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The Ohio State University

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In-Situ Morphological Study of Wustite Scale Growth
in a Hot Stage Environmental SEM

DISSERTATION

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

By

Moonyong Lee, B.S., M.S.

* * * * *

The Ohio State University
1986

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To my wife, Kyung-Ja
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I. Introduction

The importance of microstructure of metal substrates and of oxide scales has been recognised in recent studies of high temperature oxidation of metals. With the development of sophisticated equipment for surface observation and analysis, considerable progress has been made in understanding the mechanistic details of the metal oxidation process. A combination of experimental results from different techniques has certainly made a significant contribution to the understanding of the mechanisms involved in oxide scale growth at high temperatures. However, most experimental observations have been made during post-oxidation experiments and may represent transient features at that particular stage of the scale growth.

In-situ studies of scale growth at high temperature in a hot-stage environmental scanning electron microscope (HSESEM) have made possible observation of these transient morphological features at the gas/scale interface and their evolution. Such in-situ observations of the morphological features have contributed to the development of a mechanistic model for the growth of oxide scales. The development of growth whiskers, pyramids, pits, and other
morphological features caused by microstructural defects in the oxide has been reported for various metal oxide systems. In particular, in-situ oxidation studies of high purity iron at the high temperatures near 1050°C and at $P_{O_2} = 10^{-4}$ atm have revealed many interesting morphologies for wustite scale growth, including square symmetry growth-pits and microledges. In-situ observations of these morphological features helped in understanding the elemental steps for the oxide lattice extension of the wustite scale. This study was undertaken to further understand and characterize the morphological features in wustite scale growth. The initial stage of oxidation is closely examined in an effort to understand the sequence of transition from nucleation to the development of different morphologies by growth. The crystallographic orientation of the surface is also determined for these morphological features. In addition, a correlation of these morphological features with growth conditions is attempted.
II. Literature Survey

This chapter discusses literature pertinent to the study performed and reported here. The first half of the chapter, sections A, B, and C, consists of reviews of several topics in the study of oxidation of metals. The second half, sections D, E, and F, includes reviews of topics of related physical phenomena pertinent to the present work. No attempt has been made to refer in detail to all the work found in the literature. Rather, important concepts which are used in later chapters for the discussion of results pertaining to this study are briefly introduced.

A. Oxide Film Growth in Oxidation of Metals

The reaction of oxidant gases with metals and the subsequent growth of the oxide film involves a large number of phenomena and reaction steps(1-7). The usual sequence of events includes: 1) the adsorption of gas molecules on the metal surface, 2) their dissociation and ionization, 3) the development of two or three-dimensional oxide nuclei, 4) the lateral growth of these nuclei until they impinge on each other, and 5) the subsequent thickening of this oxide film.
by the transport of metal or oxygen in the appropriate form through the film. The study of each individual reaction step is a field in itself and it is not feasible to discuss all these steps here. Reviews of these topics can be found in the proceedings of a recent conference (8). Only the nucleation and the subsequent thickening of the continuous oxidation product film will be considered here.

1. Nucleation and Growth of Oxide

1-1. Nucleation of the Oxide

With the advent of modern surface tools such as LEED, HEED, A.E.S., ESCA, work function measurements and others, many studies have been made of the first stage of oxidation. For example, the formation of small domains or island structures was suggested to explain LEED data (9). Structural domains such as Ni$_3$O on Ni surfaces were reported by Garmon and Lawless (10) based on the data of superlattice reflections by both transmission and reflection HEED. The nucleation of 2D islands of a more dense phase from a less dense phase was observed by means of LEED or HEED (11-14). Work function measurements were used to precisely determine the critical concentration of adsorbed atoms on copper for such a transition from the dilute to the dense phase (15,16). In case of iron, Bardolle and Benard (17) clearly demonstrated the growth of discontinuous particles of epitaxial FeO. They also reported the variation of the
density of oxide islands with crystal orientation, the density being greatest on the \{100\} and least on the \{110\} planes. On the contrary, Bauer (18) has argued for the existence of transition structures. A transition structure during nucleation is now accepted as a fairly general phenomenon (19,20). More detailed discussions concerning the reality of such structures have been given by May (9).

The exact nature of the nucleation sites with regard to surface imperfections and impurity atoms is not clear because of experimental difficulties. Since Cabrera (22) suggested theoretically that oxide nuclei should form at points where dislocations intersect the surface, a number of workers have attempted to correlate oxide nuclei formation with dislocations. A one-to-one correlation between nuclei and dislocation sites was reported in the oxidation of Te-doped copper single crystals (23), and in sulfidation of silver (24).

In many cases, however, it was reported that nuclei do not form preferentially at dislocations. Garmon and Lawless (11) showed clearly that there was no general relationship between sites where oxide nuclei formed and dislocations, in their study of oxidation of high purity nickel. They reported that most nuclei were not associated with dislocations and many dislocations did not have oxide nuclei associated with them. Similar results were also reported for nucleation during oxidation of iron (25) and of copper.
(23,26,27). On the other hand, nucleation and growth along steps associated with the emergence of the stacking faults at the surface were observed (26-29). Other common surface defects such as kink sites, vacancies or impurity atoms can also play an important role in the formation of surface oxide, but it is very difficult to determine experimentally whether oxide nuclei nucleate at such sites of atomistic size.

According to the classical nucleation theory, surface defects due to the presence of dislocations, stacking faults, vacancies, and impurity atoms are expected to play an important role at low temperature and low pressure, where the degree of saturation is not large enough for homogeneous nucleation to be favorable. The possibility that nucleation of an oxide takes place at any given site on a surface increases when the partial pressure of oxygen is increased and temperature is increased at a fixed supersaturation ratio. This kind of behavior is typical of an activated process, characterized by the so-called Arrhenius-type relationship. An Arrhenius type relationship between the density of oxide nuclei and temperature has been confirmed by a number of workers (30-34).
1-2. Growth of Oxide Nuclei

The details of the growth mechanism of oxide nuclei are also not very well understood because of difficulties in experimental verification. A number of proposed models (35,36) assumed that the nuclei grow laterally and only the edges of oxide nuclei are active in the further growth. This process may actually involve a series of partial processes, as suggested by Orr (35), such as nucleation of the oxide, physical adsorption and chemisorption, surface diffusion, and capture of oxygen at active growth sites. Two limiting cases for the geometry of oxide nuclei were considered by Bloomer (37): (1) cylindrical disks, one monolayer high, where the active region for oxygen uptake is an annulus of one atom wide around the circumference of the island, and (2) hemispherical caps, where the whole oxide surface is active in the oxygen uptake. These limiting cases were further tested experimentally by Orr (35) in the growth of magnesium oxide islands. He concluded that only a narrow zone at the edge of the nuclei was active around two-dimensional disks for the oxygen takeup. On the other hand, Cohen (38) reported the frequent occurrence of the second case, where the whole oxide surface of hemispherical caps was active in oxygen takeup. He suggested that the variation in the nature and concentrations of surface defects, which could serve as nucleation centers, might be responsible for the scatter of incidences in the two cases.
Although the two limiting cases have not been tested further to elucidate the contribution of this growth step to the steady state morphology at a later stage, they may provide useful information on the stability of the gas/oxide interface in the initial stage of oxide film growth. A planar gas/oxide interface is formed when growth takes place only at the edge of two-dimensional disk type of nuclei, while a hill-and-valley gas/oxide interface is formed when the whole surface of the 3D nuclei is active for further growth.

The rate of oxidation is known to decrease abruptly when the oxide islands cover the entire metal surface to form a continuous thin film. Several physical phenomena can take place at this final stage of nucleation and growth of oxide nuclei, but they are not well documented. When two islands impinge, a small angle boundary or a large angle boundary will form, depending on the angle of misorientation between two grains. Grain growth will take place, once a continuous oxide layer is formed, in an effort to minimize energy by reducing the grain boundary area. Dislocations will be generated in the oxide film as well as at the metal substrate because of stresses arising from the difference in molar volume between the oxide phase and the metal substrate. Comprehensive characterization of these processes seems very essential to understand the kinetics and the structural and morphological development of the
oxide during subsequent stages of oxidation.

2. Thin Film Growth

As soon as a thin oxide film forms on a metal surface, the reactants are separated by the reaction product. In order for the reaction to proceed further, one or both reactants of appropriate form must penetrate the film. When the oxidant or metal ions are introduced into the lattice of the oxide layer, point defects such as vacancies or interstitials are formed. Since most metal oxides are ionic in nature, point defects carry electrical charge and their charge is compensated by electronic defects such as electrons and positive holes. There is an important distinction between scale growth by cation migration or by anion migration in that new film grows at the gas/film interface in case of cation diffusion and at the film/metal interface in case of anion diffusion. Figure 1 shows the two different types of oxides, and possible mobile species in the oxide film in each case.

Many theories on the kinetics of thin film growth were developed for p-type oxides (40-43). One significant theory of thin film growth was developed by Mott (40-42) and Cabrera and Mott (43), yielding direct logarithmic relations and inverse logarithmic relationships, such as:

\[ x = A \ln(Bt + 1) \]  \hspace{1cm} \text{(direct log law)} \hspace{1cm} (1)

and
**A**

Gas Phase $X_2(g)$

$\frac{1}{2}X_2 \rightarrow X \ (ads)$

$X(ads) + M_M^X \rightarrow M_M^X + V_M^{2-} + 2h^+ + X_X^X$ (Reduction)

Scale MX

$M^0 + V_M^{2-} + 2h^+ \rightarrow M_M^X$ (Oxidation)

Metal M

Overall Reaction $M^0 + \frac{1}{2} X_2(g) \rightarrow MX$

**B**

Gas Phase $X_2(g)$

$\frac{1}{2}X_2 \rightarrow X \ (ads)$

$X(ads) + V_X^{2-} + 2e' \rightarrow X_X^X$ (Reduction)

Scale MX

$X_M^X + V_X^{2-} \rightarrow X_X^X + M^0 + V_X^{2-} + 2e'$ (Oxidation)

Metal M

Overall Reaction $M^0 + \frac{1}{2} X_2(g) \rightarrow MX$

**Fig 1.** Diffusional growth of MX scale by: A. Outward cation migration (p-type) and B. Inward anion migration (n-type).
\[
\frac{1}{x} = A' - B' \ln t \quad \text{(inverse log law)} \quad (2)
\]

where \(x\) is the film thickness at time \(t\) and \(A, B, A',\) and \(B'\) are constants at constant temperature. The direct logarithmic rate law is derived based on the assumption that the diffusion of electrons through a tunnelling mechanism was the rate determining step. Cation migration under the influence of an electric field, induced by the difference in mobility between electrons and cations, is assumed to be the rate limiting step for the inverse logarithmic rate law (40-43).

Qualititatively, the direct logarithmic relationship has been observed more frequently than the inverse logarithmic relationship but very little definitive quantitative support has been found for the theory (5). This is attributed to the difficulty in performing experiments with a carefully controlled and characterized specimen surface under clean conditions. Another major difficulty is the limitations in measuring accurately the reaction rates for the formation of the initial oxide layers.

