_I P_{O_2}^{1/4}}{[V''_{Ni}]^{1/2}}
$$

(30)

With the simplified ENC, described by Eq. (27), Eq. (30) can be written as:

$$
[h] = \frac{[2K_I]^{1/4} P_{O_2}^{1/2}}{[Fe_{Ni}]^{1/2}}
$$

(31)
Figure 8 - Proposed scheme for the development of product microstructure during the initial stage of the Fe vs. O-rich NiO displacement reaction. The scales for the hole and ion concentrations differ significantly.
The $P_{O_2}$ of an O-rich NiO at the interface in contact with the Fe changes from $P_{O_2} = 0.21$ atm down to $P_{O_2} = 4.4 \times 10^{-11}$ atm, the dissociation pressure of NiO. The concentration of $Fe_{Ni}$ increases from zero up to about 10 a/o (27). Therefore, the concentration of positive holes in the NiO, according to Eq.(31), should drop drastically as the NiO is continuously doped with Fe ions and as the activity of the oxygen decreases. The concentration profiles of the pertinent species are schematically depicted in part (c) of Fig.8.

As the activity of oxygen in NiO decreases, the O anions in the NiO under a reducing atmosphere can interact with the available positive holes to form O atoms. The intrinsic defect equilibrium in NiO under a reducing atmosphere is described by:

$$0^{x}_{0} + 2h^{+} = O + V^{\prime\prime}_{0} \quad (32)$$

The equilibrium constant of Eq.(32) is

$$K_{II} = \frac{[V^{\prime\prime}_{0}]^{\frac{1}{2}}}{P_{O_2} \cdot h^{2}} \quad (33)$$

where $P_{O_2}$ represents the activity of O.
The O atoms formed from Eq.(32) are dissipated into the Fe-Ni alloy phase, as depicted in part (b) of Fig.8. Such O atoms have sufficiently high activity to oxidize the Fe-Ni alloy to form simultaneously two-phase layer of wustite and spinel. Consequently, formation of these oxide phases should be expected in the Fe-Ni alloy, as depicted in part (d) of Fig.8.

Since the wustite and spinel have limited solubility for Ni, the excess Ni atoms are rejected out of the wustite and spinel and appear as random precipitates in both matrix phases. Since the volumes of the wustite and spinel formed during the early stage of reaction are very small, the Y precipitates should likely be interconnected in a three-dimensional manner because of the constraint in the space for precipitation. This is schematically represented in part (e) of Fig.8.

Although the above discussion is for the reaction couple between Fe and O-rich NiO, it should also apply to the case of the Fe vs. Ni-rich NiO couple. The difference between the case of using a Ni-rich NiO and that of using an O-rich NiO as reactant materials is that in the former case the intrinsic hole concentration is less than that in the later case. Dissolution of Fe into NiO by interaction with the
positive holes, as described by Eq. (25) should be negligible. That is, reaction (26) becomes much more dominant. This means a much amount of Ni atoms is dissolved into the Fe-phase at the Fe/NiO interface. Since the initial activity of O in the Ni-rich is very much lower than that in the O-rich NiO, the reaction (26) should also take place in a relatively very short period of time. Therefore the depth of the penetration of Ni atoms into the Y phase is not expected to be larger than that of the previous case. Consequently, the concentration profiles of Fe and Ni atoms in the Y near the Y/NiO interface should be relatively steeper, as depicted in part (c) of Fig. 9. Once this Fe-Ni alloy is oxidized by the O atoms formed from Eq. (26) to form a two-phase layer of wustite and spinel, as depicted in part (d) of Fig. 9, the larger gradient of the Ni ions in these two-phase oxides should result in a very distinct gradation in the state of supersaturation of Ni ions with respect to the formation of Y at location A compared with that at B in part (c) of this Figure. This means, chronologically, the precipitation of Y at location A should form before that at location B. Austenite can precipitate at location A without significant interference with the local condition at B by precipitation in a planar-like
Figure 9 - Proposed scheme for the development of product microstructure during the initial stage of the Fe vs. Ni-rich NiO displacement reaction. The scales for the hole and ion concentrations differ significantly.
manner. Physically, the volume of the precipitation region is so small that the planar-like precipitation of \( \gamma \) results in sidewise interconnection of this phase. As a result, the arrangement of this \( \gamma \) in the wustite and spinel should appear more or less as a layered type structure. Between the two intermittent \( \gamma \) layers is a wustite or spinel that is in equilibrium with these \( \gamma \) phases. The microstructure of the transient product should resemble that shown in part (e) of Fig. 9.

In effect, starting with a Ni-rich NiO as a reactant material would only result in the difference in the arrangement of the \( \gamma \) phase in the wustite and spinel matrix phases.

Experimental verification of these proposed schemes for the development of the transient product morphologies is subjected to certain physical constraints. Physically, a transient time is required to heat the reaction couple from room temperature up to \( 1000 \pm 4^\circ \text{C} \). If the transient time is long, reaction steps occurring during the continuous heating of the reaction couple may prevail. Consequently, the observed product microstructures may not be the good representatives of the transient product morphologies. Experimentally, an infinitely short transient time can be approached if the furnace
is superheated to temperatures higher than 1000°C. However, actually, a finite time is required for the handling of the reaction couple and for the reading of the couple temperature. With frequent practice, this required time can be shortened to the order of 80 seconds. Thus, experimentally, the furnace temperature was superheated to about 1120°C so that the couple temperature could be raised up to 1000 ± 4°C within such a time period. The typical product microstructures observed after the reaction time between 80 to 120 seconds are shown in Fig. 10, for couple between Fe and O-rich NiO and in Fig. 11, for couple between Fe and Ni-rich NiO. At shorter reaction time, the reaction couple fell apart upon rapid cooling. In such a case, no reaction product could be observed. On the other hand, for longer reaction time, the couple could be superheated, and thus, the observed structures should not be good representatives of the transient morphologies at 1000°C. With these experimental difficulties, the microstructure shown in Figs. 10 and 11, which are consistently observed after reaction time between 80 to 120 sec., are the best available representatives of the morphologies developed during the very early stage of reaction.
Figure 10 - Product microstructure of the Fe vs. 0-rich NiO after 90 seconds at 1000°C.
(a) As polished, 2000x;
(b) 4% Nital etched, 2000x;
(c) 50% HCl etched, 2000x;
(d) 7500x
Figure 10 (continued)
Figure 11 - Product microstructure of the Fe vs. Ni-rich NiO after about 90 seconds at 1000°C:
(a) As polished, 2000 x;
(b) 4% Nital etched, 2000 x;
(c) 50% HCl etched, 2000 x;
(d) 50% HCl etched, 7500 x.
Figure 11 (continued)
The as polished product microstructures are shown in part (a) of both Figs. 10 and 11. In part (b) of these Figures the existence of the two-phase wustite and spinel was identified upon etching the specimens with 4 \% Nital solution. The wustite appears as a dark phase while the spinel, which is virtually unattacked by such a solution, appears as a gray phase. The very existence of a spinel zone in the products was further confirmed upon further etching the sample with 50 \% HCl solution. The spinel was then dissolved away and appears as a dark phase in the product. These are shown in part (c) of Figs. 10 and 11.

The difference in the arrangement of \( Y \) in the oxide phases resulting from starting with the two different types of NiO crystal can be clearly discerned in part (d) of Figs. 10 and 11. After the wustite and spinel phases were heavily etched away by the 50 \% HCl solution, the \( Y \) phases in the aggregate products in part (d) of Figs. 10 and 11 did not fall off. This suggests very strongly that the \( Y \) precipitates should be interconnected in a three-dimensional manner.

The proposed reaction steps described in parts (b) and (c) in both Figs. 8 and 9 could not be actually detected because the reaction process in the transient stage occurs so rapidly that such reaction steps cannot be physically distinguished.
C. Development of Reaction Products at a Later Stage of Reaction

Once the transient product morphologies, i.e., the well-defined adherent layers of γ-wustite, γ-spinel and Fe-doped NiO, are formed, further growth of the reaction products should be controlled by the long-range diffusion of Fe ions through the wustite, spinel and NiO phases, coupled with the short range diffusion of Ni ions in the Fe-doped NiO. This statement is justified on the basis of the diffusion data summarized in Table 2.

Although the diffusivity of 0 atoms in V appears to be competitive to that of Fe ions in wustite, the solubility of 0 in Ni is only 140 ppmw. (57) whereas those for Fe ions in wustite at P02(Fe/Fe0) and spinel at the invariant P02 corresponding to the coexisting γ-wustite-spinel phases are about 48 and 42 a/o, (24-27), respectively (24-27). As a result, the solubility-diffusivity product for 0 in Ni is 3.4 x 10^-12 mole/cm-sec, whereas, the corresponding values for Fe ions in wustite and spinel are 6.2 x 10^-9 and 1.3 x 10^-12 mole/cm-sec, respectively. It is obvious that diffusion of Fe ions in wustite should be dominant. The solubility-diffusivity products for 0 atoms in Ni and Fe ions in spinel are very competitive. Thus, localized growth of reaction product at the pre-existing γ-spinel
Table 2. Self-Diffusion of Iron, Nickel, and Oxygen in the Metallic and Oxide Phases at 1000°C

<table>
<thead>
<tr>
<th>Diffusion Species</th>
<th>Diffusion Phase</th>
<th>Self-Diffusion coefficient cm²/sec</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>&quot;pure Ni&quot;</td>
<td>$6.4 \times 10^{-12}$</td>
<td>(48)</td>
</tr>
<tr>
<td></td>
<td>&quot;pure Ni&quot;</td>
<td>$1.5 \times 10^{-11}$</td>
<td>(49)</td>
</tr>
<tr>
<td></td>
<td>$Fe_{0.94}$</td>
<td>$7.8 \times 10^{-8}$</td>
<td>(50)</td>
</tr>
<tr>
<td></td>
<td>$Fe_2O_4$ at $P_{O_2} = 10^{-11}$ atm</td>
<td>$2.5 \times 10^{-9}$</td>
<td>(51)</td>
</tr>
<tr>
<td></td>
<td>Spinel $Ni_{0.8}Fe_{2.2}O_4$</td>
<td>$2.0 \times 10^{-11}$</td>
<td>(52)</td>
</tr>
<tr>
<td></td>
<td>$NiO$ at $P_{O_2} = 0.21$ atm</td>
<td>$4.1 \times 10^{-12}$</td>
<td>(53)</td>
</tr>
<tr>
<td>Ni</td>
<td>&quot;pure Fe&quot;</td>
<td>$2.4 \times 10^{-12}$</td>
<td>(54)</td>
</tr>
<tr>
<td></td>
<td>80 a/o Fe</td>
<td>$2.2 \times 10^{-12}$</td>
<td>(55)</td>
</tr>
<tr>
<td></td>
<td>&quot;pure Ni&quot;</td>
<td>$9.3 \times 10^{-12}$</td>
<td>(56)</td>
</tr>
<tr>
<td></td>
<td>$NiO$ at $P_{O_2} = 1$ atm</td>
<td>$1.6 \times 10^{-12}$</td>
<td>(57)</td>
</tr>
<tr>
<td></td>
<td>Nickel Ferrite</td>
<td>$6.2 \times 10^{-15}$</td>
<td>(58)</td>
</tr>
<tr>
<td>O</td>
<td>Fe</td>
<td>$6.8 \times 10^{-7}$</td>
<td>(59)</td>
</tr>
<tr>
<td></td>
<td>Ni</td>
<td>$4.4 \times 10^{-8}$</td>
<td>(60)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$6.9 \times 10^{-8}$</td>
<td>(61)</td>
</tr>
</tbody>
</table>
interface should also contribute to some of the product formation. However, such a mechanism should not rule out the possibility that Fe ions can diffuse further into the NiO phase.

As reaction proceeds, the primary growth front of the γ phase should be in the Fe-doped NiO adjacent to the spinel/NiO interface. As Fe ions continuously enter the Fe-doped NiO, Ni ions should become relatively unstable with respect to γ formation. Nickel-supersaturated NiO can be achieved locally by localized withdrawal of Ni ions from the NiO crystal in the vicinity of the pre-existing γ precipitates that are present near the γ-spinel/γ-Fe-doped NiO interface, as depicted in parts (a) and (b) of Fig. 12. Thus, localized growth of γ into the NiO phase can occur. This is conceivable because the phase diagram (25), Fig. 7, allows γ and Fe-doped NiO to coexist if the partial pressure of oxygen is between \(10^{-10.36}\) and \(10^{-10.06}\), which must be the case in the vicinity of the γ-spinel/NiO interface.