An important factor to be kept in mind here relative to the early studies of thin film growth is that the theoretical and experimental studies have been done for relatively low temperatures. At such temperatures, the effects of short-circuit diffusion paths and crystal orientation on the reaction rate of film growth are more pronounced than those effects at more elevated temperatures.
where the thick film growth theory is applicable. Enhanced diffusion along dislocations and grain boundaries compared to lattice diffusion is well known and in general most oxide films contain an extensive array of dislocations and grain boundaries. The lower the oxidation temperature and the higher the density of these structural defects, the higher their contribution to the overall reaction. To take account of the contribution by short-circuit paths, Hart (47) defined an effective self-diffusion coefficient $D_{\text{eff}}$, as a weighted sum of constants for lattice and boundary diffusion such as:

$$D_{\text{eff}} = D_L(1-f) + D_B f$$  \hspace{1cm} (3)

where $D_L$ and $D_B$ are the lattice and boundary diffusion coefficients, respectively, and $f$ is the fraction of available short-circuit diffusion sites. Thus the calculation of the effective diffusion coefficient requires information about $f$ in the microstructure of the oxide film and its variation with the growth of the oxide.

The pronounced effect of crystal orientation on the rate of oxide film growth at lower temperatures have been demonstrated by many workers (48-54). Some striking features of oxidation in the thin film range were shown by Cathcart (48) for a single-crystal sphere of copper oxidized at 250°C. The variation in the rate with crystal face was vividly illustrated through the interference color pattern caused by the differing thickness of the film. He also
reported kinetic results indicating that the thickness of oxide on the (100) of copper was up to 25 times larger than that on the (311). Similar results on the crystal orientation effect were reported for the oxidation of Ni by Graham (49).

Such a big difference in reaction rate on two different crystal surfaces has been discussed by many scientists. Cabrera and Mott (43) suggested that the difference in atomistic-scale surface roughness was responsible for the reaction rate anisotropy. However, this idea was criticised because the predicted order of reaction rate did not agree with experimental results. A more plausible explanation was provided by Lawless and Gwathmey (50). They attributed the big difference to the varying diffusion rate along the different oxide grain boundary configurations on different crystal faces. In other words, oxide films developed on certain crystallographic orientations are polycrystalline in nature and contain many grain boundaries. On the other hand, oxide films formed on the surface of other orientations are nearly single-crystalline. This idea was further investigated by Cathcart et al (51-54). A detailed discussion on this subject has been given by Cathcart (48).

In summary, a knowledge of the detailed structure of the film is of great importance because the kinetics of film growth are found to vary considerably with difference in microstructure. The types of grain boundaries present,
e.g., high or low angle boundaries, and their orientations with respect to the adjacent oxide grains and the metal surface will determine the efficiency of the boundaries as diffusion paths. The evolution of these microstructural features, such as during grain growth and the formation/annihilation of dislocations due to creep processes, are also important to understand the overall processes occurring during thin film growth. These points will be addressed in greater detail in the discussion of the present work.

3. Thick Film Growth

In contrast to the studies on the thin film growth, numerous studies have been conducted on thick film growth at elevated temperatures. Since the early observations by Tammann (55) and Pilling and Bedworth (56), the most commonly observed growth mode at such temperatures has been characterized by a parabolic rate law. Wagner (45,46) has made the most important contribution to the understanding of the nature of the parabolic rate law. Wagner's model for the oxidation of metals assumes that the ambipolar diffusion of ionic and electronic species through lattice of a growing scale is the rate determining step. In other words, the rate of transport of each species is proportional to the gradient in the electrochemical potential for that species, but independent of the electrochemical potentials for the
other species. A detailed procedure for the derivation of the rate equation for parabolic scale growth can be found in his original papers (45,46). It should be noted that Wagner's theory leads to an expression for the parabolic rate constant that incorporates both the transport properties of the scale (e.g., conductivity of the film and transport numbers) and the thermodynamic driving force for scale formation (e.g., difference in chemical potential for either the metal or oxidant between the two interfaces). All these quantities can be measured independently, and the theory can be verified from the comparison of the reaction rate constant between the theoretically calculated value and those experimentally obtained. There are several review articles on this topic (3,4,7,44,57) indicating excellent agreement between the theory and the experiments at sufficiently high temperatures.

An important feature of the Wagner theory is the direct correlation with the point defect structure in the oxide film. The theory can be used to predict the expected dependency of the rate constant on the oxygen activity (58). For a p-type semiconducting cation-diffusing oxide film, the parabolic rate constant $\tilde{k}$ is expressed as:

$$\tilde{k} \propto P_{O_2}^{1/n}$$

where $P_{O_2}$ is the partial pressure of oxygen at the oxide/gas interface and $n$ is a constant. The value of $n$ varies in a predictable way, depending on the nature of the dominant
point defect in the oxide. For example, in the case of a p-type oxide such as nickel oxide, \( n \) becomes 6 for doubly charged cation vacancies and 4 for singly charged cation vacancies. For an n-type oxide, on the other hand, \( n \) assumes a negative value depending on the degree of ionization of the point defect. Deviation from the predicted oxygen pressure dependency was explained by nonideal behavior of point defects due to complex defect structures (59,60).

There are four major assumptions in Wagner's theory:

1) A pure, flat, adherent crystalline compound in a one-phase scale layer is in local chemical equilibrium at both the metal/scale and the scale/gas interfaces,
2) Independent diffusion of ions and electrons across the scale is the rate controlling process,
3) The growth of the scale is considered to occur at the metal/scale or at the scale/gas interfaces or both.
4) Thermodynamic equilibrium is established within the scale between the ions and electrons with the metal and gas at their local thermodynamic activities.

The validity of these assumptions has been studied by many workers (61-64). However, it seems appropriate to introduce briefly some of the previous observations concerning the first assumption since this study is closely related to it. More detailed discussion regarding irregular morphological features, as opposed to the assumed flat and adherent films,
will be introduced in a later section.

The first assumption listed above states that the oxide film is a homogeneous diffusion barrier. In many cases, however, a truly homogeneous diffusion barrier rarely occurs. For example, many oxide films contain voids and cracks. These physical gaps may act as barriers to the solid state diffusion process and lead to the slowing of the rate of reaction. As special cases, some oxides fail to form the homogeneous solid-state diffusion barrier because the oxidation product is either a liquid phase or has high volatility. The oxidation of metals in group IV A and V A (e.g., Ti, Zr, Hf, Ta and Nb), on the other hand, are known to be greatly affected by oxygen solubility in the substrate metal phase (3). The oxidation of metals in these groups is very complex and a careful modification is needed to take into account both the simultaneous dissolution of oxygen and oxide formation. Finally, short-circuit paths such as grain boundaries and dislocations serve as important modes of transport. As pointed out previously, the effect of short-circuit paths is less pronounced at elevated temperatures than at lower temperatures. Nevertheless, contributions from short-circuit diffusion to the overall diffusion has to be carefully considered. A number of investigators have studied the effects of these short-circuit diffusion paths within the oxide films on the kinetics of metal oxidation (65-72).
B. High Temperature Oxidation of Iron

1. Defect Structure of Iron Oxides

The oxidation of iron in air at temperatures higher than 570°C produces a multi-layered scale composed of wustite (Fe$_{1-x}$O), magnetite (Fe$_3$O$_4$) and hematite (Fe$_2$O$_3$). At temperatures below 570°C, wustite is thermodynamically unstable and a two-layered scale of Fe$_3$O$_4$ and Fe$_2$O$_3$ is formed. Wustite has a NaCl structure and is a p-type metal deficit semiconductor which can exist over a wide range of stoichiometry, from Fe$_{0.95}$O to Fe$_{0.88}$O at 1000°C (73). Cation diffusion in wustite was studied by Chen and Peterson (74), using the tracer diffusion technique. They showed that the diffusion of Fe in wustite takes place by free vacancies, which are not associated with immobile vacancy clusters. The vacancy cluster refers to a complex vacancy structure resulting from the Coulombic interaction between cation vacancies and cation interstitials. Extensive studies have been done on variable types of possible complex defect structures in wustite (59,60,75-79).

Magnetite has the inverse spinel structure, with a cubic close-packed oxygen anion sublattice. Half the number of octahedral interstices are occupied by Fe$^{2+}$ cations, and one-eighth of the tetrahedral interstices are occupied by Fe$^{3+}$ cations. Magnetite also can exist over a small range of stoichiometry. Cation diffusion in magnetite in the
temperature range of 900°C-1400°C has been studied by Dieckmann and Schmalzried (80) and Peterson and Chen (81). They reported that diffusion occurs by the movement of a doubly charged iron vacancy at high oxygen activity and by an iron interstitial at low oxygen activity. Very recently, Atkinson and Taylor (82) have shown that the same diffusion mechanism is also applicable at the lower temperature of 500°C.

Hematite has a rhombohedral structure, in which the oxygen ions exist on a close packed hexagonal arrangement with two-thirds of the octahedral interstices occupied by Fe$^{3+}$ cations. The defect structure of hematite has not been made clear because of comparable diffusion coefficients between Fe and O in bulk hematite. Oxygen vacancies (83) as well as cation interstitials (84) have been proposed for the rate controlling dominant diffusing species. However, a recent study indicates that the outward diffusion of interstitial iron ions is the dominant transport process for the growth of hematite (85). Because of the complication due to the contribution of faster short-circuit paths for inward oxygen diffusion, the current level of understanding of the diffusion process in hematite and the mechanism of film growth is poor. Figure 2 shows a schematic diagram for the oxidation mechanism on the basis of information about the transport process in each phase.
Fig 2. Schematic diagram showing diffusion steps and interfacial reactions in a three-layered oxide scale growth of iron. Two possible diffusing species Fe$^{3+}$ are shown in the hematite scale.
2. Experimental Observations

Since the iron self-diffusion coefficient for wustite is orders of magnitude larger than those for the higher oxides as shown in Fig. 3, the steady-state thickness of wustite would be expected to greatly exceed the combined thickness of magnetite and hematite if the scale growth were controlled by diffusion. Paidassi (86) confirmed this prediction in the oxidation of iron in air in the temperature range of 700°C-1200°C, showing that the combined thickness of magnetite and hematite amounts to only 5% of a scale formed. He reported that the relative thicknesses of layers in the multi-layered scale attained a steady-state value from the very early stage of oxidation and remained unchanged during oxidation. The nature of steady-state oxidation was reported as parabolic.

The growth kinetics of multi-layered scales of iron at the same temperature range but at low oxygen pressures, about $10^{-4}$ atm, were studied by Goursat and Smeltzer (87). They found that the increasing initial reaction rate was followed by a linear oxidation rate. A parabolic rate was reported to start later with the nucleation and growth of the magnetite scale. The initial increasing rate was explained on the basis of the growth of wustite islands to form a continuous layer. The linear reaction rate was attributed to the uniform thickening of wustite, controlled by a phase boundary reaction involving the adsorption and
Fig 3. Iron and oxygen self-diffusion coefficients in iron and iron oxides (44).
dissociation of oxygen molecules. The oxidation of iron at even lower partial pressures was studied by Pettit et al. (88,89). They oxidized iron in the temperature range of 700°C-1100°C in CO-CO₂ mixtures where wustite is the stable phase, and found that the oxidation kinetics obey a linear rate law up to a scale thickness of 100 μm. They reported that the parabolic rate law was obeyed subsequently. For the transitional linear reaction at the initial period, a hundred micrometers of oxide scale thickness is certainly a very large value compared to the other oxide scales; it is interesting to note that the supply of cations to the wustite/gas interface by diffusion is so rapid that the overall reaction is controlled by phase boundary reactions.

The initial stages of the oxidation of iron at high temperatures (570°C-1200°C) have been seldom investigated compared to studies of steady-state oxidation. It is important to consider the structure of the substrate in the studies of wustite scale growth because iron transforms allotropically from alpha-bcc to gamma-fcc above 910°C. Since the structure of the metal surface affects the nucleation and growth behavior greatly, the distinction between alpha and gamma seems very important for the initial stage of oxidation. The nucleation and growth kinetics in the gamma range were investigated by Charbonnier and Bardolle (90) for the oxidation of zone-refined iron at 950°C. They found a variation in the number and size of the
wustite crystals on differently oriented iron grains. They also reported that the number of nuclei on a given metal face decreased with temperature at fixed oxygen pressure and increased with oxygen pressure. The oxidation of alpha iron at 604°C by Paidassi (91) showed that the wustite islands appeared on the metal surface and that they later transformed into a layer covered by magnetite. Because of the lack of experiments focused on the initial stage of oxide scale growth, it is difficult to draw any conclusions which might be helpful in interpreting the physical phenomena occurring in this study. Although, there are a number of experiments performed for the study of nucleation and growth in the case of low temperature oxidation (less than 570°C) (19,92-95), these are not very helpful because magnetite nucleates on the substrate of alpha iron.

C. Morphological Study of High Temperature Oxidation

It has been assumed so far that the oxide film is morphologically ideal such that the film has flat and dense interfaces and grows at one of its interfaces by the solid-state diffusion of reactant through it. In practice, many different deviations from this ideal case have been reported in thick film (called scale hereafter) growth of metals at high temperatures. Detachment at the scale/metal interface is possible due to several reasons, discussed later in this
section, and introduces complications in the understanding of the further growth of the scale. Development of a duplex structure, which consists of two well-defined layers, an inner equiaxed layer and an outer columnar layer, requires additional consideration for the analysis of the oxide grain structure in the scale. Finally, the development of irregular morphologies at the scale/gas interface such as whiskers, blades, pyramids and pits requires further understanding of the mechanism of scale growth. In this section, growth processes in the three cases mentioned above which deviate from the ideal morphology assumed will be discussed in detail.

1. Detachment at Scale/Metal Interfaces

The separation at scale/metal interfaces occurs in many ways. When the oxide scale grows by outward cation migration (or by inward cation vacancy migration), there exists the possibility of void formation at the scale/metal interface by condensation of vacancies (3,4). The migrating vacancies can be accommodated in the scale and metal substrate by processes such as the generation of dislocation loops, formation of dislocation jogs and annihilation at grain boundaries and second phases in the metal when the scale is sufficiently thin. When such vacancy sinks are exhausted, the continuing arrival of cation vacancies can lead to void formation at the scale/metal interface. On the
other hand, stress-induced spalling or cracking can also cause separation at the scale/metal interface during high temperature oxidation. For example, the observation of the development of highly convoluted films detached from the metal substrate has been reported by many workers for the growth of \( \text{Cr}_2\text{O}_3 \) and \( \text{Al}_2\text{O}_3 \) (96-100). It has been suggested that the convoluted scale morphology occurs because of a large amount of lateral growth within the scale, with resulting compressive stresses on the scale. A detailed mechanism for lateral growth can be found in literature (96-100).

When separation of the scale from the metal substrate occurs, solid-state diffusion is no longer possible through that physical gap. Three different types of transport mechanisms are known to contribute to the transport of the reactant through the voids. Firstly, for metals with a high vapor pressure at the high temperatures (Cr and Al, for example), metal vapor is supplied to the scale. Cations then diffuse through the scale and further growth of the scale take place at the scale/gas interface (96). Secondly, for metals with a low vapor pressure, scale dissociation at the scale/void interface provides oxidant to the void/metal interface according to following reaction:

\[
\text{MO} + \text{V}^n_{\text{M}} + 2 \text{h}^* \rightleftharpoons \text{M}^0_{\text{M}} + 1/2 \text{O}_2 (\text{g}) \quad (\text{in void})
\]

where \( \text{V}^n_{\text{M}} \) is a doubly charged cation vacancy, \( \text{h}^* \) is an electron hole, and \( \text{M}^0 \) is a cation in a normal cation site.
Then, new scale is formed both at the void/metal interface by the reaction between dissociated oxygen and the substrate metal, and at the scale/gas interface by the reaction between the liberated cations (formed by dissociation mechanism) and oxygen. The overall reaction is known to be controlled by the diffusion of cations through the scale (101-107). Finally, the development of grain boundary fissures which serve as microchannels for inward transport of oxygen to the scale/metal interface has reported by Mrowec and Werber (7). Channels are most probably created at the junction of 3-point grain boundaries because vacancies are expected to condense preferentially at those sites. The actual presence of such fissures is demonstrated by a two-stage reaction procedure (108-111) and by recent in-situ observations (112). As will be discussed subsequently, the last two mechanisms are closely related and are attributed to the development of a duplex scale structure (113-119).

2. Development of the Duplex Structure

A duplex structure refers to the morphology of an oxide scale which consists of a layer of fine-grained equiaxed inner grains and a layer of large columnar outer grains. The inner layer of grains was thought to be porous, but recent studies using transmission electron microscopy have shown that the inner layer is not greatly porous (120-122).
The occurrence of this duplex structure has been reported mainly for oxides which grow by the outward diffusion of metal ions. However, the conditions that favor the growth of duplex scales are not very clear. There are two major points of view about the mechanism for duplex scale growth. The first view was mentioned earlier when the dissociation mechanism was explained. The basic idea is that if for some reason, the scale lost adherence at the scale/metal interface, the growth of the scale would proceed by the continuing supply of oxygen to the void/scale by the dissociation mechanism. The morphology of oxide grains formed thereby at the void/metal interface would consist of small equiaxed grains. The cations liberated by the dissociation mechanism at the scale/gas interface would migrate toward the scale/gas interface by solid-state diffusion and form new oxide on top of columnar oxide grains. This bimodal growth has been reported frequently since the early work by Dravnieks and MacDonald (123).

The second view is suggested in terms of different recrystallization and grain growth behavior of oxide grains during oxidation. This mechanism was put forward because of recent observations of the transverse sections of oxide scales in TEM. At this moment, the exact condition for the development of the duplex structure is not clear. Sawhill and Hobbs (122) investigated the effect of substrate surface on the morphology of oxide scales on high purity nickel at
1000°C using TEM. They found that a duplex structure was observed for the scale on the electrochemically polished surface, and a columnar oxide grain structure on the mechanically polished surface. The reason for the development of the columnar structure in the case of the mechanically polished sample was explained as due to a high driving force for recrystallization induced by the mechanically deformed substrate metal layer.

The effect of impurities on the grain growth characteristics was studied by McKee and Druschel (124) for the sulfidation of pure and 'not-so-pure' iron at 700°C. They found that the silicon impurity in iron reduced the reaction rate and altered the microstructure from a columnar scale growth to a layered duplex structure. Similar results on the development of the duplex structure due to impurity was also reported on the scale growth of NiO on nickel at 1000°C by Atkinson et al (102) and the magnetite scale growth on iron at 500°C by Atkinson and Taylor (103).

The effect of temperature on the morphology of oxide grains during scale growth of NiO was studied by Douglas (125). At lower temperatures he observed a well-developed duplex oxide structure. However, at high temperatures of around 1000°C a dense adherent oxide was observed. The compressive stresses in the oxide caused voids at the scale/metal interface at lower temperatures due to a lack of plasticity of the oxide. Recently, single layer growth of
wustite scale at the high temperature at 1000°C and 1200°C in a CO/CO₂ environment was reported by Kofstad and Bredesen (126).

In many cases, the distinction about causes of the duplex structure between the dissociation mechanism and the recrystallization behavior of the oxide scale has not been made clear. However, there is general agreement on the importance of the two different microstructures in understanding overall oxidation reactions. Another interesting observation on the possible consequences of the different morphology between single-layered columnar and duplex structure was made by King et al (127). In their recent study by TEM on the reactive element effect in Fe-Cr-Y alloys at 1000°C, they found that a Y addition changed the oxide scale structure from mainly single-layered columnar to a well-developed duplex structure. Considering the well-known effect of Y on enhancing scale adherence, among many other beneficial effects, this observation is quite interesting in understanding the mechanism of scale adherence. Unfortunately, the reason for the transition in the oxide grain structure is not discussed in detail in that work.

3. Irregular Scale Morphologies

Different types of oxide morphologies obtained by altering the experimental conditions slightly during high
temperature oxidation have been studied extensively during recent years. Facets, growth pyramids, platelets, whiskers, and growth pits were observed in the scale growth of cation-diffusing oxides. The growth of such irregular morphologies at the scale/gas interface will be briefly discussed.

The oxidation of nickel has been a favorite model for the kinetic and morphological studies of oxidation because it forms only one oxide phase, NiO. This avoids complications in morphological changes which arise from different oxide structures, as in the oxidation of iron (128). Morphological changes in NiO scale growth induced by modifications in experimental conditions such as surface pretreatment, metal purity, temperature, oxygen pressure and its water vapor content have been reported (57,129-131). The effect of purity at 1100°C showed that a morphology composed of flat columnar grains was obtained only when very impure nickel (99.5% Ni) was used. Facets and growth ledges were the main morphological features for pure nickel (99.999% Ni) (129). Water vapor in oxygen was shown to enhance the growth of whiskers during NiO scale growth.

The most significant contributing factor controlling morphological features at the scale/gas interface is temperature, as seen from the recent in-situ observation of the scale morphology for the oxidation of Ni, Fe and Cu (130-134). As the temperature range of scale growth changes from low to intermediate to high temperatures, morphologies
related to dislocations also change from whiskers to pyramids to pits. In the low temperature range, a hollow dislocation core provides rapid surface diffusion to the whisker tip. Lateral whisker growth via lattice diffusion is very limited at low temperatures, and whisker or blade growth is preferred. In the intermediate temperature range, lateral lattice diffusion becomes appreciable but is still less than the surface diffusion along dislocation pipes and hence, pyramidal growth is preferred. In the high temperature range, however, throughput (flux times area) via lattice diffusion is greater than surface diffusion through dislocation pipes resulting in the formation of growth pits.