The direct forward growth of γ nodules into the NiO phase to form rods, eventually resulting in lamellar-aggregate, is not favorable in this case because the growth tips of these γ nodules are some distance behind the leading Fe-doped zone in the NiO.
Figure 12 - Schematic representation of the physical picture for the γ growth process to produce interwoven microstructure in the reaction between Fe and NiO. The relative dimensions of the product phases are greatly exaggerated.
There exists a statistical distribution of Ni-ion clusters, in the atmosphere surrounding these γ nodules. Only clusters with sufficiently large radii should be eligible to form γ and accrete to the pre-existing γ nodules. Therefore, the direction of growth of these nodules is governed by the localized condition of supersaturation of the Ni ions, i.e., depending on where the eligible Ni-ion clusters are located.

However, the process discussed above can only release some of the Ni ions from the meta-stable Fe-doped NiO. As a result of continuous supply of Fe ions into this phase from the adjacent spinel phase, the NiO becomes supersaturated. According to the phase diagram of Fe-Ni-O system at 1000°C, Fig. 7, supersaturated NiO should decompose to a spinel of about 10 a/o Ni, γ of about 0.5 a/o Fe, and NiO saturated with Fe of about 10 a/o Fe.

The reaction products add on to the existing product phases and consequently cause the γ-spinel/γ-NiO interface to advance toward the NiO, as depicted in part (c) of Fig. 12. Both cation position change and plastic deformation of oxides must occur in order to accommodate the change in the oxide structure and the precipitation of γ. Newly formed γ should preferentially add to the existing γ phase because in doing so less surface energy of formation of new
precipitates is required, and thus this is thermodynamically favorable.

Approximately three moles of Ni form for each mole of \( \text{NiFe}_2\text{O}_4 \), i.e.,

\[
2\text{Fe} + 4 \text{NiO} \rightarrow \text{NiFe}_2\text{O}_4 + 3\text{Ni} \quad (34)
\]

However, because its molar volume is greater, the total volume formed of \( \text{NiFe}_2\text{O}_4 \), 44.8 cm\(^3\)/mole (31), is greater than the total volume of Ni, 19.8 cm\(^3\) (31). Thus, spinel appears as the dominant phase in the aggregate product.

Because Fe ions continuously enter the product oxide at the Fe/product interface, the spinel should be converted to wustite containing about 0.5 to 2 a/o Ni in solution and \( \gamma \) alloy of varying composition, as depicted in part (d) of Fig. 12.

\[
\text{Fe} + \text{"NiFe}_2\text{O}_4" \rightarrow \text{Ni}_{a} \text{Fe}_{1-a} \text{ alloy} + \text{Ni}_{m} \text{Fe}_n \quad (35)
\]

and

\[
\text{Fe} + \text{Ni}_{m} \text{Fe}_n \text{O}_4 \rightarrow \text{Ni}_{b} \text{Fe}_{1-b} \text{ alloy} + \text{"FeO"} \quad (36)
\]

where the trend reactions (35) and (36) are the qualitative explanation of the reaction process. No attempt is made to balance these trend reactions.
In effect, the growth mechanism of the reaction products is primarily associated with the diffusion of Fe ions through the wustite and spinel into the NiO crystal between the initial metallic precipitates. Consequently, the oxygen activity in the Fe-doped NiO near the $\gamma$-spinel/NiO interface decreases causing some $\gamma$ to precipitate in the Fe-doped NiO and subsequently $\gamma$ and spinel and even later, $\gamma$ and wustite to form. During the reaction, the dominant transport species are the Fe cations, cation vacancies, and positive holes in the oxide phases. Most of the electrons should transport via the metallic precipitates.

The generalized growth mechanism of the reaction products described above represents a simplified overview of the reaction process. It is important to note that the arrangement of the $\gamma$ in the $\gamma$-wustite or $\gamma$-spinel aggregate is dictated by the local condition of supersaturation. To be explicit, let us consider the schematic representation depicted in Fig. 13 in which the Fe-doped NiO region in the product zone is given in detail for the purpose of the present discussion.

Part (a) of Fig. 13 represents some of the interconnected $\gamma$ particles formed during the very early stage of reaction. Since Fe ions can dissolve
Figure 13 - Schematic representation of the effect of the local condition of supersaturation on the arrangement of the $r$ phase in the $r$-oxide aggregate.
into the NiO, a very thin layer of Fe-doped NiO should form between the \( \gamma \)-spinel and the un-doped NiO. The concentration of Fe ions in this doped NiO is about 10 a/o Fe (27) at the interface in contact with the \( \gamma \)-spinel aggregate and about zero in the undoped zone. Because the thickness of this doped NiO is very small at the early stage of phase transformation, the gradient in the concentration of Fe ions in this phase should be very large, as depicted in part (b) of Fig.13. As a result, a very distinct gradation in the state of supersaturation of Ni ions with respect to \( \gamma \) alloy should be realized between the region at plane 1 and that at plane 2, in Fig. 13(b), as the spinel/NiO interface advances toward the NiO phase during the growth process. Consequently, the localized flux of Ni ions migrating toward the growing nodule of \( \gamma \) along plane 1, indicated by A in part (c) of Fig. 13 should be more dominant than that of Ni ions migrating toward the growing nodule of \( \gamma \) along plane 2, indicated by B in the same Figure. Therefore, sidewise growth of the \( \gamma \) nodule should be prevalent, although slight thickening of this \( \gamma \) nodule is possible. This is depicted in part (d) of Fig. 13. As the \( \gamma \) nodule grows, the Fe ions that were initially located in this region are dissipated by diffusion either sidewise or forward,
ahead of the growing $\gamma$ nodule. Dissipation of Fe ions backward into the spinel phase is unlikely because that would require Fe ion to migrate up its own concentration gradient. The rejection of Fe ions in the sideward direction, indicated by C in part (d) of Fig. 13 would cause a greater degree of supersaturation of Ni ions in the doped NiO with respect to the formation of $\gamma$ because the concentration of the Fe ions in this region is already very high compared to that in the region slightly ahead of it. Consequently, the $\gamma$ nodule should prefer to grow sidewise while the Fe ions are pushed ahead of the $\gamma$ phase as indicated by D in part (d) of Fig. 13. In effect, the growing $\gamma$ nodule is always sandwiched by spinel at its back and Fe-rich NiO at its front. This condition eventually leads to the formation of an intermittent arrangement of $\gamma$ in the $\gamma$-oxide aggregate, as depicted in part (e) of Fig. 13.

A coherent layer of $\gamma$ cannot be formed because the interface between $\gamma$-spinel and $\gamma$-NiO keeps advancing toward the NiO phase as the reaction proceeds. The untransformed supersaturated NiO will eventually transform, via a diffusion process, into $\gamma$ and spinel. Such a spinel will interrupt the continuity of the layer.
After some period of reaction time, the reaction products, especially the Fe-doped NiO phase, grow thicker while the concentration of Fe ions and the partial pressure of oxygen at the γ-spinel/NiO and the Fe-doped/undoped NiO interfaces remain constant at equilibrium values. The gradients of the Fe ion and the partial pressure of oxygen in the Fe-doped NiO phase then should become less, as depicted in part (f) of Fig. 13. In this stage, the γ-spinel/NiO interface moves relatively more slowly toward the NiO phase because the diffusion distance, x, is greater while the diffusivity is assumed constant. Thus D/x, which is the rate of interface migration, is decreased. Then the rate of supersaturation of Ni ions with respect to formation of γ alloy in the Fe-doped NiO phase at plane location 3, as shown in part (f) of Fig. 13 become less significantly different from that at plane 4 in the same Figure. As a result, the preferential sidewise growth of γ phase in the Fe-doped phase in the vicinity of the spinel/NiO interface should become less prevalent. Rather, the growing γ nodules should experience a more competitive short range flux of Ni ions surrounding them, as depicted in part (g) of Fig. 13, and they should start to grow in a three-dimensional manner along a poorly defined tortuous route in the Fe-doped NiO
phase by localized withdrawal of Ni ions from the Fe-doped NiO. As this condition begins to dominate, a breakdown of the relatively well-defined intermittent layered arrangement of $\gamma$ alloy is expected, as depicted in part (h) of Fig. 13. The further growth of $\gamma$ phase in this manner should result in a poorly defined interlocking aggregate of $\gamma$ and oxide phases, called the interwoven aggregate (4), as depicted in part (i) of Fig. 13.

Figure 14 represents close-up views of the product microstructure at the product/NiO interface of the Fe/NiO reaction after 5 minutes and 30 hours, respectively, at 1000°C. These microstructures were taken after the samples were etched by 50 % HCl to distinguish the Fe-doped NiO zone from the other product zones. The microstructures clearly indicate that the first growth of $\gamma$ is in the Fe-doped NiO from the region near the spinel/NiO interface toward the NiO phase. They also clearly show the major difference in the growth mechanism of the $\gamma$ in the Fe-doped NiO phase which can result in a different arrangement of the phase in the two-phase aggregate. These microstructures clearly support the growth mechanism proposed earlier.

Although the newly formed $\gamma$ alloys in part (b) of this Figure appear as discrete particles in the
Product microstructure near the product/NiO interface of the Fe vs. NiO displacement reaction at 1000°C after:

(a) 5 minutes; 1000 x;
(b) 30 hours; 600 x.

Figure 14 - Product microstructure near the product/NiO interface of the Fe vs. NiO displacement reaction at 1000°C after:
(a) 5 minutes; 1000 x;
(b) 30 hours; 600 x.
Fe-doped phase, it is important to realize that the growth of such a phase is three dimensional. The discrete particles seen should be parts of the tortuous tentacles extending locally from some predominant growth of $\gamma$ nodules. A discrete precipitate of $\gamma$ cannot be formed in the middle region of the Fe-doped NiO because the greatest supersaturation of Ni ions in NiO should be achieved near the spinel/NiO interface rather than in the middle region in NiO, and consequently, the first $\gamma$ to form should be close to the spinel/NiO interface rather than in the middle of NiO.

Figure 15 represents a typical microstructure in the $\gamma$-wustite aggregate where the arrangement of the $\gamma$ in the aggregate starts to deviate from the intermittent layered pattern. This corresponds to the transition step to the formation of the tortuous interwoven pattern of $\gamma$ observed in the product microstructure after long reaction times.

The product microstructures which resulted after Fe was reacted with NiO for 2, 3, 5, 10 min., 4 hr. and 30 hr., at 1000°C are represented, respectively, in parts (a) to (f) of Fig. 16. All the product microstructures shown in this Figure comprise three zones all of which are interwoven aggregates. The first one is a two-phase
Figure 15 - Typical microstructure of the \(\gamma\)-wustite aggregate in the region where the arrangement of the \(\gamma\) in the aggregate starts to deviate from the intermittent layered pattern. 1330 x.
Figure 16 - Chronological development of the product microstructure of the Fe vs. NiO reaction at 1000°C after: (a) 90 sec; (b) 3 min; (c) 5 min; (d) 10 min; (e) 4 hours; and (f) 30 hours.
Figure 16 (continued)

(c) 1330 x

(d) 1330 x
Figure 16 (continued)
zone which exists adjacent to the reactant Fe and consists of wustite and $\gamma$ alloy. Spinel and $\gamma$ constitute the second zone. The last zone comprises a Fe-doped NiO containing little $\gamma$. The $\gamma$ alloy in all zones is assumed to be continuous. The $\gamma$ alloy is rich in Fe in the region near the reactant Fe and its Fe content gradually decreases towards the NiO, see the phase diagram in Fig. 7. The Fe content in the oxides and spinel is rich in the region near the Fe phase and gradually decreases across each oxide-$\gamma$ aggregate phase toward the NiO phase.

The arrangement of $\gamma$ in the $\gamma$-oxide aggregate near the Fe/product interface is the intermittent layered pattern while in the region further away from this interface, the arrangement of $\gamma$ is in the tortuous interwoven pattern. A view of product microstructure along the growth direction should be helpful in envisioning of the difference between these two types of arrangement of the $\gamma$ phase.

Part (a) of Fig.17 shows a cross-sectional view of the microstructure of the Fe vs. NiO displacement reaction after 30 hours at 1000°C. Also shown in parts (b) and (c) of this Figure are the typical structures of $\gamma$ phase in the $\gamma$-wustite aggregate product at location approximately indicated by the arrows in the
Figure 17 - Typical product microstructure of the Fe vs. NiO displacement reaction at 1000°C:
(a) Cross-sectional view of reaction products.
(b) and (c) Structure of $\gamma$ in the $\gamma$-wustite aggregate product at indicated locations when being viewed along the major growth direction of the reaction products.
Figure when being viewed along the major growth direction of the reaction products. The wustite phases in parts (b) and (c) of Fig. 17 were selectively dissolved by a 4% Nital solution so that the three-dimensional growth of the $\gamma$ phase can be emphasized. Notice from parts (b) and (c) of Fig. 17 that small particles of $\gamma$ are still present even though the oxide matrixes have been etched away. This supports the idea that precipitates of $\gamma$ alloy should prefer to accrete to the pre-existing phase.

A typical view of the steady-state product microstructure resulting from reacting Fe with polycrystalline NiO at 1000°C is represented in Fig. 18. As in the case of single crystalline NiO vs. Fe, the product microstructure comprises three zones, all of which are interwoven aggregates. The first is a two-phase zone which exists adjacent to the reactant Fe and consists of wustite and $\gamma$ alloy. Spinel and alloy constitute the second zone. The other zone comprises Fe-doped NiO with little $\gamma$ precipitates in it. Parts (a) and (c) of Fig. 19 represents the Fe/product and product/NiO interface regions. Such morphologies are essentially those observed in the case of single crystalline NiO vs. Fe. This suggests that the growth mechanism of the products in the two-cases is essentially the same.
Figure 18 - Typical product microstructure of the Fe vs. NiO polycrystal displacement reaction after 7.5 hours at 1000°C. 100 x.
Figure 19 - Typical product microstructure of the Fe vs. NiO polycrystal displacement reaction after 7.5 hr. at 1000°C:
(a) The Fe/product interface region, 1000 x;
(b) The product/NiO region, 600 x.
The apparent difference in the product microstructures resulting from using single crystal and polycrystalline NiO as starting materials is that when a polycrystalline NiO is used as reactant, the $\gamma$ phase forms preferentially along the pre-existing NiO grain boundaries and voids in the NiO crystal. This $\gamma$ phase that formed along pre-existing grain boundaries of NiO results in a "Chinese-script" structure across the product zones. On the other hand the $\gamma$ phase that formed at the pre-existing void in the NiO appears as a large white phase, such as that shown in the upper-right corner of the product zone in Fig. 18. It is apparent from this Figure that $\gamma$ eventually displaces the pre-existing voids, which were eventually transported to the Fe/product interface, represented by the dark region in the upper-right corner of this Figure.

Despite the presence of the grain boundaries in the polycrystalline NiO, where new $\gamma$ formed preferentially, it is apparent, upon examining the microstructure showing the product/NiO interface region in part (b) of Fig. 19, that the growth of the $\gamma$ nodule along the grain boundaries, i.e., that with a sharp spike in the Figure, is not significantly faster than the growth of the $\gamma$ nodule which extends from within the grain of NiO, i.e., the one that has relatively round
shape in this Figure. An extending $\gamma$ nodule growing within a grain can grow at approximately the same rate as an extending $\gamma$ nodule advancing along the grain boundary of NiO if the newly formed $\gamma$ in the former case adds to the pre-existing phase which serves also as a preferential site for precipitation. All these evidences add further support to the postulate that all of the $\gamma$ phases are interconnected in a three-dimensional manner and that newly formed $\gamma$ should prefer to accrete to the pre-existing phase rather than precipitate as a new discrete nucleus.

D. Phenomenological Observation of the Product Phases near the Fe/Product Interface.

It is apparent from Figure 20, which shows the chronological development of product microstructure near the Fe/product interface, that as the displacement reaction between Fe and NiO proceeds the $\gamma$ phase in the $\gamma$-wustite aggregate in this region becomes thicker. In this section, the mechanism that is responsible for this thickening process is discussed.

As the reaction product grows thicker, the gradient of oxygen activity across an aggregate product becomes less because the activities of oxygen at the aggregate boundaries must be fixed thermodynamically.
Figure 20 - Chronological thickening of the $\gamma$ and the wustite phases in the $\gamma$-wustite aggregate near the Fe/product interface:
(a) 90 sec;  (b) 5 min;
(c) 10 min;  (d) 60 min;
(e) 7.5 hr;  (f) 30 hr;
Consequently, the partial pressure of oxygen at a given point in the product zone decreases as the reaction proceeds. This process is schematically represented in Fig. 21.

From the phase diagram of the Fe-Ni-O system at 1000°C, the equilibrium concentrations of Ni both in the oxides and alloys in the coexisting γ-wustite aggregate decrease substantially as the activity of oxygen in these products decreases. Thus, as Fe ions continuously enter the product oxide phases from the Fe/product interface, a localized displacement reaction, primarily the substitution of Fe ions for the Ni cations in wustite in the γ-wustite aggregate should take place. The supersaturated Ni ions are reduced locally to form Ni atoms and add to the pre-existing γ at the localized γ/wustite interface in the γ-wustite aggregate. The reduction of Ni ions results in the creation of cation vacancies in the oxide phase. These cation vacancies transport toward the Fe phase and oxidize more Fe atoms to form more Fe ions. Thus, the redox reaction is a closed circuit one. This process is schematically depicted in part (a) of Fig. 22. As more Ni atoms are added to the pre-existing γ phase, the concentration of Ni in the γ phase tends to build up locally. This is prohibited by the phase diagram.
Figure 21 - Schematic representation of the variation of the activity of oxygen across the γ-wustite aggregate product. The invariant partial pressures of oxygen at the Fe/product and the γ-wustite/γ-spinel interfaces are represented by A and B. $x_1$, $x_2$, and $x_3$ represent the thickness of the γ-wustite aggregate after reaction time $t_1$, $t_2$, and $t_3$, respectively, where $t_1 < t_2 < t_3$.
Thus, dissipation of the excess Ni atoms in the $\gamma$ phase must take place. This can be achieved in part by the localized reduction of Fe ions in the oxide phases, as depicted in part (a) of Fig. 22. Dissolution of more Fe into the $\gamma$ phase can of course dilute the Ni content in the alloy. However, another process is also possible, i.e., the interdiffusion of both Fe and Ni atoms in the $\gamma$ phase. Nickel atoms in the $\gamma$ diffuse in response to the activity gradient within the $\gamma$ toward the Fe phase, which acts as an infinite sink for the Ni atoms. At the same time Fe atoms from the Fe phase can also diffuse in the $\gamma$ in this region in order to minimize the local build up of the Ni content in this $\gamma$ phase. This process is represented in part (b) of Fig. 22.

As this process is going on another mechanism should also operate. As discussed earlier, $\gamma$ particles that form during the transient stage are in the form of interconnected precipitates. Such a structure is schematically represented by part (c) of Fig. 22. These precipitates have a large surface to volume ratio, such a product morphology should be thermodynamically metastable. At 1000°C, diffusion can be significant. Thus, these $\gamma$ precipitates can undergo an Ostwald ripening process; that is the coalescence of small
Figure 22 - Schematic drawing representative of the thickening of $\gamma$ and wustite near the Fe/product region.
precipitates to form bigger ones in order to reduce the surface to volume ratio of the precipitates. This is depicted in part (d) of Fig. 22.

In effect, the accumulation of Ni atoms and the Ostwald ripening are responsible for the apparent thickening of the $\gamma$ phase near the Fe/product interface. At a later period of time when the thickening $\gamma$ becomes the dominant phase in the $\gamma$-wustite aggregate, as shown in part (e) of Fig. 22, an additional mechanism should become active. That is the dissociation of wustite, say at A in part (e) of Fig. 22, into Fe and O atoms which dissolve into the $\gamma$ alloy. The Fe atoms dilute the Ni content in the $\gamma$ alloy, while the O atoms diffuse toward the reactant Fe and cause more wustite to form at the Fe/product interface. Thus, the wustite at the Fe/product interface grows thicker at the expense of some of the adjacent wustite in the $\gamma$-wustite aggregate.

Some of the previously-existing interwoven wustite must remain in the $\gamma$-wustite aggregate because they serve as the diffusion paths for Fe ions to enter into the product phase and contribute to further growth of the reaction products. That the thickening of $\gamma$ phase in the $\gamma$-wustite aggregate cannot eventually squeeze out all the previously-existing wustite and shut down the
reaction process is supported experimentally. When a relatively thick Ni layer is electroplated on the Fe before letting the Ni-plated Fe react with the NiO, it has been found, as will be discussed in detail later in this chapter, that the interwoven reaction products can also be formed and some wustite is found in this plated $\gamma$ phase.

Although the wustite particles in the thickening $\gamma$-wustite aggregate, in Fig. 20, appear as discrete precipitates, it should be realized that these structures are indeed continuous in a three dimensional way. What appear to be discrete particles on a sectioned sample are part of the tortuous threads of the wustite in the thickening $\gamma$ phase.

Thus, the reaction process can always proceed regardless of $\gamma$ accumulation near the Fe/product interface. The wustite phases in the (thickening $\gamma$)-wustite aggregate are eventually restricted by the dominant $\gamma$ phase, and consequently, the local flux of Fe ions, in equiv./cm$^2$-sec, through the wustite phase must be very high in order to maintain a "steady-state" current of Fe ions during the reaction process. This process represents a kinetic, rather than equilibrium, constraint on the growth process.
E. Effect of a Pre-existing Ni layer on the Product Microstructure

With regard to the morphology of the reaction products resulting from the displacement reaction between a metal and an oxide, it is interesting to compare the product morphologies resulting from the Fe vs. NiO reaction couple with those resulting from the Fe vs. Cu$_2$O couple, where a lamellar-aggregate product comprised Cu and iron oxide phases, as shown in part (a) of Fig. 23, has been observed (2).

To provide a background for discussion, the situation of the Fe vs. Cu$_2$O couple is recapitulated here as follows:

In the case of Fe vs. Cu$_2$O reaction couple, Cu$_2$O can accommodate essentially no Fe in solution (2), and the Cu-Fe alloy system has limited mutual solid solubility. According to Yurek (2), the steady-state displacement reaction proceeds by the dissociation of Cu$_2$O into 2Cu and O at the Cu$_2$O/product interface. Oxygen atoms diffuse through the Cu phase toward the Fe phase, eventually causing oxidation of Fe to magnetite and wustite. Eventually, a continuous layer of Cu forms between the Cu$_2$O/product interface while iron oxides grow as lamellar rods penetrating into the Cu phase near the Cu$_2$O phase. The reaction front is at
Figure 23 - Displacement reaction between Fe and Cu$_2$O at 1000°C:
(a) Lamellar-aggregate product microstructure.
(b) Schematic representation of the model for the growth of reaction products. After Yurek, et al. (2,18).
the tip of the lamellae where magnetite grows upon the simultaneous arrival of O atoms via the Cu phase and of Fe ions through the oxide phases. The growth model is recapitulated in part (b) of Fig. 23. In this particular system, the rate-limiting step for the reaction process, as deduced from the comparison of the rational rate constant for O in Cu, \( k_r(Cu) \) and that for Fe ions in oxides, represented approximately by \( k_r(FeO) \), is the arrival of O atoms at the reaction front. Consequently, according to Rapp et al., (4), a lamellar-aggregate product morphology should be formed. This is consistent with that observed experimentally (2).

Now, an interesting question arises if a sufficiently thick layer of Ni pre-exists between the Fe and NiO couple before any displacement reaction product forms, so that such a layer of Ni is analogous to the Cu layer formed during the reaction of Fe vs. Cu\(_2\)O. Then the very first oxide formed might involve, in some degree, the diffusion of O into the pre-existing Ni phase. The issue is then whether or not a lamellar-aggregate product microstructure, like that of Fe vs. Cu\(_2\)O couple, can be formed in the "Fe"/NiO system. In other words, it is interesting to examine whether or not the interwoven-aggregate product morphology
normally observed in the Fe vs. NiO couple can be altered to form a lamellar-aggregate arrangement by surface pretreatment of the reaction couple.