In summary, a number of studies on the oxidation of metals have shown that the morphological features of oxides depend greatly on the experimental conditions during the reaction. Morphological changes, in turn, are expected to affect the kinetics and the adherence of oxides during the high temperature oxidation of metals. However, morphological characterization has seldom been performed for most kinetic studies. Since experimental factors such as metal purity, pretreatment, oxidation procedure, temperature and the environment affect the morphological and transport characteristics of scale growth, it is imperative to note limitations in evaluating any scale growth model proposed.
D. Structure and Energy of Grain Boundaries

The oxide scale on a metal is generally found in the form of a polycrystal, which is an aggregate of randomly oriented single crystals (or grains) bonded together by a grain boundary. Single crystalline grains, in turn, usually contain subgrains, which have slightly different orientations, and are joined by subboundaries or low angle grain boundaries. The structure and energy of grain boundaries and related phenomena occurring at the onset of recrystallization are reviewed briefly in this section with a view to demonstrating important concepts which are used later for discussion of the grain growth characteristics in wustite scale growth.

1. Grain Boundary Structure

The description of a simple low angle boundary as an array of dislocations, formulated by Burgers, Frank, Read, and Shockley (135), is a very satisfactory model for the interpretation of the microstructure and energy of boundaries with misorientations below about 10-20 degrees. This topic has been reviewed extensively by Amelinckx and Dekeyser (136) and by Shewmon (137). The tilt boundary is formed when the two grains on either side are related by rotations about an axis lying in the boundary, as shown in Fig. 4A. If a boundary consists solely of edge dislocations
Fig 4. A: Low angle symmetrical tilt boundary (141).
B: Grain boundary energy of [100] tilt boundaries in copper as a function of the tilt angle $\theta$ (145).
of Burgers vector equal to the step height, \( b \), as shown in Fig. 4A, the dislocation spacing, \( D \), decreases as rotation angle \( \Theta \) increases up to a certain degree where dislocation cores start to overlap and lose their physical significance.

The alternative type of simple low-angle boundary arises when the boundary lies at right angles to the axis of rotation. This is called a twist boundary and is made up of screw dislocations. In reality, however, it is important to realize that the dislocation structure of a low-angle boundary cannot be fully or accurately modelled on the basis of simple tilt or twist arrays of dislocations. Some examples of complex dislocation networks in low-angle boundaries are discussed by Jones (138).

The geometrical structure of a high angle boundary (\( \Theta > 15-20 \) degrees) is best described by the Bollmann O lattice (139), which was developed from the original coincidence site lattice (C.S.L.) approach (140). High angle boundaries can be classified into three types according to the degree of deviation of the grain boundary lattice from an exact coincidence: (1) exact C.S.L. orientation, (2) close to but not precisely at a C.S.L. orientation, and (3) large deviation from the C.S.L. orientation. This classification is very convenient and provides a good understanding about the energies of boundaries. For high angle boundaries close to the C.S.L. orientation, the deviation from the exact C.S.L. orientation is taken up by
secondary intrinsic grain boundary dislocation, referred to as D.S.C. vectors (139). The structure of high angle boundaries at large deviation from the C.S.L. orientation can still be described within the Bollmann model but their physical significance is more difficult to grasp. A large percentage of boundaries in well-annealed polycrystalline materials is found to have structures which include periodic arrays of grain boundary dislocations.

2. Grain Boundary Energy

Grain boundaries possess energies which govern their stability and structure. The relationship between the boundary energy and the misorientation in low-angle tilt boundaries in an infinite medium of shear modulus \( \mu \) and Poisson's ratio \( \nu \) is given by Read and Shockley (141) as follows

\[
E = E_0 \Theta (A - \ln \Theta)
\]

where

\[
E_0 = \frac{\mu b}{4 \pi} \left(1 - \nu \right)
\]

and \( A \) is an integration constant. Physically, the equation predicts the energy of the boundary to be the sum of total core energy in unit area of boundary (first term) and the elastic energy (second term). The energy of a twist boundary will increase with the angle of twist in the same general way as the energy of a tilt boundary increases with the angle of tilt. A plot of Eq. 5 is shown in Fig. 4B for low-angle (100) tilt boundaries in copper at 1065°C. The
agreement with experiment appears to be quite satisfactory for the curves labeled Read-Shockley at small angles. Note the sharp cusp at $\theta = 0$ degree, where the boundary disappears.

Unlike the case of low angle grain boundaries, the relationship between the boundary energy and the misorientation angle in high angle boundaries is not well established. One of the basic problems in discussing the energy of high angle boundaries is that the energy depends on many factors such as misorientation angle, temperature, and segregation which can not be defined accurately in a simple way. The misorientation angle has five degrees of freedom itself, three rotation angles between the grains and two angles for describing the inclination of the boundary plane. Because of the complexity of the boundary energy function, gross simplifications are needed. A notable exception is the tilt boundary of a pure metal whose energy is expressed in terms of a single misorientation angle at a given temperature.

As will be seen from the review of surface energy measurement in the following section, most of the measurements of grain boundary energy are comparative rather than absolute. Various types of experimental method employed to measure grain boundary energies are found in the previous reviews (142,143). Typical relations between grain boundary energy and angle of misorientation are shown in
Figs. 5A and 5B. The variation of the boundary energy with tilt angle $\theta$, as predicted by Read and Shockley (141), is shown in Fig. 5A. Figure 5B shows the same relationship based on the original data by Gjostein and Rhines (145). In both cases, the cusps are located at a higher order twin, or at a boundary which has a high density of coincidence sites. The variations are not very appreciable at high misorientation angle (about 10-15\%). The presence of these cusps in the boundary energy plot is particularly helpful in understanding the rotation of a single crystal sphere in sintering experiments, suggested by Shewmon (137) and tested by Herrmann et al (146-148).

According to Shewmon (137), when two spheres are sintered together to form a boundary, the initial orientations of the lattices of two spheres are arbitrary. In this case, five degrees of freedom of the boundary can be used in the movement of the spheres during annealing so as to decrease the grain boundary energy. After long annealing times, a thermodynamically stable grain boundary will form. Shewmon further pointed out that his model is, in principle, identical to the subgrain boundary coalescence model proposed by Hu (149) and Li (150) for the nucleation process in recrystallization. The implication of the presence of a cusp at coincidence orientations and energy minimum at zero degree will be discussed more in detail later with experimental observations.
Fig 5. Variation of grain boundary energy with misorientation angle attributed to A: Shockley and Read (141), and B: Gjostein and Rhines (145).
E. Anisotropy of Surface Energy in Solids

The influence of surface energy and its anisotropy on metallurgical processes have been known to be very important for a long time. However, there has been very little success in experimentally determining the surface energy of a single crystal. One needs to evaluate the dependence of surface energy on the orientation of a crystalline surface, and some relative measurements based on theoretical calculations have proved useful in studying the anisotropy in surface energy, \( \gamma \). Various distinctive microscopic features resulting from the anisotropy of surface energy have been observed during the study of wustite scale growth. In view of the importance of anisotropy in surface energy to this work, it is worthwhile to discuss the current understanding of surface energies in metals and NaCl-type crystals.

Measurement of surface energies has been reviewed extensively in a number of books (151,152) and articles (153-156). In principle, all methods for determining surface energy can be divided into two groups depending on whether an absolute or a relative value of energy is determined. Two of the most popular methods in the absolute measurement of surface energy are the zero-creep technique (157) and the controlled cleavage technique (158). Measurement in the zero-creep technique is made by balancing
the capillary forces which are to be determined against a known external force. Determination of the external load required to balance the surface tension of a polycrystalline wire yields an absolute value of \( \gamma \). Since the specimen must be polycrystalline, according to theory (159) and experiments (160), the value \( \gamma \) so determined will be an average value of the surface energies of all surface orientations. Therefore, determination of \( \gamma \) for a known orientation is not possible with this technique.

Surface energy in the controlled cleavage experiment is determined by measuring the reversible work for creating unit area of a new surface. The first serious application of this technique was by Gilman (158) for the planes of LiF (100), MgO (100), Si (111), and Fe-3% Si (100). In order to ensure that the amount of plastic deformation is minimal during measurement, the experiment is done either at liquid nitrogen or liquid helium temperature. Results for ionic crystals were in good agreement with theoretically expected values from simple ionic theory, but the measured values of surface energy for Fe-3% Si were unreasonably high due to energy dissipation by plastic deformation; hence this method is limited to a few inherently brittle ionic crystals.

The relative evaluation of surface energy, on the other hand, has proved very successful in measuring the anisotropy in \( \gamma \). The techniques most frequently used are: 1. the measurement of dihedral angles at twin boundary-surface
intersections (161-163), 2. the study of the equilibrium shapes of solids of small mass (164), 3. observations on faceting of planar surfaces (165,166). All three methods are based on the fact that the geometry of the equilibrated system provides a measure of the ratio of the unknown energies. Although these techniques are not very complicated, precautions should be taken in their use and in the analysis of the results. Some critical aspects of the methods are discussed by Shewmon and Robertson (153).

As a typical example, the third method, evaluation of faceting of planar surfaces, will be discussed briefly because of the faceting observed here during wustite scale growth. If the surface energy is sufficiently anisotropic, the planar surface will break into facets during annealing. The facets consist of one or more planes with low value of \( \gamma \) (low-index plane) and planes of higher \( \gamma \) (high-index planes). During this process, reduction of surface energy is achieved and the average surface orientation is kept parallel to that of the original surface. Figure 6 shows a section normal to the new surfaces where the surfaces are labeled simple and complex. For a particular thermally etched crystal of known surface orientation (and hence known \( a \)), the ratio of the surface energy of the simple plane to that of a random plane is found by measuring the angle \( \beta \). Moore (165) found that \( \gamma(100)/\gamma_r = 0.90 \) and \( \gamma(111)/\gamma_r = 0.84 \) for silver heated in air to about 900°C. These ratios, which indicate the degree
Fig 6. Schematic diagram of a thermally etched surface (165).

of anisotropy of surface energy for silver, are very small compared to those for ionic crystals.

Theoretical calculation of the surface energies for alkali halides was done by many workers (154), and more recently by Racmann (167) and by Tasker (168). Theoretical evaluation was done by calculating the mutual potential energy across two halves of a cleavage plane and lattice sums using the appropriate potential energy function for like or unlike ions. The uncertainties in the choice of the potential function and approximation of the surface distortion are two major difficulties in the calculation of surface energies of ionic crystals. Recent results by
Tasker (168) show a striking degree of anisotropy in surface energy between (100) and (110) planes of NaCl crystal. He reported that \( \gamma(100)/\gamma(110) \) was about 0.5.

The most straightforward representation of surface energy anisotropy is a polar diagram of surface energy, which is called a \( \gamma \)-plot. Figure 7 gives a \( \gamma \)-plots for gold and NaCl showing the variation of \( \gamma \) with orientation. The difference of surface energies between maximum and minimum values for NaCl is dramatic compared to that of gold, as already mentioned earlier.