In an attempt to answer this question, a layer of Ni between the reaction couple was introduced by electroplating a Ni layer on the Fe samples. The Ni-plated Fe samples were reacted with NiO crystal discs for various times at 1000°C. Then the product morphologies formed from such reaction couples were studied.

The photomicrograph shown in Fig. 24 is a typical structure of the unreacted Ni plating and the Fe substrate taken from the region where the Ni-plated Fe was held against the alumina disc in the Mo holder. The adhesion of the plated Ni and the Fe substrate in Fig. 24 was excellent and there was no observable peeling or crack in the Ni-plating resulting from the rapid heating and cooling process.

The product microstructure which resulted after an Fe sample with about a 1 µm thick Ni plate on its surface was reacted with a NiO single crystal for 4.5 min at 1000 °C is presented in part (a) of Fig. 25. Part (b) of the same Figure is the product microstructure resulting from reacting unplated Fe with the other surface of the NiO single crystal.
Figure 24 - Typical microstructure of the unreacted Ni plating and the iron substrate of a Ni-plated Fe. 4% Nital etched, 3000 x.
Figure 25 - Product microstructure resulting from reacting the two surfaces of a NiO single crystal with:
(a) an 1-μm thick, Ni-plated Fe, and
(b) a pure Fe,
respectively, for 4.5 minutes at 1000°C.
When a thicker, about 10 μm thick, Ni layer was plated on the Fe before letting it react with a polycrystalline NiO for about the same reaction time at 1000°C, no reaction product could be metallographically observed from this reaction couple. This is shown in Fig. 26. Since the contact at the reacting interface is excellent, only the pre-existing Ni layer should be the cause for the inhibition of reaction product. Figure 27 show the product microstructure observed on the other side of the surface of the NiO sample where it was reacted against unplated Fe. Such a product microstructure should have been observed in the case we have just discussed should the Ni layer not have existed between the Fe and NiO reactants.

In summary, results from short-time experiments on the Ni-plated Fe vs. NiO couple indicate that: (i) an essentially interwoven aggregate product morphology resulted from the reaction process; (ii) the pre-existing Ni layer between the Fe and NiO phases retards the nucleation process of the reaction products.

The morphologies of the reaction products of Ni-plated Fe vs. NiO single crystals after long reaction times are shown in Fig. 28. The iron reactants used in the reaction were plated with 0.015 and 0.025 mm thick Ni layers. These Ni-plated Fe samples were
Figure 26 - No metallographically observable product was formed when a Fe plated with 10 μm thick Ni was reacted against a NiO polycrystal. (a) As polished, 1330 x; (b) 4% Nital etched, 1330 x.
Figure 27 - Product microstructure resulting from reacting pure Fe against the other surface of the NiO sample used in Fig. 26. 4% Nital etched, 1330 x.
Figure 28 - Product microstructure of the Ni-plated Fe vs. NiO displacement reaction at 1000°C.
(a) Thickness of plating = 0.015 mm
   Reaction time = 8 hr
(b) Thickness of plating = 0.025 mm
   Reaction time = 11 hr
Figure 29 - Typical product microstructure resulting from the Ni-plated Fe vs. NiO displacement reaction at 1000°C.
(a) The Fe/product region;
(b) The middle region of the product zone;
(c) The product/NiO region.
Figure 29 (continued)
reacted with NiO single crystals for 8 and 11 hours, respectively. The morphology of the reaction products shown in Figs. 28 and 29 is in a more or less periodic arrangement between the γ and oxide phases. This kind of structure has not been observed for the unplated Fe vs. NiO couple. Thus, it is interesting to examine this peculiar structure with the aid of the SEM.

Part (a) of Fig. 30 represents the product microstructure shown in part (b) of Fig. 29 after the wustite was selectively dissolved away by 4% Nital solution. A typical product microstructure when viewed along a direction normal to that in part (a) of this Figure is also shown in part (b). These microstructures reveal that the periodic pattern of the γ-oxide aggregate product morphology, seen in Fig 28, is in fact a result of the tortuous growth of γ nodules which have originated from a relatively flat plane and swung up-and-down, in a three-dimensional manner during the growth process.

It is interesting to consider how the interwoven product morphology develops despite the presence of a pre-existing Ni layer between the reactant Fe and NiO.

At the early stage of the reaction process, interdiffusion between Ni and Fe at the interface between the Ni-plating and the Fe substrate takes
Figure 30 - Typical microstructure of Y in the Y-wustite aggregate product after the wustite was selectively dissolved away: (a) Cross-sectional view, and (b) Viewed in the direction normal to that in part (a).
place; consequently, a Fe-rich zone in the original Ni-plating moves toward the NiO. At the same time, some Ni atoms in contact with the O-rich NiO are oxidized locally by filling into the vacant sites in the cation sublattice of NiO. This increases the cation/anion ratio to form Ni-saturated NiO. At the early stages, reaction between Ni and NiO does not stop once the localized equilibrium between Ni and NiO is achieved because gradients in the activity of oxygen and nickel near the Ni/NiO interface still exist. Consequently, the localized Ni-saturated NiO dissociates to form Ni and O atoms so that O can diffuse into the Ni-plating, and Ni atoms protrude into the NiO phase in order to dissipate, respectively, the activity gradients of the O and Ni atoms across the bulk phases. The dissociated Ni atoms should add readily to the pre-existing Ni plating adjacent to the Ni-saturated NiO, leading to growth into the NiO phase, whereas the dissociated O atoms which have a potential equal to the $P_{O_2}$ for the coexistence of Ni and NiO diffuse through the Ni-plating towards the Fe phase. This process should proceed spontaneously to achieve a Ni-saturated NiO and an O-saturated Ni in the bulk product. This process is schematically depicted in parts (a) and (b) of Fig. 31.
Figure 31 - Proposed scheme for the development of product microstructure of the Ni-plated Fe vs. NiO displacement reaction.
Since the partial pressure of oxygen at the γ/Ni-saturated NiO interface is respectively about 4 and 2 orders of magnitude greater than those of wustite and spinel (25,34), most of the O atoms dissolved in the Ni-plating have a sufficiently high potential to internally oxidize the Fe-rich γ to form two-phase layer of wustite and spinel particles when they encounter the Fe-rich during diffusion.

The solubility and diffusivity of O atoms in Ni have been reported to be $4.4 \times 10^{-8}$ cm$^2$/sec and 140 ppmw, respectively (60). With the density of Ni, 8.9 g/cm$^3$ (31) and the molar weight of oxygen, 16 g/mole, the solubility-diffusivity product of oxygen in Ni is calculated to be $3.4 \times 10^{-12}$ mole/cm-sec.

The self-diffusion coefficient of Fe in the Ni-Fe alloy as extrapolated from the result of Kristal et al. (62) is about $1.5 \times 10^{-11}$ cm$^2$/sec. With the molar volume of Fe, 7.09 cm$^3$/mole (31), the solubility-diffusivity product of Fe in the γ is calculated to be $2.1 \times 10^{-12}$ mole Fe/cm-sec, which is slightly less than that for O in Ni. Thus, the depth of penetration of O atoms is slightly greater than that of the Fe atoms in this γ phase. Thus, it is expected that the confrontation between the two active species, i.e., the O and the Fe, should take place about the middle
region, but slightly shifted toward the Fe phase, of the \( \gamma \)-plating. Consequently, internally oxidized wustite-spinel particles, with the wustite facing the Fe phase and the spinel in the opposite direction, are formed there. This process is depicted in part (b) of Fig. 31.

As reaction proceeds, further dissociation of NiO takes place as discussed earlier. The newly formed Ni should add to the pre-existing \( \gamma \). In so doing the surface energy required to create a new free-surface can be reduced. Consequently, the coexisting \( \gamma \) and NiO should form side by side in a periodical manner as the growing nodules of \( \gamma \) swing tortuously into the NiO phase. The \( \gamma \) nodules are a three dimensional structure because these phases grow by localized withdrawal of the Ni ions from the Ni-ion cloud in the NiO host lattice surrounding them. In other words the point effect of diffusion always prevails.

At the same time, more dissociated O atoms dissolve into the \( \gamma \). However, once the Ni tentacles coexisting with Ni-saturated NiO grow longer, the dissociated O atoms must diffuse over a greater length in the \( \gamma \) phase. Consequently, these newly formed O atoms should encounter the incoming Fe-rich at some position shifted toward the NiO phase. Thus, the newly formed
wustite-spinel particles should precipitate nearer to the NiO phase in the $\gamma$ phase, as depicted in part (c) of Fig. 31.

The diffusivity of Fe ions in the wustite is about 4 orders of magnitude greater than that of Fe atoms in the $\gamma$. Therefore, when the Fe atoms diffusing through the $\gamma$ matrix encounter the $\gamma$/wustite interface of the internally oxidized precipitates, it should be more favorable for these atoms to be oxidized to form wustite and diffuse therein rather than diffuse further in the $\gamma$ matrix toward the NiO phase. This is described in part (c) of Fig. 31. Thus, the internally oxidized wustite-spinel particles can grow very rapidly toward the NiO phase as Fe atoms are oxidized at the Fe/wustite interface. This statement is certainly true despite the fact that the diffusivity of Fe ions in spinel is very slow (44). This is because growth of the two-phase oxide is virtually controlled by the growth of the major wustite phase (see Reference 63 for the formation of two-phase wustite-magnetite for example). Eventually, bridging of the internally oxidized particles, as depicted in part (d) of Fig 31, occurs. Because of this rapid growth of internally oxidized particles, the tips of the two-phase oxide can meet the coexisting $\gamma$ and Ni-saturated NiO in a short period of time, as
depicted in part (e) of Fig. 31.

Once these nodules reach the Ni-saturated NiO, Fe ions from the spinel can dissolve into the Ni-saturated NiO displacing its Ni ions which eventually precipitate out of the Fe-doped NiO, as depicted in part (e) of Fig. 31. Then, further dissolution of Fe ions causes the supersaturated NiO to decompose into spinel and \( \gamma \), as depicted in part (f) of Fig. 31. Because Fe ions continuously enter the wustite at the Fe/wustite interface, the spinel should be converted eventually to wustite and small amount of \( \gamma \), as required by the phase diagram \((24,25)\). Once the three aggregate product zones, i.e., \( \gamma \)-NiO, \( \gamma \)-spinel and \( \gamma \)-wustite are formed, the growth mechanism of the reaction product can essentially be described by the mechanism postulated for the growth of the unplated Fe vs. NiO, which has been discussed in detail and is not repeated here.

As the displacement reaction proceeds, the \( \gamma \) nodules in the \( \gamma \)-oxide aggregates are likely extended from the very first \( \gamma \) tentacles that were formed from the dissociation of NiO and rooted on the very flat previously-existing plated Ni. The extending \( \gamma \) tentacles are likely to swing tortuously side by side up and down in the NiO phase in a very competitive manner driven by the point effect of diffusion as they
grow into the NiO phase. Such a competitive growth should result in the periodic pattern in the \( \gamma \)-oxide aggregate.

The amplitude of this periodic pattern appears to increase as the thickness of the plated-Ni increases, see parts (a) and (b) of Fig. 28. This is understandable because as the thickness of the plated Ni increases the distances for the \( \text{O} \) and Fe atoms to diffuse in the plated \( \gamma \) phase increase. Consequently, a longer time is required for the very first internally oxidized wustite-spinel particles to form in the plated \( \gamma \) phase. A longer time should result in longer Ni nodules formed by the dissociation of NiO before the actual displacement reaction between Fe and NiO starts to take place, as compared with the case of thinner plated Ni on Fe. This is schematically represented in Fig. 32. Presumably, it is the difference in the length of the starting \( \gamma \) nodules between the case with thicker plated Ni and the one with thinner plated Ni that results in the apparent difference in the amplitude of the periodic pattern in the \( \gamma \)-oxide aggregates. A typical photomicrograph of the reaction product near the Fe/product interface is shown in part (a) of Fig. 33, in which the wustite phase was selectively dissolved away by a 4\% nital solution. The voids in this
Figure 32 - Schematic representation of the effect of the thickness of the Ni-plating on the length of the Ni tentacles formed from the dissociation of NiO.
(a) Thinner plating;
(b) Thicker plating.
Figure 33 - Typical product microstructure near the Fe/product interface of:
(a) Ni-plated Fe vs. NiO displacement reaction at 1000°C. 800 x
(b) Unplated Fe vs. NiO displacement reaction at 1000°C. 800 x
The wustite phase was selectively etched away.
photomicrograph represent the previously-existing wustite in the aggregate. The roots of the $\gamma$-tentacles on the thickening $\gamma$ are apparent in this Figure.