The general relationship between the \( \gamma \)-plot and the equilibrium shape of the crystal is called Wulff's theorem. Three types of surfaces are possible based on the theorem (144): (1) Smooth singular surfaces like (111) or (100) plane which represents a minimum (cusp) in the \( \gamma \)-plot; (2) vicinal surfaces which have an orientation close to a singular surface with ledges and kinks on them; (3) diffuse surfaces which are atomistically rough. Because kinetic and other nonequilibrium effects can affect the crystal habit, it is possible that an actual crystal has faces that are not the equilibrium ones of the Wulff construction. Manifestations of kinetic effects, particularly for the presence of a dislocation, will be discussed later.

In summary, an examination of literature on surface energies of solids indicates that the present understanding is still nebulous in spite of its fundamental importance in
Fig 7. γ-plot for A: gold at 1030°C in a hydrogen atmosphere and B: for NaCl (144).
many physical phenomena. Determination of the surface energy by the zero-creep method and the cleavage method has limited applicability because the experiments are done at extreme temperature ranges of $T/T_m > 0.7$ and $T/T_m < 0.1$, respectively. Since the effect of temperature on surface energy has not been studied extensively, care has to be taken when values of $\gamma$ are interpolated. The evaluation of relative surface energies for different orientations by theoretical calculations seems to provide useful information.

F. Dislocations in the NaCl Crystal Lattice

Wustite exhibits the NaCl-type crystal lattice which is an fcc crystal lattice with an anion-cation pair as the basis. Because of the presence of ions of opposite charge in the lattice, complicated electrical effects for dislocations have been observed. One notable effect is that the ionic bonding in the dislocation core modifies the Peierls energy and suppresses stacking fault formation$^{169}$. In addition, the dislocation charge in ionic crystals accentuates the interaction between dislocations and charged point defects. The present work involves the influence of dislocations on the morphological features during wustite scale growth.
The dislocations which have been identified in NaCl-type crystals have a \(\langle 110\rangle\) Burgers vector with the slip direction \(\langle 110\rangle\). Figure 8 is a schematic illustration of a curved dislocation forming the boundary of a region of plastic glide in a crystal. Dislocations of screw, edge, and mixed character, depending on the angle between dislocation line vector, \(\xi\), and Burgers vector, \(b\), are illustrated on the glide plane of (110). The major slip planes are \{110\}, as shown in the Fig. 8, while \{100\} slip planes are reported to be prevalent in crystals with high ionic polarizability (169).

The popular and very simple technique of dislocation etch pitting is utilised in the study of the slip system of NaCl-type crystals. This method has been reviewed extensively by Johnston (170) and Amelinckx (171). One result of a dislocation etch pit experiment is shown in Fig. 9, illustrating the slip systems on the \{100\} surface of an NaCl crystal. From the information on the slip systems illustrated in Figs. 8 and 9, a dislocation with a line vector \(\langle 100\rangle\) is possible geometrically for a pure edge but not for a pure screw dislocation. According to this simple geometrical understanding, the screw dislocation will have a \(\langle 110\rangle\) line vector, and a dislocation whose line vector is perpendicular to the \{100\} free surface has to be of mixed character. However, it has been shown that image forces pull the dislocations via kink formation out of a screw
Fig 8. A: Schematic diagram of a curved dislocation and B: Three types of dislocation formed by a curved dislocation (144).
orientation toward a perpendicular orientation (135). The implications of the orientation of the dislocation line vector with respect to the \{100\} surface will be discussed in a later chapter.

Fig 9. Slip Systems and Their Glide Band Traces in an Etch Pit Experiment (172).
III. Experimental Procedures

A. Introduction

Modifications of the scanning electron microscope (SEM) for in-situ high temperature oxidation studies have been made by many researchers (173-176). In general, the modifications comprise a heated stage, a gas injection system, and temperature measuring devices. The details of these modifications differ from each other, but they provide valuable information about factors for the development of the hot-stage environmental scanning electron microscope (HSESEM). Details on the major modification of a Cambridge Stereoscan S4 SEM done by previous workers (130,132,177,178) will be described in this chapter. In addition, post-oxidation analyses for further characterization of the oxidized sample, such as two-stage replication technique and X-ray diffraction analysis, will be presented.

B. Modification of the SEM

1. Arrangement of Specimen Stage

The specimen stage used for this study is shown in Fig. 10. A type 304 stainless steel cylindrical shell with a thickness of about 3.2 mm (3.17 cm ID and 3.81 cm OD) is...
Fig 10. Specimen stage showing specimen holder surrounded by tungsten coil furnace (A), Pt gas leak pipe (B).
Fig 11. Cross-sectional view of the heating stage showing cylinder, radiation shields, tungsten coil furnace and the thermocouple.
used to contain the specimen holder, which is surrounded by a heater coil and radiation shields. The disk-shaped specimen of 1.15 mm thickness sits at the top of the specimen holder. The specimen and the specimen holder are surrounded by a doubly-wound tungsten wire (0.5 mm diam.), insulated with ceramic tube segments, as shown in Fig. 11. Three concentric sets of radiation shields are used. The innermost cylinder is made of molybdenum foils. The other two radiation shields are made of nickel foil and are separated by a ceramic ring as indicated by cross-hatching mark in the Fig. 11.

Three cap-type radiation shields are also used to maintain the temperature more effectively and to prevent tungsten evaporation and condensation on top of the specimen during heating. A larger outer shield covers the entire specimen assembly and protects the light pipe from damage caused by the heat generated in the specimen assembly. The arrangement of radiation shields, three concentric shells and three caps was found to be very effective in raising the temperature of the specimen to 1200°C and maintaining it reasonably constant.

The temperature was monitored using a Pt/Pt-10%Rh thermocouple located beneath the specimen, inside the hollow specimen holder. Calibration was done according to the procedure described in the next section. To avoid the buildup of electrostatic charge on the specimen surface, a
grounded platinum wire was wrapped around the specimen holder. The gas was leaked to the top surface of the specimen through a platinum capillary pipe (0.5 mm ID and 0.25 mm ID). The gas flow rate was adjusted by the microvalve attached to the outside of the SEM chamber.

The image was recorded using either a 35 mm camera or a videotape recorder. The videotape recorder was particularly useful for wustite scale growth considering the rapidly changing features of the scale/gas interface. A sequence of photographs was taken later from the screen of the TV monitor as the videotape was played.

2. Temperature Calibration

As described previously, a doubly wound tungsten wire is used to heat the specimen holder to the desired temperature, using a DC power supply (Hewlett-Packard 6264B). The double winding was intended to eliminate any magnetic field generated by the passage of current, which might interfere with the electron beam. The number of turns for the tungsten coil furnace to attain the temperature of 1400°C was calculated by a previous worker (130). It is very important to maintain the number of turns consistent for the temperature calibration. In the present study, the wire was wound exactly to 10 turns.

Initially, molybdenum was chosen as the material for the radiation shields due to its low emissivity at high
temperatures. However, molybdenum oxidizes very quickly in the SEM atmosphere and its emissivity increases drastically once oxidized(179). In addition, oxidized molybdenum is very difficult to clean and is brittle and difficult to handle. Nickel, on the other hand, turned out to be a good material for radiation shields because of its lower tendency to be oxidized in the SEM atmosphere and its low emissivity even when oxidized. However, the innermost radiation shield was made of molybdenum because of the high working temperatures.

An accurate measurement of the specimen temperature was ensured by several complementary calibration methods. Because of space limitation and the chemical instability of the specimen, the thermocouple had to be inserted into the hollow specimen holder rather than in contact with the specimen itself. Also, the specimen could not be located in the uniform temperature zone in the middle of the coil furnace because of possible contamination and electrical noise, so the current thermocouple arrangement was inevitable. Clearly, an appreciable temperature difference exists between value indicated by the thermocouple located inside the hollow of the specimen holder underneath the specimen and the actual temperature of the specimen. The inset in Fig. 12 shows the arrangement used to calibrate the temperature difference between measuring thermocouple and actual temperature of a specimen obtained from an attached
thermocouple. The temperature calibration curve shown in the Fig. 12 shows the temperature difference over different temperature ranges.

As shown in Fig. 12, a difference of 200°C was recorded at the temperature range of interest in this study. This temperature difference was also confirmed by checking in-situ the melting point of gold placed inside a groove on top of the specimen, as shown in the inset of Fig. 12. The response time for thermal equilibration of the specimen was also very short. This is a fortunate situation because one can immediately make a correction to the temperature measured by the thermocouple. In order to further ensure the reliability of temperature measurement, the specimen thickness (1.15±0.02 mm) and arrangement of radiation shields and coil furnace were kept constant, and the calibration was rechecked occasionally.

3. Gas Pressure Estimation

For the normal operation of the SEM, a gas pressure of $10^{-4}$ Torr or less has to be maintained in the specimen chamber. Two different systems with the ability to sustain an appreciable oxygen pressure without causing vacuum failure in the SEM have been developed. Ramanarayanan and Alonzo (176) used a differential pumping system, permitting a dynamic gas flow over the sample, with an auxiliary mechanical vacuum pump for the small environmental chamber
Fig 12. The arrangement of temperature calibration shown in the inset and calibration curve.
surrounding the specimen. They sustained the partial pressure of oxygen as far as \(2.5 \times 10^{-3}\) atm. On the other hand, Castle and Hunt (174) reported that high pressure could be maintained locally at the specimen surface through capillary pipes without disturbing the entire vacuum system. They obtained an oxygen gas pressure up to \(3.7 \times 10^{-4}\) atm. The second method was adopted in the present study to obtain a high local pressure (flux) of oxygen.

To calculate the effective gas pressure at the specimen surface, the Hertz-Langmuir equation given by Eq. (7) was used from the kinetic theory of gases.

\[
J_{\text{max}} = \frac{A P_i}{\sqrt{2\pi M_i RT}}
\]  

(7)

where \(J_{\text{max}}\) is the maximum molecular flow rate in moles/sec, \(P_i\) is the pressure in dynes/cm\(^2\), \(M_i\) the molecular weight of the gas (for \(O_2\), 32 gm/mole), \(R\) the gas constant (8.314 \(\times 10^7\) gm cm\(^2\)/sec\(^2\)mol °K), \(T\) the temperature in °K, \(A\) the exposed area of specimen. The flow rate \(J_{\text{max}}\) and exposed area \(A\) should be known to calculate the effective gas pressure \(P_i\) at the specimen surface using this equation.

The volume flow rate of the gas was obtained from a calibrated capillary flow-meter attached to a U-type manometer. The oxygen flow rate (cm\(^3\)/min), as a function of the displacement in a U-tube manometer, was obtained from the calibration curve shown in Fig. 13. The maximum flow rate possible without causing vacuum failure was 1.5 cm\(^3\)/min. This maximum flow rate can be converted to proper
Fig 13. Calibration curve for the oxygen flow rate with respect to height difference in a U-tube manometer.
units for equation (7), mole/sec, according to the following calculation

\[
1.5 \text{ (cm}^3/\text{min}) \times 10^{-3} \text{ (liter/cm}^3) \times 273^\circ\text{K} \\
60 \text{ (sec/min)} \times 22.4 \text{ (liter/mole)} \times 298^\circ\text{K}
\]

The exposed area of the specimen was obtained by measuring the reduced area of a NiO scale on a Ni specimen under a hydrogen gas beam. The distance between the tip of the platinum gas pipe and the specimen was kept constant at 1 mm and the exposed area of the specimen was measured to be 2.0 \( \times 10^{-2} \text{ cm}^2 \). With these two values, the effective gas pressure directly beneath the center of the pipe was calculated and to be 1.0 \( \times 10^{-4} \text{ atm} \).