A typical microstructure of the corresponding region of the product zone resulting from the reaction between unplated Fe vs. NiO is shown in part (b) of this Figure, for comparison purposes. Notice that no $\gamma$ tentacles extending from the thickening $\gamma$ are present in this case. This is why the periodic aggregate pattern is not pronounced in the case of unplated Fe vs. NiO.

The intermittent layered pattern of $\gamma$ in the $\gamma$-wustite aggregate near the Fe/product region is not found in the present case. This is because the intermediate stage of the growth process, which gives rise to such an intermittent layered pattern of $\gamma$ in the $\gamma$-wustite aggregate, in the present case is suppressed by the presence of the pre-existing $\gamma$-tentacles which were formed from the dissociation of NiO. The newly formed $\gamma$ should add to the tips of these $\gamma$ tentacles in a manner to lengthen them and not to preferentially widen them. Sidewise growth of these $\gamma$ tentacles is unlikely because each $\gamma$ tentacle is sandwiched by the coexisting NiO which cannot tolerate more $\gamma$ phase in it.
To complete this discussion, the phenomenon near the product/Fe interface resulting from the Ni-plated Fe and NiO should be mentioned in more detail. As the displacement reaction between the Fe and NiO proceeds, a gradual buildup of Ni atoms near the Fe/product interface takes place. The buildup of Ni content in this region is the result of rejection of Ni from the alloy and oxide phases as the potential of oxygen decreases, as discussed earlier. Consequently, apparent thickening of $\gamma$ and dissociation of some wustite in this region take place. The dissociated Fe atoms add into the $\gamma$ while the dissociated O atoms move toward the Fe and oxidize more Fe to form wustite. In effect, as reaction proceeds, thickening of $\gamma$ and wustite near the Fe/product zone can occur by the same mechanism as that described for the case of unplated Fe vs. NiO.

In conclusion, the mechanism for the growth of reaction products from the displacement reaction between Ni-plated Fe and unplated Fe vs. NiO are essentially the same. Each results in interwoven-aggregate products. Plating a Ni layer on the Fe causes an additional early mechanism to operate before the "steady-state" growth process can occur. The overall kinetics for the growth process are significantly slowed by the presence of the pre-existing Ni phase. The
pre-existing Ni phase between the reactants Fe and NiO can also result in a periodic pattern in the γ-oxide aggregate product.

Putting an artificial layer of Ni on Fe sample does not result in the formation of a lamellar-aggregate product morphology, such as that observed in the case of Fe vs. Cu₂O (2). This is primarily associated with the fact that NiO can tolerate many Fe ions in its cation sublattice while Cu₂O virtually cannot dissolve any Fe ions. The growth front of the lamellar-aggregate in the Fe vs. Cu₂O couple is at the oxide/Cu interface, where a predominantly one-dimensional diffusion flux of O atoms in Cu is drawn to the tips of the oxide rods in the lamellar-aggregate. On the other hand, the growth front of the product in the Fe vs. NiO system is in the NiO phase, in which the leading γ tentacles feel free to tortuously swing into the NiO matrix. This situation favors the formation of interwoven-aggregate products and suppresses the possibility of the formation of the lamellar-aggregate products.

F. Diffusion Path for the Displacement Reaction between Fe and NiO at 1000°C

A plot of the variation of the composition on the corresponding equilibrium diagram, such as that in
Fig 7, should constitute one of the effective methods of representing experimental results in the present study of the displacement reaction between Fe and NiO in which multiphase aggregate products are formed. Such a plot is conventionally known as a diffusion path.

To trace a diffusion path for the displacement reaction between Fe and NiO at 1000°C on an equilibrium diagram represented by a $P_{o_2}$ vs. $X_{Ni}$ plot, where $X_{Ni}$ is the atomic fraction of Ni, the partial pressure of oxygen and the molar partition between alloy and the corresponding oxide or spinel must be known.

Qualitatively, since the partial pressures of oxygen at the boundaries of each two-phase aggregate, where three phases are coexisting, are invariant and known from thermodynamic data, the partial pressure of oxygen at any location in the two-phase aggregate can be approximated by assuming a linear gradient of the logarithmic value of the partial pressure of oxygen, $d \log P_{o_2} / dx$, across each two-phase aggregate. The logarithmic gradient, $d \log P_{o_2} / dx$, is used instead of $d P_{o_2} / dx$ because the difference in the partial pressure of oxygen across an aggregate, such as the $\gamma$-spinel aggregate, may be many orders of magnitude. In such a case, logarithmic gradient should be more meaningful. Consequently, the $\log P_{o_2}$ at any location within the two-phase aggregate can be approximated
by interpolation.

The molar partition between the alloy and the coexisting oxide or spinel at any location in the two-phase aggregate product is determined from the photomicrograph that represents the typical microstructure of the reaction product, such as that shown in Fig. 34, as follows. The volume fraction of $\gamma$ alloy at any location in the two-phase aggregate is determined by point counting the fraction of grid intersections lying on the $\gamma$ alloy phase, from a grid network which was superimposed onto the photomicrograph of the product microstructure. Then, with the assumption that the volume fraction of $\gamma$ in the aggregate can be fairly represented by the point fraction of that phase at the same location, the volume fraction of $\gamma$, and consequently the volume fraction of the corresponding oxide or spinel, can be determined. With the available data of molar volume of $\gamma$, approximated from the data of pure Fe and Ni, and oxide or spinel (31), the numbers of moles of $\gamma$, oxide or spinel can be calculated. Thus, the molar partition of components between the $\gamma$ and oxide or spinel in the aggregate can be determined.

Once the $P_{O_2}$ and the molar partition of the two phases in the aggregate are known, representative points can be traced on the equilibrium diagram of the type $P_{O_2}$ vs. $X_{Ni}$. 
Figure 34- Typical product microstructure of the displacement reaction between Fe and NiO at 1000°C. The partial pressures of oxygen and the volume fractions of $\gamma$ in the $\gamma$-wustite aggregate at various locations are approximated on the right hand side of this Figure.
The approximated values for the partial pressure of oxygen and the corresponding volume fraction of $\gamma$ phase at various locations in the aggregate product phases are given together with a typical microstructure of the reaction product from the displacement reaction between Fe and NiO in Fig. 34. With such values, points along the diffusion path on the $P_{O_2}$ vs. $X_{Ni}$ diagram are traced as shown in Fig. 35.

The diffusion path, represented in Fig. 35 indicateds that when a couple of essentially O-free Fe and an O-rich NiO was reached at 1000°C, the product microstructure at steady-state condition consists of three two-phase aggregates; that is, the $\gamma$-wustite, $\gamma$-spinel and $\gamma$-NiO. The first aggregate is present adjacent to the Fe, the last one close to the NiO and the second present in between the former two aggregates. Each two-phase product zone is known to be in an aggregate arrangement, instead of in a well-defined planar layer arrangement. This is so because the diffusion path cuts the tie lines in the two-phase field, which can be represented by the iso-activity lines, i.e., lines of constant $P_{O_2}$. Consequently, the compositions of the two phases in the aggregate change along the path. This situation can happen only when the two phases in the aggregate arrange themselves in an aggregate manner.
Figure 35 - A diffusion path for the displacement reaction between Fe and NiO at 1000°C. Phase diagram after Davies and Smeltzer (25).
The very first $\gamma$ forms in the $\gamma$-NiO aggregate zone. The mole fraction of the $\gamma$ in the aggregate gradually increases along the path as the partial pressure of oxygen decreases until the invariant partial pressure of oxygen for the coexisting phases between $\gamma$-spinel-NiO is reached. Then the supersaturated NiO undergoes a eutectoid decomposition to form approximately a 3 to 1 molar ratio of $\gamma$ and spinel. Thus, the molar fraction of the $\gamma$ in the aggregate drastically increases from about 10% in the $\gamma$-NiO aggregate to about 70% in the $\gamma$-spinel aggregate. Across the $\gamma$-spinel aggregate, the molar fraction of the $\gamma$ slightly increases, presumably because the localized reaction between the $\gamma$ and the spinel takes place when more Fe ions are added into the aggregate, as the equilibrium partial pressure of oxygen decreases along the diffusion path toward the Fe phase.

Finally, when the invariant partial pressure of oxygen for the coexistence of $\gamma$-wustite-spinel is reached, the unstable spinel decomposes to a structure containing mostly wustite and very little $\gamma$. Upon the accommodation of the sudden increase in the molar fraction of wustite, the molar fraction of $\gamma$ in the $\gamma$-wustite aggregate drops to about 50%. Along the diffusion path toward the Fe phase, the molar fraction
of $\gamma$ in the aggregate increases rapidly as the partial pressure of oxygen decreases until the dissociation pressure for the wustite is reached. Then wustite is in contact with the Fe phase. Such a rapid increase in the mole fraction of $\gamma$ in the aggregate near the Fe/product interface is a result of increasing Fe content in the $\gamma$ which can be achieved by both the dissolution of more Fe atoms from the Fe phase and by the dissociation of the pre-existing wustite. Thus the apparent mole fraction of $\gamma$ in the aggregate increases. Such an increase in the mole fraction of $\gamma$ in the aggregate in this region is compensated by the increase in the mole fraction of the wustite in the same aggregate at the Fe/product interface. Physically, the drastic change in the mole fraction of $\gamma$ and wustite near the Fe/product zone is associated with the thickening of $\gamma$ in the aggregate, as discussed in detail earlier.

A diffusion path that represents the displacement reaction between Fe and NiO can also be traced on an isotherm of a ternary diagram. Actually, the diffusion path shown in the $P_{O_2}$ vs. $X_{Ni}$ plot can be easily transferred onto an isothermal section of the ternary diagram because each point on the two-phase field of the $P_{O_2}$ vs. $X_{Ni}$ plot describes the composition of the $\gamma$ coexisting with the corresponding oxide or spinel and
the molar fraction of $\gamma$ in the aggregate. Such information is necessary and sufficient to transfer that point onto an 1000°C section of the Fe-Ni-0 ternary diagram if the tie lines in the two-phase field are known.

Thus, such a diffusion path has been drawn on the isotherm, from the experimental results of Dalvi and Smeltzer (24), as shown in Fig 36. Such a diffusion path has the same physical meaning as that described earlier. That is, three two-phase aggregate zones are formed from the reaction between Fe and NiO because the path cuts the tie-lines in the two-phase fields.

Along the diffusion path the average concentration of oxygen in the $\gamma$-NiO aggregate drops drastically as the Fe ions displace the Ni cations in the NiO and cause $\gamma$ to precipitate out of the oxide phase. The presence of the $\gamma$ in the NiO results in the apparent decreases in the average concentration of Ni in the aggregate. The apparent increase in the average concentration of Ni in the aggregate is understandable because when the $\gamma$ precipitates out of the Fe-doped NiO, it appears as if more Ni atoms are formed while the NiO which becomes doped heavily with Fe ions (increasing the vacancy concentration) does not shrink.
Figure 36 - A diffusion-path for the displacement reaction between Fe and NiO at 1000°C. Phase diagram after Dalvi and Smeltzer (24).
When the unstable NiO transforms to $\gamma$ and spinel there is a discontinuous change in the average concentration of O because the apparent mole fraction of alloy increases drastically from the phase transformation. Then, proceeding along the path toward the Fe phase, the average concentration of oxygen decreases only slightly, presumably since more Fe ions are added into the aggregate. It should be noted here that, actually the activity of oxygen decreases drastically across the spinel-$\gamma$ aggregate.

At the interface between the $\gamma$-spinel and the $\gamma$-wustite, unstable spinel transforms to a large amount of wustite and very little $\gamma$. This results in the increase in the average oxygen concentration in the aggregate. The average content of oxygen in the $\gamma$-wustite aggregate gradually decreases proceeding along the path toward Fe phase because more $\gamma$ is formed from the addition of Fe to the aggregate. However, near the Fe/product interface the average content of O in the aggregate drops drastically followed by a sudden increase in its content at the Fe/product interface. This peculiar behavior is the result of the buildup of Ni atoms near the Fe/product zone and coupled with the dissociation of the pre-existing wustite in this region. The oxygen atoms from the
dissociated wustite are pushed toward the Fe/product interface. Physically, this peculiar behavior is the result of the thickening of the Y in the aggregate near the Fe/product interface.