C. Specimen Preparation

A 0.5 inch diameter rod of purity 99.993 at. pct iron was reduced to 0.25 inches by a cold swaging process. A disk 1.20 mm thick was cut from the rod using a diamond saw. The surface of the disk was mechanically polished up to 600 grit SiC paper followed by 3 um and 1 um diamond polish. Additional polishing using 0.05 um alumina powder suspended in distilled water was also done. After finishing the surface polishing, the specimen was cleaned ultrasonically in acetone and rinsed with methyl alcohol. A few specimens were made from the unswaged rod in order to study the effect of cold work on the morphological characteristics of wustite scale growth. Otherwise, all specimens were taken from the
cold swaged rod.

The specimen was placed at the top of the specimen holder and the distance of the gas pipe to the specimen was carefully adjusted. The three radiation shield caps and the large outer shield were put into position. The complete specimen stage was slid into the chamber, and the vacuum pump was actuated. After the chamber vacuum was far less than $10^{-4}$ Torr, hydrogen gas dried in a liquid nitrogen trap was admitted into the chamber just before heating up the stage. Once the desired temperature was reached, the hydrogen gas was replaced by oxygen gas and oxidation began. In some cases, heating under the condition of chamber vacuum ($2 \times 10^{-5}$ Torr) or with flowing oxygen was done to study differences in nucleation behavior.

D. Post-Oxidation Experiments

Several post-oxidation experiments were carried out to further clarify questions raised during in-situ observation. An X-ray diffractometer was used to identify the phases of oxide scale formed and also to established the preferred growth directions. Post-oxidation SEM observations were made for geometrically well defined morphologies at the gas/scale interface. The oxide was spalled from the underlying metal by quenching the oxidized specimen into liquid nitrogen and impacting the specimen. The metal side and scale side of the scale/metal interface were examined.
under the SEM for any significant morphological features leading to an understanding of the mechanism of scale growth.

Two-stage carbon replicas of the oxidized surfaces shadowed by gold were observed in a JEOL 200 CX STEM to reveal submicroscopic details on the scale/gas interface. The preparation technique for two-stage replicas has been well established (180,181) because of its extensive use in the study of surface features, which are not resolved in SEM. Hence, details of the preparation steps are not listed here.

The most difficult step during preparation was determining the optimum carbon film thickness. Because the morphology of interest in the present work consisted of microscopically deep sharp pits, replicas easily broke into tiny pieces during the dissolution of 5 mil thick plastic replicating tape in cool acetone. Kerrick et al (182) reported the interference colors of carbon films on polished brass substrates as shown in the Table 1. In their study, a polished brass substrate was located next to the replicating tape during vacuum evaporation of carbon to estimate the thickness of the carbon film. Various thicknesses of carbon film were tried to determine the optimum condition for obtaining the reasonable size of carbon replica. Interference colors of bluish green (300 Å to 350 Å film thickness) were found to give the best results. In some
cases, the two-stage replicas were heated at 150°C, 10^{-5} Torr to permit the migration of Au by surface diffusion to decorate the shadowed area of the replica. Enhanced contrast was observed by this additional treatment.

Table 1. Interference Colors of Carbon Films on a Polished Brass Surface (182)

<table>
<thead>
<tr>
<th>Approximate Thickness (in Å)</th>
<th>Colors</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>Orange</td>
</tr>
<tr>
<td>200</td>
<td>Indigo Red</td>
</tr>
<tr>
<td>250</td>
<td>Blue</td>
</tr>
<tr>
<td>300</td>
<td>Bluish Green</td>
</tr>
<tr>
<td>350</td>
<td>Greenish Blue</td>
</tr>
<tr>
<td>400</td>
<td>Pale Green</td>
</tr>
<tr>
<td>450</td>
<td>Silver Gold</td>
</tr>
</tbody>
</table>
IV. Results and Discussion

A. Initial Stages of Oxidation

As mentioned earlier, the initial stages of oxidation include several processes. Here, the initial stages of oxidation refer to the nucleation of 3D oxide nuclei on the surface of the metal and their subsequent growth until they impinge on each other. This stage of the oxidation of metals is very important because the initial reaction of the gas with the metal has a considerable influence on the subsequent morphology and growth rate of the oxide scale. To interpret properly the initial stages of the oxidation reaction, experiments were planned under several experimental conditions. Four different temperatures were chosen even though the major experiments for the study of oxide scale growth were done at 1050°C; two of these temperatures were in the alpha iron range (750°C and 850°C) while the other two were in the gamma iron range (950°C and 1050°C). At each temperature, different environmental conditions were applied ranging from the SEM vacuum atmosphere to the various levels of oxygen gas flux.

Experimentally, controlled amounts of oxidation at high temperature was followed by post-oxidation observation at room
Fig 14. Equilibrium oxygen partial pressures for different iron oxides at 1050°C. (calculated from Rapp and Shores (183))
temperature because of the very low contrast and extremely fast reaction during the early stages of oxidation in the HSESEM. The degree of dosage of oxygen flux was varied from exposure to the ambient SEM vacuum atmosphere to several seconds of controlled exposure, at which time the morphology becomes distinguishable during hot stage in-situ observation. The SEM vacuum atmosphere was obtained by pumping down the instrument overnight. In this case, the partial pressure of oxygen was estimated to be somewhat higher than $10^{-9}$ atm because a Penning gauge indicated a vacuum of about $10^{-6}$ mm Hg and perhaps 0.2 percent of that atmosphere is composed of oxygen. The estimated SEM vacuum atmosphere is indicated in Fig. 14, along with the equilibrium partial pressures of oxygen for the different iron oxides.

1. Experiments in the SEM Vacuum Condition

The main purpose of these experiments was to reveal the substrate grain boundaries by thermal etching and thus permit the measurement of the grain size of the substrate alpha or gamma iron. This information about the grain size at the temperature of oxidation provides basis for understanding mechanisms involved in nucleation and growth of the oxide nuclei and their subsequent growth to a large scale. For example, the grain size of the substrate iron may influence the grain growth characteristics of the oxide
grains if epitaxy of the oxide phase is important. In addition, nucleation in the SEM vacuum atmosphere can be studied since the partial pressure of oxygen in the SEM vacuum is several orders of magnitude larger than either the Fe$_3$O$_4$/FeO or FeO/Fe equilibrium partial pressures at the temperature of reaction as shown in Fig. 14. Thermodynamically, therefore, wustite or magnetite nuclei can be formed under these conditions.

During heating in the SEM vacuum atmosphere, grain boundaries suddenly appeared at a temperature around 700°C as a result of thermal grooving. This was rather surprising since the thermal grooving process requires time for atoms at the boundary to evaporate and/or migrate via surface diffusion. When the desired temperature was reached, the specimen was maintained 30 minutes and the grain boundary morphology was monitored in-situ. After the first few minutes at the reaction temperature, changes in grain boundary morphology did not occur.

Figure 15 shows some of the morphologies developed during heating in the SEM vacuum for the period of 30 minutes. Fig. 15A and 15B, for specimens heated to 750°C and 850°C, respectively, clearly show a uniform grain size of about 100 µm in alpha iron. However, Figs. 15C and 15D do not show the grain boundaries for gamma iron very well because of the complication caused by the $a/\gamma$ transformation during both heating and cooling. Both clear grain
Fig 15. Metal grain morphologies developed during heating in the SEM vacuum for the period of 30 min at
A: 750°C (200x),  B: 850°C (400x),
C: 950°C (400x),  D: 1050°C (200x).
Fig 16. Grain boundary morphologies developed in alpha iron in the SEM atmosphere for 30 min at A: 750°C (1kx), B: 850°C (1kx).
boundaries (indicated by "a") and traces of what are probably former austenite grain boundaries (indicated by "b") are shown in Figs. 15C and 15D. Clear grain boundaries are believed to be current grooved grain boundaries of alpha iron because the sudden appearance of surface relief took place during cooling at around 800°C. The grain size of the clear grain boundaries appears almost as same as that of alpha iron as seen in Fig. 15B. The trace of the austenite grain boundaries shows roughly same size around 100 μm. The austenite grain size was confirmed by another method, by measuring the grain size of the substrate at the area far away from the gas pipe which had been oxidized at the austenite temperature for 1 hr.

Other interesting grain boundary morphologies associated with recrystallization and grain growth of cold-worked specimens were observed, as seen for 750°C in Fig. 15A and Fig. 16A. However, the traces of grain boundaries formed by recrystallization and grain growth is not so evident at 850°C (Figs. 15B and 16B). This difference can be explained by the difference in the recrystallization kinetics at the two temperatures. The kinetics of recrystallization is sigmoidal in nature and the rate increases dramatically as the temperature increases as shown in Figs. 17A and 17B for the case of 60% cold worked 3.25 % Si-steel. Consistent with information given in Fig. 17 the surface seen at 750°C represents the morphology when
Fig 17. Kinetics of recrystallization of 60% cold worked 3.25% Si-steel from 550°C to 1000°C (184).
recrystallization is still incomplete during the period of the experiment. However, during the same period for the experiment at 850°C, recrystallization seems to have been completed. Even faster recrystallization kinetics occur at the temperature of 1050°C. This rapid recrystallization may explain why the morphology and mechanism of scale growth are not different for heavily cold worked specimens and fully annealed specimens at 1050°C.

At 850°C, morphological features typically reported in the study of Diffusion Induced Grain Boundary Migration (DIGM) were seen, as marked by the arrows in Fig. 16B. It is not clear whether this morphology is truly a consequence of DIGM caused by the interstitial solute oxygen in iron. In fact, DIGM in interstitial alloy systems is still in doubt, and has been reported only for the Ni-C (185), Ag-O (186), and Cu-O (186) systems. Further analysis, such as Auger electron spectroscopy measurements of the oxygen contents in the area swept by the grain boundaries and in the bulk, are required to verify the exact nature of this phenomenon.

After 30 minutes, no discrete oxide nuclei were observed for any of the four temperatures shown in Fig. 15 and Fig. 16. The surface of the specimens maintained their metallic luster even after the high temperature exposures to vacuum. This may indicate that either the oxide nuclei forms at a very slow rate for these conditions, or that the
oxide nuclei comprise a thin film which is not resolvable at normal SEM magnifications (up to 20,000x). On the other hand, the surface of iron may be covered with a chemisorbed oxygen layer. Also, there is a likelihood of oxygen dissolution into the iron substrate. The special feature of grain boundaries suspected to have undergone DIGM might be a strong indication of oxygen dissolution in the early stages of the experiments under these conditions. Actually, this is the stage that is least understood.