The reaction process and the product morphologies between the Fe and NiO couple can be the reverse, the paths are deduced from the description presented in Figs. 35 and 36.

However, it should be borne in mind that the diffusion paths provide only some necessary but not sufficient information. Explicitly, it cannot be concluded from such paths what the arrangement of the two-phase aggregates are, i.e., whether they are interwoven, lamellar or discrete precipitates. A criterion proposed by Rapp et al. (4) should be of great help in answering this question.
V. KINETICS OF THE DISPLACEMENT REACTION BETWEEN Fe AND NiO AT 1000°C

A quantitative theory for the steady-state growth of the interwoven-aggregate product phases resulting from the Fe vs. NiO displacement reaction must take into account: (i) the variation in the compositions of all product phases across the aggregate product zones; (ii) the complexity of the defect structure in oxides that can tolerate high contents of foreign species; and (iii) the localized short-range diffusion of cations, say Ni ions in the Fe-doped NiO for example. If the growth process is assumed to be controlled by the long-range diffusion of Fe cations through the oxide phases, then the quantitative model has to account for the change in the mobilities of Fe ions along the diffusion path as the compositions in oxides and the partial pressure of oxygen change. It must also consider the fraction of the Fe cations that are locally reduced and added into the Y alloy. This necessary information is not available in the literature. The situation is so complicated that a mathematical
theory for such a growth process appears to be intractible. Thus, no attempt is made in this dissertation to develop such a theory. Instead, the experimental results on the growth kinetics of the product phases will be interpreted qualitatively but as critically as possible.

The thicknesses of various aggregate products have been measured as a function of time at 1000°C. The parabolic plots of the thickness vs. $\sqrt{t}$, where $t$ is the time in furnace are presented in Figs. 37 to 41. The time in furnace is defined as the duration of time from which the reaction couple was put into the hot zone of the furnace to the time it was withdrawn to the cold zone of the furnace. The intercepts on the $\sqrt{t}$-axis of the thickness vs. $\sqrt{t}$ plots in Figs. 37 to 41 are arbitrarily set at $\sqrt{t} = 0.22 \sqrt{\text{hr}}$, or $t = 3$ minutes. This value was chosen because the temperature of the reaction couples reached 1000 ± 4°C in about 3 minutes after they were put in the furnace.

The slope of each line on the thickness vs. $\sqrt{t}$ plot was calculated by the least-squares method, with the intercept on $\sqrt{t}$ being forced to be $0.22 \sqrt{\text{hr}}$ as mentioned earlier.

The kinetic results show that the parabolic growth law was followed for each type of aggregate
Figure 37 - Time dependence of the thickness of the overall product zones for the Fe vs. NiO displacement reaction at 1000°C.
Figure 38 - Time dependence of the thickness of \( \gamma \)-wustite and \( \gamma \)-spinel zone in the aggregate morphology for the Fe vs. NiO displacement reaction at 1000°C.
Figure 39- Time dependence of the thickness of the $\gamma$-wustite zone in the aggregate morphology for the Fe vs. NiO displacement reaction at 1000°C.
Figure 40 - Time dependence of the thickness of the $\gamma$-spinel zone in the aggregate morphology for the Fe vs. NiO displacement reaction at 1000°C.
Figure 41 - Time dependence of the thickness of the Y-Fe-doped NiO zone in the aggregate morphology for the Fe vs. NiO displacement reaction at 1000°C.
product, as well as the overall product aggregates, despite the fact that the actual mechanism of the reaction process is very complicated. This suggests that the rate of growth of overall product phases is virtually controlled by the long-range diffusion across zones with time-independent boundary conditions.

The results in Figs. 37 to 41 also show that there is a slight difference between the growth rate of the reaction products formed from couples consisting of single crystalline NiO vs. Fe and those consisting of polycrystalline NiO vs. Fe. This discrepancy in the growth rate may be explained in terms of the mole fraction of γ phase in the product aggregates as discussed in detail later in this chapter after the kinetics are qualitatively clarified.

Since the actual growth of the two-phase aggregates follows a parabolic growth law, the thickening of each aggregate can be represented by

\[
\frac{d\xi}{dt} = \frac{k_p}{\xi} \quad (37)
\]

Upon integration,

\[
\xi^2 = 2k_p t \quad (38)
\]

where \(\xi\) represents the thickness of the two-phase aggregate at time \(t\) and \(k_p\) is the so-called parabolic rate constant for the growth process. Thus, the square
of the slope on a thickness vs. $\sqrt{t}$ plot is equal to $2k_p$ in Eq. (38). Such a value for each curve is given in the thickness vs. $\sqrt{t}$ plots in Figs. 37 to 41.

A. Simplified Model for the Growth Kinetics

In an attempt to qualitatively describe the growth kinetics, a simplified model is presented in this section. This model describes the simultaneous growth of the oxide phases and the $Y$ alloy by the long range diffusion of Fe ions in the oxide.

The following assumptions are made for the model. First, growth of the products is diffusion controlled through the oxide, spinel, and NiO and the diffusivity of Fe ions is much greater than the diffusivities of Ni cations and O anions in the binary oxides and spinel phases. This statement is justified, based on the diffusion data summarized in Table 2. Secondly, local equilibrium exists at the phase boundaries at all times. Thirdly, capillarity has a negligible effect on the equilibrium activities at the phase boundaries.

The qualitative growth kinetics are explained in terms of the partitioning of Fe ions between the product oxides. This partitioning can be demonstrated by considering the reaction at each interface in the
product zone. The total displacement reaction is the sum of these interfacial reaction steps, which are given here as defect equations. The defect equations are introduced to illustrate one possible, and simplified, mechanism for the present case of predominant cation diffusion in the binary oxides and spinel. To aid the discussion, the typical product microstructure of the displacement reaction between Fe and NiO together with a schematic description of the product zones are recapitulated in Fig. 42.

The predominant ionic defects in wustite, spinel and NiO are assumed to be cation vacancies _V^w_{Fe(w)}_, _V^s_{Fe(s)}_ and _V^w_{Ni}_, which have negative relative charges of 2, 3 and 2, respectively, relative to the normal site occupation. The symbols _Fe^w_{Fe(w)}_, and _Fe^s_{Fe(s)}_ represent normally-charged cations on cation sites in wustite and spinel, respectively. Iron ions situated in the cation sublattice of NiO are represented by _Fe^1_{Ni}_, which indicates a plus one charge relative to the defect-free lattices. Positive holes which have a single positive charge, are represented by _h_. The oxide and spinel compositions are based on one mole of oxygen per mole of oxide. The symbols for the Ni-doped wustite, spinel and Fe-doped NiO are defined in Fig. 42. The number of moles involved in the
Figure 42—Typical product microstructure from the displacement reaction between Fe and NiO at 1000°C.
reaction steps are represented by $\beta, \delta, \lambda, \eta, p, q, r$.

The consumption of the Fe phase by oxidation at the Fe/wustite interface, labelled I in part (b) of Fig. 42 can be represented by

$$(\beta+\delta)\text{Fe} + (\beta+\delta)\text{V}_{\text{Fe}(w)} + 2(\beta+\delta)\text{h} = (\beta+\delta)\text{Fe}_{\text{Fe}(w)} \quad (39)$$

At the $\gamma$-wustite/$\gamma$-spinel interface, labelled II in part (b) of Fig. 42, wustite and alloy grow at the expense of the spinel; however, not all the Fe cations which arrive at the $\gamma$-wustite/$\gamma$-spinel interface through wustite contribute to the growth of the wustite. The excess Fe ions diffuse further into spinel. The reaction at the $\gamma$-wustite/$\gamma$-spinel interface can be written as:

$$\delta\text{Fe}_{\text{Fe}(w)} + p\text{Ni}^m_{m}\text{Fe}^o_n = p\text{Ni}^x_{x}\text{Fe}^y_0 + \frac{p(m-x)}{a}\text{Ni}_{a}\text{Fe}_{1-a}$$

$$+ \delta\text{V}_{\text{Fe}(w)} + 2\delta\text{h} \quad (40)$$

The excess Fe-ion flux is oxidized to higher valence at this interface according to

$$\beta\text{Fe}_{\text{Fe}(w)} + \beta\text{V}_{\text{Fe}(s)} + \beta\text{h} = \beta\text{Fe}_{\text{Fe}(s)} + \beta\text{V}_{\text{Fe}(w)} \quad (41)$$

The spinel and alloy grows at the $\gamma$-spinel/$\gamma$-NiO interface at the expense of the supersaturated NiO:
The excess Fe ions change cation sites when entering NiO:

\[(p+q+r)\eta \text{Fe}_\text{Fe}(s) + \eta(p+q+r) V'\text{Ni} = (p+q+r)\eta \text{Fe}^{III}_\text{Ni} + (p+q+r)\eta V''\text{Fe}(s) \quad (43)\]

Finally, Fe-doped NiO grows at the doped and undoped NiO interface, labelled III in part (b) of Fig. 42.

\[(p+q+r)\eta \text{Fe}^{III}_\text{Ni} + (p+q+r) \text{NiO} = (p+q+r)\text{Fe}_\text{wNi}_\text{v} \]

\[+ (p+q+r)^{1-V\text{c}} \text{Ni}_\text{cFe}_\text{1-c}^{1-}\]

\[+ \eta(p+q+r) V'\text{Ni} \]

\[+ 3(p+q+r)\eta \hat{\eta} \quad (44)\]

The molar numbers, \(\beta, \delta, \lambda,\) and \(\eta\) contain parameters that describe the composition of the oxides, spinel and alloy as follows:
\[ \beta = (p+q+r)(w+v-1+\frac{1-v}{c}) + (p+q)(m+n-w-v+\frac{v-m}{b}) \]

\[ \delta = p(x+y-m-n+\frac{m-x}{a}) \]

\[ \lambda = (m+n-w-v+\frac{v-m}{b}) \]

\[ \eta = (w+v-1+\frac{1-v}{c}) \]

Combining all the reaction steps represented by Eqs. (39) to (44), the overall reaction process can be written as:

\[ (\beta+\delta)Fe + (p+q+r)NiO = pNi_xFe_yO + p\frac{m-x}{a}Ni_{a}Fe_{1-a} \]

\[ + qNi_{m}Fe_{n}O + (p+q)\frac{v-m}{b}Ni_{b}Fe_{1-b} \]

\[ + rFe_{w}Ni_{v}O + (p+q+r)\frac{1-v}{c}Ni_{c}Fe_{1-c} \]

Thus, the simplified defect model can essentially describe the simultaneous formation of the oxide or spinel an \( \gamma \) alloy. Equation (45) indicates that the products comprise three two-phase zones; that is the \( \gamma \)-wustite, the \( \gamma \)-spinel and the \( \gamma \)-Fe-doped NiO.
B. An Evaluation of the Kinetic Results

Since the overall displacement reaction process is virtually driven by the gradient of the activity of oxygen across the "bulk interface" of the two reactants, i.e., \( P_{O_2} = P_{O_2}^{(Ni/NiO)} \) at the product/NiO interface and \( P_{O_2} \) is virtually zero within the Fe phase. Thus, the rate of growth of the product phases resulting from the displacement reaction between Fe and NiO should be compared to the rate of the growth of the corresponding products formed during the oxidation of Fe-Ni alloy under the same partial pressure of oxygen, i.e., about \( 4 \times 10^{-11} \) atm and at 1000°C.

Phenomenological observations on the oxidation characteristics of the Fe-Ni alloys over the entire composition range have been carried out in pure \( O_2 \) and controlled atmospheres containing \( CO_2 \) and water vapor as oxidizing reactants by several workers (64-70). The types of scales formed on this alloy system depend on the Ni content in the alloy. It appears that the following trend is observed: (i) alloys containing up to 2 w/o Ni exhibit scales similar to those found on iron; (ii) alloys containing approximately 2-30 w/o Ni form predominantly slow growing spinel with some internal oxide precipitates; (iii) alloys containing 30-75 w/o Ni form predominantly
spinel and Fe$_2$O$_3$ scales, although the presence of some NiO in the scale has also been observed (69); and (iv) alloys containing 75-100 w/o Ni exhibit scales consisting of nickel oxide and spinel. All alloys show nickel enrichment at the alloy/scale interface and, in addition, exhibit subscale formation. Information on the kinetics of scale formation is not extensive and the results of kinetic studies have been neither reproducible nor of a continuous pattern (71).