2. Nucleation and Growth of Oxide Nuclei

The experimental procedures adopted in this group of experiments were basically the same as those just described. The specimen was heated to the desired temperature and held there for 20 minutes in the SEM vacuum atmosphere. The intent of this first 20 minutes exposure was to stabilize a grain size and surface condition similar to those obtained in the experiments of the previous section. Then, controlled amounts of oxygen were leaked to the specimen surface for periods of 3 seconds and 1 minute. After 3 seconds, differing extents of oxidation were seen between the area directly beneath the gas pipe and areas far from the pipe. The experimental results for 1050°C is particularly chosen for discussion because the study of scale growth discussed in a later chapter was done mainly at 1050°C.
Figure 18 is a post-oxidation SEM micrograph at low magnification of a specimen heated to 1050°C showing a varying extent of nucleation on the surface of the iron. The area marked by "a" is the area which is hidden by the gas pipe during in-situ observation. Grain boundaries of the metal in the area "a" appear as a network of white lines. This morphology results from the less oxide nuclei density near the metal grain boundaries compared to the grain interior. The area "b", outside the periphery of area "a", is the area that is not hidden by the gas leak pipe and can therefore be studied during in-situ oxidation. Grain boundaries of the metallic phase appear as thermal grooves as in the case of the area "c", which is far away from the oxygen gas source. After a short exposure to oxygen, as for Fig. 18, the surface morphology in the area "c" is essentially identical to that for exposure in the SEM vacuum atmosphere. But when the oxidation time is long enough, nucleation of the oxide phase starts in the area "c".

More detailed morphologies in these three regions are shown at higher magnifications in Fig. 19 through Fig. 22. Figure 19 shows an evidence for a difference in the oxygen availability during 3 seconds of exposure in the transitional area between "b" and "c" of Fig. 18. From the area far away from the oxygen source to the area close to the oxygen source, different morphologies ranging from a smooth bare metal surface, to striations in the metal
Fig 18. A post-oxidation micrographs of a specimen heated to 1050°C for 20 min. (exposed to oxygen for 3 sec)
Fig 19. Post-oxidation micrographs showing morphological details at the transitional area between "b" and "c" of Fig. 18. (1kx)
grains, and to the "incipient" discrete oxide nuclei along the striations were observed. Finally, discrete oxide nuclei in the absence of striations were seen in the area closest to the oxygen source in all four cases. Although the striations were not seen in this area, it is interesting to note that these nuclei are aligned in the same manner as the "incipient" nuclei.

The density of oxide nuclei depended on both the oxygen availability and on the orientation of the iron grains. The dependence of the nuclei density on oxygen availability is understandable. But the reasons for the dependence of nuclei density on the orientation of the substrate metal grain are less obvious. If nucleation of the oxide takes place at imperfections in the surface of a metal grain, the nuclei density would depend on the surface structure of a given metal grain. The metal grains which have a larger number of imperfections such as dislocations, stacking faults, or ledges at the surface, could exhibit a higher density of oxide nuclei.

On the other hand, if oxide nucleation is not favored by such imperfections, those metal grains where the oxygen concentration near the surface reaches a critical value of supersaturation faster should form oxide nuclei faster. In this case, the rate of oxygen dissolution in different grains would become the controlling factor. Mitchell and Lawless (188), in their study of copper oxide nucleation,
explained the difference in the nuclei density on different grains in terms of a differing rate of oxygen dissolution depending on the orientation of metal grains. For a grain that has a high rate of oxygen dissolution, the time required for the oxygen concentration near the surface to reach a critical value at which oxide nuclei suddenly form by a precipitation process would be longer. This explanation seems more plausible for this experiment because the density of oxide nuclei near the metal grain boundaries, where the oxygen dissolution rate may be faster than at a grain interior, is much less than that in grain interior as shown in Figs. 18 and 19.

Generally, the oxide nuclei have the shape of polyhedra with little differences in different grains. These nuclei are seen to be aligned along certain directions, as is more clearly shown in Fig. 20. The occurrence of such polyhedral oxide nuclei are not unique to iron oxide and have also been reported in the low pressure oxidation and sulfidation studies of copper (189,190) and in the oxidation of nickel (13,14). A highly aligned arrangement of oxide nuclei for iron oxidation was also shown elsewhere (92). These two features, polyhedral shape of the oxide nuclei and their aligned arrangement, probably result from the epitaxial relationships between the oxide and the metal. These well oriented oxide nuclei are comprised definite crystal habit planes for the oxide nuclei. However, the epitaxial
Fig 20. Post-oxidation SEM micrographs showing oxide nuclei aligned of different metal grains. Specimen was heated to 1050°C for 20 min followed by exposure to O₂ for 3 secs. (1kx)
relationships between the oxide and the metal in iron oxidation under the same experimental conditions (gamma iron and wustite) have not been studied previously. The epitaxial relationships between alpha iron and the wustite phase are well known (92,191,192). For 1050°C, the oxide phase is believed to be wustite because experiments done by Gulbransen et al (93,94) under similar experimental conditions showed that the oxide nuclei were indeed the wustite phase. Nucleation of the magnetite phase takes place on top of the wustite scale at a later stage of oxidation, and will be described later.

An important problem in the study of oxide nucleation has been the nature of nucleation sites. As described previously, it has been suggested that the oxide nuclei would most likely nucleate at areas where imperfections on the surface of metal already existed. Explicitly, the role of dislocations in the metallic phase as nucleation sites has been the focus of discussion. From the information presented so far, it is questionable whether dislocations in the metal substrate act as nucleation sites. First of all, dislocations may act as a short-circuit path for oxygen dissolution at the initial stages of oxidation, as shown by the absence of oxide nuclei in the area near metal grain boundaries. In that case, they would not serve as a center of locally high supersaturation in oxygen concentration for nuclei formation. The strong epitaxial relationship between
the oxide nuclei and the metallic phase, illustrated by the same nucleus shape and their highly aligned arrangement in a given grain, also indicates that an area locally disturbed by the emergence of dislocations might represent an unfavorable site for nucleation. A number of discussions which favor dislocations as nucleation sites base their arguments on the fact that the density of nuclei is about the same order of magnitude as that for dislocation intersections at the surface (47). The average density of oxide nuclei in this experiment was about $10^7-10^8$ per cm$^2$, which is about the same order of magnitude as the density of dislocations in a well annealed metal. However, surface imperfections due to dislocations do not seem to have an influence on the nucleation sites at high temperatures. In this temperature range, the reactivity is so strong that nucleation seems to be unassisted by surface defects and thus epitaxy becomes the more important factor to be considered. Surface imperfections could have a role as nucleation sites at rather low supersaturations. In that case, the epitaxial relationship between oxide nuclei and metal becomes less important.

3. Grain Growth Characteristics of Wustite Scale

Once discrete 3-D oxide nuclei were formed, they grew laterally until they touched each other. During this process, no substantial further nucleation seemed to occur.
This kind of behavior, characterized by a sudden nucleation burst and lateral growth of the nuclei without further nucleation, has been reported in many oxide nucleation studies (3). Some of the analysis characterizing this stage were described in the previous chapter. In this section, features observed during the lateral growth of the nuclei will be discussed, with an emphasis on the phenomena occurring at the stages immediately following the impingement of oxide nuclei.

The four SEM micrographs of Fig. 21 were taken at the transitional area between "a" and "b" of Fig. 18, showing morphologies of the oxide nuclei at different stages during their growth. As shown in Figs. 21A and 21B, the oxide nuclei grew laterally and well-defined crystallographic shapes became rounded during this event. In particular, Fig. 21B shows three different nuclei morphologies at the critical moment when two approaching oxide nuclei contact each other. Some of oxide nuclei appear to be sintered together, while others are just in contact with each other, and some are still physically separated. Figs. 21C and 21D show morphologies believed to be the next stages of Fig. 21B. In these figures, all the oxide grains on a given metal grain substrate appear to be sintered.

When two oxide nuclei are sintered together, an oxide grain boundary is formed between them. Grain boundaries thus formed change their shape from elongated to pyramidal
Fig 21. Post-oxidation micrographs showing morphological details at the transitional area between "a" and "b" of Fig. 18. Pictures of A and B were taken from different metal grains. (all 1kx)
Fig 21. (continued) Pictures of C and D were taken from different metal grains. (all 1kx)
equiaxed as shown in Fig. 22, which was taken after an exposure of 1 minute at the reaction temperature. The size of these equiaxed grains are about twice that of the oxide nuclei shown in Fig. 19. Even though all these micrographs in Fig. 18 through Fig. 22 were not taken sequentially in-situ, they still demonstrate that the growth kinetics differ for different orientations of the metal substrate. This enables one to deduce a sequence of growth steps for the oxide nuclei. In fact, all the characteristics in different stages of nuclei growth observed in these pictures were later confirmed in in-situ experiments. From the moment equiaxed oxide grains covered the whole metal surface, the rate of morphological changes slowed down considerably and the contrast of the SEM image was so much improved that in-situ observation under HSESEM became more meaningful.

As stated previously, the rate of the morphological changes during wustite scale growth was so rapid that a videotape recorder was used to resolve them, and photographs were taken from the TV screen later. Even though one can videotape the entire sequence of processes occurring during oxidation, the quality of the images are not as good as the ones taken from the SEM monitor with a slow scan. The sequence of micrographs taken from the TV screen in Fig. 23 show the morphological features developed during the initial period of oxidation in a HSESEM. The quality of the image in these in-situ SEM micrographs is not good enough to
Fig 22. Post-oxidation SEM micrographs of the specimen heated to 1050°C for 20 min followed by 1 min exposure to oxygen. A: 400x, B: 800x.
distinguish individual nuclei. However, all the morphological features described by the post-oxidation experiments (of Figs. 19 through 22) can also be seen in these micrographs. The development of morphology from discrete elongated nuclei on the metal substrate to equiaxed oxide grains are illustrated by this sequence. Figure 23D is the stage when equiaxed oxide grains were first apparent. These oxide grains of 10 to 20 μm diameter grew to about 100 μm diameter in the next 20 minutes of oxidation. After this period, the grain growth kinetics became very sluggish.