No kinetic data for the growth of wustite underneath the spinel is available for comparison with the results of this study. However, the rate of growth of the two-phase aggregate of γ-wustite and γ-spinel can be compared with the simultaneous growth of two-phase layer wustite and spinel scales that form on the pure iron during the oxidation process at $P_{O_2} \approx 10^{-11}$ atm. However, most experiments (72-76) for the scaling of iron were either carried out in a very low partial pressure of oxygen or in air and consequently either only one layer of wustite was formed on iron or a three-phase layer oxide of wustite, magnetite and hematite was simultaneously formed on the iron. It appears that the experimental results for the growth kinetics of the simultaneous formation of wustite and magnetite on iron are not available.
Fortunately, the rate of growth of a two-phase layer scale formed on metal can be calculated based on a quantitative theory proposed by Yurek et al. (63). Such a theory calculates the parabolic rate constants for the simultaneous growth of two oxides based on diffusion and thermodynamic data. The growth rate of the wustite, magnetite and two-layer oxide, being oxidized at \( P_{O_2} = 4.4 \times 10^{-11} \) atm, which is very close to the value \( P_{O_2} = 2.5 \times 10^{-11} \) atm in the present case of Fe vs. NiO, have already been calculated as an example. The corresponding results are reported in Table 3. The pertinent discussion will be presented later in this section.

Although the parabolic rate constants mentioned above have not yet been directly measured from the conventional oxidation experiment, such rate constants have been indirectly measured from the kinetic study of the displacement reaction between Fe and CuO at 1000 °C (2,18,23), where the two-phase oxide grows as rods into the Cu matrix. The typical product microstructure and the schematic model for the growth process were recapitulated in Fig.43. Physically, in the Fe vs. CuO system, the oxide rods have to protrude into the Cu matrix not growing into the gas phase as they do when being oxidized in gaseous oxidant. However, the growth
Table 3. Comparison of the Parabolic Rate Constants for the Growth of Reaction Products Resulting from the Displacement Reactions between Fe and NiO and Fe and Cu2O and from the Oxidation of Fe at 1000 °C (23)

<table>
<thead>
<tr>
<th>Parabolic Constant cm²/sec</th>
<th>Fe vs. NiO ( P_0^2 = 2.5 \times 10^{-11} ) atm</th>
<th>Fe vs. Cu2O ( P_0^2 = 4.4 \times 10^{-11} ) atm</th>
<th>Oxidation of Fe ( P_0^2 = 4.4 \times 10^{-11} ) atm</th>
</tr>
</thead>
<tbody>
<tr>
<td>( k_p ) (wustite)*</td>
<td>1.62 \times 10^{-7}</td>
<td>2.83 \times 10^{-7}</td>
<td>2.89 \times 10^{-7}</td>
</tr>
<tr>
<td>( k_p ) (spinel)*</td>
<td>1.10 \times 10^{-10}</td>
<td>1.01 \times 10^{-10}</td>
<td>5.91 \times 10^{-11}</td>
</tr>
<tr>
<td>( k_p ) (two-phase oxide)*</td>
<td>1.71 \times 10^{-7}</td>
<td>2.94 \times 10^{-7}</td>
<td>3.07 \times 10^{-7}</td>
</tr>
</tbody>
</table>

* \( k_p \) (wustite) for the Fe vs. NiO couple means the \( k_p \) for the \( \gamma \)-wustite aggregate. Accordingly, this is also applied for \( k_p \) (spinel) and \( k_p \) (two-phase oxide).
Figure 43 - Displacement reaction between Fe and Cu₂O at 1000°C:
(a) Lamellar-aggregate product microstructure.
(b) Schematic representation of the model for the growth of reaction products.
After Yurek, et al. (2,18).
of these oxide rods should not be significantly retarded by the Cu phase because the Cu is at 0.92 of its homologous temperature, $T/T_m$, where $T_m = \text{melting point of Cu, 1083°C.}$ At such a high temperature the Cu should be so soft that it can be deformed easily once the advancing oxide rods penetrate it. Thus, in effect, the observed growth rates of the two-phase oxide rods in the case of Fe vs. Cu$_2$O reaction should be excellent representatives of the growth rates of the corresponding oxide during the gaseous oxidation process. The measured parabolic rate constants (23) are reproduced in Table 3.

It can be seen from Table 3 that the values for the $k_p$ of the $\gamma$-wustite aggregate from the Fe vs. NiO displacement reaction is slightly less than the calculated and experimental $k_p$'s for the oxidation of Fe to form wustite underneath magnetite. Physically, the $k_p$ for the $\gamma$-wustite represents the simultaneous growth rate of both $\gamma$ and wustite in the aggregate underneath the $\gamma$-spinel. Thus, despite some contribution of the small amount of $\gamma$ to the growth of this aggregate zone, its growth rate is still slightly less than the rate of growth of wustite under the magnetite during oxidation in oxygen gas. This suggests that the mobility of Fe ions in the wustite is slightly retarded
by the presence of the dopant Ni ions. There is also a retarding tortuosity (geometric) factor for the irregular wustite structure.

Since the growth rate of the $\gamma$-wustite aggregate controls the growth of the overall product zones, the $k_p$ for the overall product zones should also be less than that for the simultaneous formation of a two-layered oxide during the oxidation of Fe under about the same $P_{O_2}$ and at the same temperature. This is the case as shown in Table 3.

It is interesting to note, from the results in Table 3, that although the diffusivity of Fe ions in the iron-nickel-spinel is about one order of magnitude lower than that in magnetite (44), the growth kinetics for the $\gamma$-spinel aggregate appears to be very close to that for the growth of magnetite during an oxidation process under the same temperature and $P_{O_2}$. Such an apparent higher rate of growth of this $\gamma$-spinel aggregate is understandable since the formation of the spinel is a result of eutectoid decomposition of supersaturated NiO which yields approximately 3 additional moles of $\gamma$ per mole of spinel formed, see Fig.7. The apparent thickness of spinel in the $\gamma$-spinel zone should be increased considerably to accommodate this large amount of $\gamma$ phase. The contribution to the
growth of the aggregate by the presence of $\gamma$ appears to counteract the slower diffusivity of Fe ions in the spinel.

The rate of thickening of a scale consisting of predominantly spinel with a small amount of hematite on the outer scale formed on nominally 30 and 41 w/o Ni Ni-Fe alloys in a $P_{O_2} = 0.21$ atm, $O_2-N_2$ mixture at 1000°C have been reported to be $3.3 \times 10^{-9}$ and $3.51 \times 10^{-9}$ g$^2$/cm$^4$-sec, respectively (67). With the relation between $k_m$, in g$^2$/cm$^4$-sec and $k_p$, in cm$^2$/sec, given by Kofstad (77), the corresponding $k_p$'s are $1.27 \times 10^{-10}$ and $1.35 \times 10^{-10}$ cm$^2$/sec, respectively. The numerical values of these $k_p$'s are close to the experimentally observed $k_p$ for the growth of $\gamma$-spinel aggregate in the Fe vs. NiO displacement reaction system. However, the physical difference between the two cases should be noticed; that is $k_p$ of the $\gamma$-spinel is the measurement of the simultaneous growth of $\gamma$ and spinel zone whereas $k_p$ for the oxidation process is the measurement of the rate of growth of all scales, i.e., including the smaller thickness of hematite on the outer scale. Therefore, it can be concluded that the intrinsic growth rate of spinel, excluding the $\gamma$, should be much lower than that of magnetite.
Now, the growth kinetics of the Fe-doped NiO layer in the NiO are interpreted. If the thickening mechanism for such a doped phase is solely associated with the diffusion of Fe ions into the NiO phase, as schematically depicted in Fig. 42, then the parabolic rate constant for this phase should be on the order of the solubility-diffusivity product for Fe ions in the doped NiO.

The solubility of Fe ions at $P_{O_2}$ corresponding to the coexisting of NiO, spinel and alloy has been reported ranging from 0.065 to 0.145 atomic fractions (24, 25, 26, 27). Measurements of the diffusivity of impurity Fe in NiO at various $P_{O_2}$ and temperature have been made by several workers (78-81). The results are summarized in Table 4. The result of Dalvi and Smeltzer (81) differs markedly from the trend of the other data.

If the extrapolated diffusivity result of Crow (79) at $P_{O_2} = 5 \times 10^{-5}$ atm and the recent solubility data of Dalvi and Sridhar (26) are used, the calculated solubility-diffusivity product of Fe ions in NiO is $7.96 \times 10^{-12}$ cm$^2$/sec, which is about one order of magnitude less than the parabolic rate constant obtained experimentally, i.e., $4.65 \times 10^{-11}$ cm$^2$/sec. This discrepancy arises from the fact that the diffusivity
Table 4. Diffusivity of Impurity Fe in NiO at 1000°C

<table>
<thead>
<tr>
<th>$P_{O_2}$ (atm)</th>
<th>$D$ (cm$^2$/sec)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>$4.14 \times 10^{-11}$</td>
<td>(78)</td>
</tr>
<tr>
<td>$5 \times 10^{-5}$</td>
<td>$5.49 \times 10^{-11}$ *</td>
<td>(79)</td>
</tr>
<tr>
<td>$10^{-3}$</td>
<td>$9.94 \times 10^{-12}$ *</td>
<td>(79)</td>
</tr>
<tr>
<td>1</td>
<td>$5.69 \times 10^{-11}$ *</td>
<td>(79)</td>
</tr>
<tr>
<td>0.011</td>
<td>$1.18 \times 10^{-11}$ *</td>
<td>(80)</td>
</tr>
<tr>
<td>0.21</td>
<td>$2.11 \times 10^{-11}$ *</td>
<td>(80)</td>
</tr>
<tr>
<td>1</td>
<td>$2.48 \times 10^{-11}$ *</td>
<td>(80)</td>
</tr>
<tr>
<td>1</td>
<td>$2.00 \times 10^{-9}$</td>
<td>(81)</td>
</tr>
</tbody>
</table>

* Extrapolated values
of Fe was for a very dilute Fe content in NiO and that both the diffusivity and "solubility" of Fe in NiO depend upon $P_{O_2}$. Thus, the solubility-diffusivity product calculated from the presently available data has not much significance in the verification of the postulate that the thickening of the Fe-doped NiO layer is virtually controlled by the diffusion of Fe ions in the NiO.

C. Comparison of the Kinetics of Reaction Process Resulting from Using Single and Polycrystalline NiO as Reactant Materials

As noticed from the kinetic results shown in Figs. 37 to 41 that there is a slight difference between the growth rate of corresponding products resulting from couples starting with single crystalline NiO and those starting with polycrystalline NiO. Couples with single crystalline NiO exhibit faster growth rates of the $\gamma$-wustite aggregate, and of the overall product phases, whereas those with polycrystalline NiO show faster rates of growth of $\gamma$-spinel and the $\gamma$-Fe-doped NiO aggregate. The slight difference in the growth kinetics between these two types of couples is likely associated with the fact that polycrystals of NiO which were prepared by
oxidizing Ni metal contain voids, present as inherent faults in the oxidized samples. Typical voids in the polycrystals of NiO are shown in part (b) of Fig. 44 whereas part (a) of the same figure represents the typical structure of the single crystalline NiO. The voids that appear in the single crystalline are probably etch-pits developed after the crystal was etched in 4% Nital solution. These pits have well-defined square shapes.

Within polycrystalline NiO, when the reaction front encounters a void, as depicted in part (a) of Fig. 45, $\gamma$ can easily form at the surface of that void by dissociation of NiO. At the same time growth of $\gamma$ in the bulk by short-range diffusion of Ni ions in NiO surrounding the growing $\gamma$ nodule still takes place. In effect, more $\gamma$ is formed in the Fe-doped phase at a given time as compared to that formed in the corresponding phase in single crystalline NiO.

The pre-existing void is eventually healed, to some extent, by further growth of $\gamma$ into the void. This is a preferable process because space in the void relaxes elastic constraints on the growth of $\gamma$. Also the void can be healed by gradually dissipating vacancies toward the Fe phase. Healing of a void through plastic deformation driven by the hydrostatic
Figure 44 - Typical voids observed in the NiO crystals used in this study:
(a) "Voids" in single crystalline NiO.
(b) Voids in polycrystalline NiO.
Figure 45—Schematic representation of the effect of the existing voids in the polycrystalline NiO on the growth of γ nodule.
pressure exerted during the phase transformation process is also expected. The growth of \( Y \) into the void is depicted in part (b) and (c) of Fig. 45. It should be noted that \( Y \) is also formed preferentially along pre-existing grain boundaries in the polycrystalline NiO. Thus, enhancement in the rate of formation of this \( Y \)-Fe-doped NiO aggregate should also be caused by the presence of a grain boundary in NiO.

At the \( Y \)-spinel/\( Y \)-Fe-doped NiO interface, supersaturated NiO decomposes to form spinel and \( Y \). Since there are more pre-existing \( Y \) particles in the polycrystalline samples, as discussed above, the apparent rate of formation of the spinel-\( Y \) aggregate is expected to be higher in these crystals because more preferential sites for precipitation of newly formed \( Y \) are available. A slightly greater amount of \( Y \) in the \( Y \)-spinel aggregate in the case of polycrystalline NiO is also expected because of the same reason. Such an apparent increase in the amount of \( Y \) does not violate the local equilibrium condition because the phase diagram can only dictate the equilibrium composition in the coexisting \( Y \) and spinel. It does not control the molar partition between the two phases because the mass in the system is conserved by the rapid supplying of the Fe ions into the
aggregate. Therefore, the rate of growth of the \( \gamma \)-spinel aggregate is found to be greater in the couples using polycrystalline NiO as compared with those using single crystalline NiO.

At the interface where \( \gamma \), spinel and wustite coexist, supersaturated spinel decomposes to form mostly wustite with very little \( \gamma \), see the phase diagram in Fig. 7. Therefore, the growth rate of this aggregate should not be controlled by the formation of the \( \gamma \) phase. Rather, it should depend on how fast the Fe ions can diffuse through the Ni-doped wustite to form new products. As a consequence of the greater amount of initially formed \( \gamma \) in the \( \gamma \)-NiO aggregate, the apparent mole fraction of \( \gamma \) in the \( \gamma \)-wustite aggregate is also higher, as compared with that formed from Fe vs. single crystal NiO. These \( \gamma \) particles should occupy more space in the \( \gamma \)-wustite aggregate, and consequently, Fe ions diffusing through the wustite coexisting with these \( \gamma \) should experience more resistance to the ion transport because the crossectional area for the diffusion in wustite has been narrowed. Since the rate of growth of the aggregate is controlled virtually by the diffusion of Fe ions through this wustite phase, the slower growth rate of the \( \gamma \)-wustite aggregate starting with
polycrystalline NiO should be expected, consistent with experimental observation.

Since the growth rate of the overall products is virtually controlled by the growth rate of the $\gamma$-wustite region, the slower growth rate of the overall product phases resulting from using polycrystalline NiO should also result. This is again consistent with the experimental results.

Finally, it is noteworthy that the growth rate of the overall product phases is on the order of magnitude of the growth rate of wustite scale on iron during oxidation process. Since wustite on iron is known to be one of the fastest growing oxide scales, the rate of formation of reaction products from the displacement reaction between Fe and NiO should also be ranked in the fast category. Thus, if a composite material consisting of $\gamma$ and oxide aggregate should be considered for engineering applications, not much energy (time at temperature) should be required to manufacture this type of material by a solid-state displacement reaction process.

D. Condition of the "Quasi-Steady-State" Growth

It is interesting to examine the "quasi-steady-state" condition in the Fe vs. NiO displacement
reaction system where all products formed have a relatively high solubility for foreign species.

By definition, a quasi-steady-state model (82) neglects the distance dependence of the diffusional flux associated with the moving boundary condition. In effect, this model assumes that the diffusional flux of the reacting species is independent of the distance along the path.

To aid the following discussion, the typical product microstructure resulting from the displacement reaction between Fe and NiO is recapitulated in Fig. 46.

If the growth process of the reaction product in this reaction system is the long range diffusion of the Fe ions through the various oxide phases, the currents of Fe ions at various locations in the products represented by \( J_I, J_{II}, J_{III}, \) and \( J_{IV} \), should be virtually the same if the quasi-steady-state condition for the growth process is achieved.

Physically, the current of Fe ions, \( J_I \), entering the product at interface I, is accommodated not only by the growth of the wustite, spinel and Fe-doped NiO, but also by solution in the \( \gamma \) alloy all across the product zone. This means that there are localized reductions of the Fe ion concentration in the product phases. Consider the fact that the \( \gamma \) alloys across
Figure 46 - Typical product microstructure from the displacement reaction between Fe and NiO at 1000°C.
the overall product phases have composition ranging
from virtually pure Fe near the Fe reactant to virtually
pure Ni near the NiO side, a significant divergence of
the diffusion current of Fe ions should be anticipated.
This implies that the quasi-steady-state condition is
not achieved in this reaction system. The extent of
the divergence of the diffusion currents of Fe ions
is examined in the following section.

If \( J_{\|} \) is said to be the average or effective
current of Fe ions, in equiv./sec, passing through the
wustite that gave rise to the growth of wustite in the
\( \gamma \)-wustite aggregate product, then from the flux
equation in the form described by Eqs. (13) to (15):

\[
J_{\|} = \frac{k_p(\text{wustite})}{\xi} \cdot \frac{z}{V} \cdot f
\]  

(46)

where \( k_p(\text{wustite}) = \) the parabolic rate constant for
the \( \gamma \)-wustite aggregate

\( z = \) the effective valence of the
diffusing Fe ions in wustite

\( V = \) molar volume of wustite expressed
per mole of oxygen

\( f = \) the fraction of cross-sectional
area of wustite in the \( \gamma \)-wustite
aggregate
Accordingly, the corresponding expressions are also true for $J_{III}$ and $J_{IV}$ if they represent the effective current of Fe ions passing through the spinel and Fe-doped NiO in the $\gamma$-spinel and $\gamma$-Fe-doped NiO, respectively. The effective currents of Fe ions diffusing through the oxides and spinel phases in the aggregate phases, calculated from Eq. (46) using pertinent parameters, are given in Table 5.

The results in Table 5 indicate that the average current of Fe ions drops substantially from wustite to spinel and it also drops slightly from spinel to Fe-doped NiO phase. This is understandable from the fact that the $\gamma$ alloy in the $\gamma$-wustite aggregate varies from almost pure Fe at the Fe/product interface to about 20 a/o Fe at the $\gamma$-wustite/$\gamma$-spinel interface, see the phase-diagram in Fig. 7. Although some Fe atoms can be directly supplied into the $\gamma$ alloy from the Fe phase via the $\gamma$ channels in the product in contact with the Fe phase, most of the Fe in the $\gamma$ alloy, especially in the region far from the Fe reactant phase, should come from localized reduction of Fe ions at the $\gamma$-wustite interface. This is because the diffusivity of Fe ions in wustite is about 4 orders of
Table 5. The Effective Current of Fe-Ions across the Wustite, Spinel, and Fe-Doped NiO in the Pertinent Two-Phase Aggregate Products

<table>
<thead>
<tr>
<th>Phase</th>
<th>$k_p$ (cm$^2$/sec)</th>
<th>$z$</th>
<th>$\xi$ (mm)</th>
<th>$V$ (cm$^3$/mole O)</th>
<th>$f$</th>
<th>$J$ (equiv/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wustite</td>
<td>$1.62 \times 10^{-7}$</td>
<td>2</td>
<td>2.484$^a$</td>
<td>12.04$^b$</td>
<td>0.58$^c$</td>
<td>$6.3 \times 10^{-8}$</td>
</tr>
<tr>
<td>Spinel</td>
<td>$1.10 \times 10^{-10}$</td>
<td>3</td>
<td>0.058</td>
<td>11.03</td>
<td>0.74</td>
<td>$3.8 \times 10^{-9}$</td>
</tr>
<tr>
<td>Fe-doped NiO</td>
<td>$4.65 \times 10^{-11}$</td>
<td>3</td>
<td>0.043</td>
<td>10.97</td>
<td>0.91</td>
<td>$2.7 \times 10^{-9}$</td>
</tr>
</tbody>
</table>

a. Data after 47 hours  
b. From reference 31  
c. Estimated from the typical product microstructures.
magnitude greater than that of Fe atoms in $\gamma$. In effect, substantial numbers of Fe ions are withdrawn from the wustite before the remaining Fe ions enter the spinel phase. The profile of the current of Fe ions in the product zone is depicted in Fig.47.

On the other hand, $\gamma$ in the $\gamma$-spinel aggregate contains only about 20 a/o Fe at the $\gamma$-wustite/$\gamma$-spinel interface and varies to smaller values of about 0.5 a/o Fe at the $\gamma$-spinel/$\gamma$-Fe-doped NiO interface. The localized reduction of Fe ions in the spinel at the $\gamma$/spinel interface is also expected in this case. However, such divergence in the Fe-ion current is effectively compensated by the dissolution of Ni ions into the spinel, i.e., 14 a/o Ni at the $\gamma$-spinel/$\gamma$-NiO interface varying to 0.5 a/o Ni at the $\gamma$-spinel/$\gamma$-wustite interface. Thus, it appears that very little change in the current of Fe ions across the spinel in the $\gamma$-spinel aggregate is observed.

In summary, an evaluation of the kinetic data suggests significant divergence of the Fe ion current across the wustite in the $\gamma$-wustite aggregate. The current decreases because of divergence into the alloy. Thus, the quasi-steady-state condition in a kinetic sense is not achieved in this Fe vs. NiO displacement reaction system where all product phases
Figure 47 - Schematic representation of the diffusional current of Fe ions passing through the oxide phases during the growth process. Dotted-lines represent the average diffusional currents of Fe ions.
have significant solubility for foreign species. The term steady-state can only be used in describing the long time morphological aspects of the reaction product. It does not have the meaning as conventionally understood in the kinetic study of growth process.
VI. CONCLUSIONS

Results from the present study of the displacement reaction between Fe and NiO at 1000°C lead to the following conclusions:

(1) Reaction products comprise three interwoven-aggregate zones; namely, γ-wustite, γ-spinel, and γ-Fe-doped NiO.

(2) A pre-existing Ni-layer between the two reactants cannot suppress the formation of the interwoven-aggregate product morphology.

(3) The early stage of reaction involves the dissolution of Fe into NiO, the dissociation of NiO and the oxidation of the Fe-Ni alloy; whereas in the later stage the reaction is virtually controlled by the solid-state diffusion of Fe ions through the wustite, spinel, and the NiO phases.

(4) The active reaction front is in the Fe-doped NiO phase where the growing γ nodules always experience the point effect of diffusion, which influences the growth morphology.
(5) The spontaneous adjustment of the system to satisfy the local equilibrium condition during the growth process results in the localized thickening of the $\gamma$ and wustite phases near the Fe/product interface.

(6) The arrangement of the $\gamma$ in the $\gamma$-oxide aggregate depends greatly on the local supersaturation condition.

(7) The rate of growth of the overall product zones is comparable to the rate of scaling of iron in gaseous oxygen under the same $P_{O_2}$ and the same temperature.
VII. SUGGESTION FOR FUTURE WORK

Since the interwoven-aggregate arrangement of reaction products has some promising engineering application, future studies in this area should also emphasize those reaction couples that give rise to the interwoven-aggregate product morphology. The reaction couple between Cr and NiO would be very interesting to study with regard to mechanistic aspects because it exhibits features of both lamellar- and interwoven-aggregate morphologies (2). Furthermore, with regard to practical aspects, a composite material consisting of $\gamma$ and Cr$_2$O$_3$ aggregate should serve as a better structural material in high temperature service than that consisting of $\gamma$ and mostly wustite. This is because the corrosion resistance of Cr$_2$O$_3$ is much better than that of wustite, which can be easily dissolved by a Nital 4% solution.
LIST OF REFERENCES


17. R. Metselaar, Private Communication.