During the first 20 minutes of oxidation, a very interesting mode of oxide grain growth was observed and this is illustrated in Fig. 24. The area indicated by an arrow in this sequence of micrographs shows a typical example of this interesting behavior. The oxide grain boundary revealed by the groove between grains "a" and "b", converted into an array of dislocations as shown in Fig. 24B. (In fact, evidence for the existence of dislocations is provided by the formation of dislocation pits. This was observed and explained by Jungling and Rapp (134), and will be discussed in detail in the next chapter.) This array of dislocations then dissociates into two groups of dislocations. One group of dislocations migrated into the interior of grain "a" while the other group migrated into the interior of grain "b" by glide, as shown in Figs. 24C and 24D. Subsequently, the original grains "a" and "b" constituted only one grain.
Fig 23. In-situ HSESEM micrographs taken at the initial stages of oxidation at 1050°C. (all 1kx)
A: during heating in H₂  B: 3 min before oxidation
C: 1 min of oxidation  D: 5 min of oxidation
Fig 24. Sequence of micrographs showing oxide grain coalescence (continuation of Fig. 23)
A: 7 min of oxidation  B: 8 min and 20 sec
C: 9 min and 5 sec    D: 9 min and 20 sec
By this process, the three-fold grain boundary junctions of equilibrium shape (120° degree three-fold nodes) at both ends of the original oxide grain boundary were released and changed their shape into two straight lines. Also, the orientation of the dislocation pits, which were originally different because they were located in two different grains, then became identical. This mode of grain growth is also seen in the middle right of the pictures in this sequence.

The area originally composed of grain boundaries (Figs. 24A and 24B) becomes covered with a high density of dislocation pits localized near the original grain boundaries (Figs. 24C and 24D). Later, this entire area became one large grain.

In some occasions, the array of dislocations formed at a grain boundary seemed to migrate by climb as shown in left center of Fig. 25. In this case, chevron marks first appeared at the grain boundary and later developed to individual dislocation pits. Climb of individual dislocations continued until the density of dislocations at the original boundary decreased substantially. The climb motion of dislocations is believed to be activated by the stresses generated by a moving grain boundary "m", which is situated at the bottom of the pictures in Fig. 25.

These two different types of motion of grain boundary dislocations essentially result in grain coalescence or growth. However, these may be two extreme cases. Depending on the nature of grain boundaries (e.g., symmetrical/
Fig 25. Sequence of micrographs showing climb motion of dislocation pits at the grain boundary after
A: 8 min of oxidation  B: 9 min
C: 10 min  D: 10 min and 30 sec
asymmetrical, tilt/twist, or mixed grain boundary) various combinations of these two kinds of motion are possible. Unfortunately, it is very difficult to follow exactly the movement of individual dislocation pits because many dislocation pits frequently repeat the cycle of the active/inactive transition, and some new pits are generated in the matrix of the oxide grains.

Dissociation of a grain boundary into grain boundary dislocations was also observed in the later stages of scale growth as shown in Fig. 26 (see also Fig. 28D). Because of the extremely low mobility of dislocations in thick oxide scales, annihilation of those grain boundary dislocations could not be observed. The grain coalescence is believed to be more critical during the early stages of oxide grain growth, i.e., from the moment when the elongated oxide grains are sintered together to the moment when they convert into equiaxed grains of size up to about 20 μm. Because of the large grain boundary area, at these early stages of oxidation, the driving force for grain growth is the greatest. At this stage, however, dislocation pits are hard to be resolved (or may not be developed) and hence the presence of this kind of grain growth could not be observed.

The characteristics of grain growth described so far are very similar to that of the subgrain coalescence during the process of recrystallization of cold-worked metals, which was reported by Hu (149,193,194) and modeled by Li
Fig 26. Sequence of micrographs showing sudden appearance of dislocation pits at the grain boundary after A: 22 min of oxidation B: 22 min and 30 sec
In Hu's extensive study of recrystallization of 3%-silicon-iron single crystals in a hot stage TEM, he observed gradual disappearance of the boundaries between neighboring subgrains. During this sequence the relevant regions showed decreasing contrast, indicating that they were merging into a common orientation. He also found that the orientation of the "coalesed group" differed in general from that of the original subgrains from which it was formed. This process was explained as a gradual migration of dislocations from the disappearing subgrain boundary into other boundaries neighboring the subgrains.

The rotation of the subgrains involved in the coalescence during the recrystallization process was further studied by Li (150). Figure 27 shows a schematic description of Li's model for the process. The two slightly misoriented grains are marked by cross lines in Fig. 28A. In order to eliminate the common boundary, CH, one grain (the right-hand grain in this example) has to rotate as shown in Fig. 27B. According to Li, this process is achieved by the diffusion of atoms, along the boundaries, from the shaded area to the unshaded area, i.e., climb of grain boundary dislocations. Figures 27C and 27D show the final stage of the process after the rearrangement of the affected boundaries (BC, CD, IH and HG) in order to remove the unstable re-entrant angles (at C and H). Thus a limited amount of subgrain boundary migration occurs as an integral
Fig 27. Schematic representation of subgrain coalescence by subgrain rotation (150).
part of the coalescence process. However, mere diffusion of materials from one region to other region does not explain the necessary grain rotations involved in the process. While it can explain the shape change of the subgrain, rotation of subgrains can only happen when dislocation density at the boundary (CH) also changes. Hence the decrease of dislocation density, by glide and climb, at the boundary (CH) results in the grain rotation necessary for the disappearance of a subboundary and the associated grain coalescence.

The thermodynamic implications of the subgrain agglomeration process were explained in terms of the misorientation angles and energies of the subgrain boundaries as given by Read and Schockley (141) (see Fig. 4B). The plot of the energy of a grain boundary versus its misorientation indicates that there is very drastic energy change in the range of low misorientation angles. One of the most important conclusions from Li's analysis is that a subgrain can rotate naturally in directions for which low angle boundaries decrease in angle while high angle boundaries increase their angle. Experiments done to test Shewmons suggestion (137) by Gleiter et al (194,195), showed clearly the physical significance of this decrease in energy of a boundary as the driving force used to eliminate it. In their sintering experiment of small single crystal spheres on a single crystal plate, they observed that the spheres
rotated to the same orientation as the plate and thereby eliminated the grain boundary. However, there are opposing opinions about the possibility of subgrain coalescence, on a basis that the coalescence process is possible only in 2-D case such as in thin film TEM specimens (196,197). The extensive experimental results both favoring and opposing the existence of boundary coalescence were critically reviewed recently by Jones (198).

The oxide grain boundaries in the initial stages, which showed behavior similar to those exhibiting subgrain coalescence in these experiments, are also believed to be low angle boundaries. As shown in the nucleation studies, nominally parallel elongated oxide grains were developed from the growth of epitaxially nucleated crystallites whose orientations were approximately the same if they were grown in the same grain of the metal substrate. Therefore, all the oxide nuclei on a metal grain have almost the same orientation and a small misorientation could exist as the grains impinge. Another crucial contributing factor for rotation of grains involved in the process of coalescence in these experiments compared to subgrain coalescence proposed by Li (150) might be the epitaxial stress acting on the oxide grains at the interface with the metal substrate. For the oxide grains on the same substrate iron grain, the epitaxial stress would be applied continuously during high temperature reaction in a way to promote grain coalescence.
This epitaxial stress may make the thermodynamically possible process of coalescence kinetically even more feasible.

Evidence for grain coalescence presumably facilitated by an epitaxial stress, can be found elsewhere. The agglomeration of gold deposits formed by evaporation inside a TEM on top of a molybdenum disulphide substrate showed similar re-orientation and recrystallization of the crystallites (199). When two discrete adjacent nuclei contacted each other, rapid coalescence of nuclei was observed. This particular behavior was termed as the "liquid-like coalescence" by Pashley (199) even though the nuclei were crystalline. During the process, rotation of the nuclei or islands about the surface normal was detected by the change of Moire fringe patterns.

In summary of the current studies, various processes were observed during the initial stages of oxidation of iron at 1050°C in a HSESEM. Discrete wustite nuclei developed which were epitaxially related to the substrate austenite iron grains. These nuclei did not form at the area close to the grain boundaries of the iron substrate until the last stage of nucleation, perhaps because of the more rapid dissolution of oxygen at the boundaries. In the same sense, dislocations in the metallic substrate are not believed to act as a favorable nucleation sites under these experimental conditions.
Oxide nuclei were seen to grow laterally in contact with the adjacent nuclei. Elongated oxide grains formed in this manner were then transformed into equiaxed grains of about same size. These oxide grains on the same metal substrate grain were separated by low angle grain boundaries. At this stage, very rapid oxide grain growth occurred. Grain coalescence by annihilation of grain boundary dislocations is believed to be the major mode of grain growth. The influence of this type of grain growth on the development of scale structure and on the reaction kinetics will be discussed in the following chapters.
B. Morphological Development of Wustite Scale during the Steady-State Oxidation

As shown in the previous chapter, interesting morphological features of the wustite scale became discernable in in-situ observation once wustite nuclei have covered the entire iron substrate. These morphological features are associated with various microstructural defects of the growing oxide scale such as grain boundaries, dislocations, and phase boundaries (e.g., boundaries between magnetite and wustite). In particular, dislocations in the wustite phase provided valuable morphological features for understanding the growth steps of the wustite scale. This chapter describes the formation of different types of morphological features during steady-state oxidation, namely dislocation growth-pits and microledges, and their contributions to scale growth. In addition, the correlation between these two distinctive morphological features is discussed.

A. Scale Growth by Dislocation Growth-Pits

The morphologies shown in Figs. 23 and 24 represent the initial stages of wustite scale growth, which later lead to development of dislocation growth-pits. During the period of lateral growth of discrete wustite nuclei shown in Fig. 23, it was difficult to observe any indication of
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morphological features caused by the presence of dislocations in the oxide phase. However, as soon as the oxide nuclei formed equiaxed oxide grains, some geometrical irregularities believed to be caused by dislocations in the oxide phase were observed as shown in the lower right corner of Figs. 23D and 24A. These features transformed their shape to pits with four-fold symmetry. Some, but not all of the pits shown in the sequence of pictures were related to the transitory geometrical irregularities.

As shown in Fig. 24, the sources of dislocation pits were either low angle grain boundaries of the oxide scale or interior of the oxide grain. In the early stage of the scale growth, dislocation growth-pits migrated actively by processes of glide or climb as discussed in the previous chapter. The mobility of these dislocation pits decreased substantially as the thickness of the scale increased. The movement of dislocation pits by glide ceased at the later stages, and only limited movement probably associated with dislocation jog segments was observed. The dislocation growth-pits were seen to interact actively in the early stages with other pits and oxide grain boundaries. As a result, only one orientation of growth-pits could be formed in a given oxide grain as will be shown in the next series of figures.

A sequence of micrographs, from the moment a high density of growth-pits first appeared at the gas/scale
interface to the moment they started to disappear, is shown in Fig. 28. This sequence of micrographs was taken over a period of about 30 minutes, from 10 minutes and 5 sec of oxidation in Fig. 28A to 38 minutes and 40 sec in Fig. 28H. The reference point in the figures is indicated by an arrow at the junction of three grain boundaries in the first four pictures (Figs. 28A, 28B, 28C, and 28D). The exact location of the reference point in the next four pictures was very difficult to pinpoint because the junction disappeared upon its coverage by a high density of growth-pits. Figures 28D through 28F show such a transition of grain boundary area to dislocation pits.

Detailed information about the physical processes associated with this continuously changing morphology is difficult to infer from this sequence of pictures because they were taken at a low magnification. However, one can observe the general trend indicating that the area covered by dislocation growth-pits increased continuously up to a certain stage (e.g., Fig. 28E) and then started to decrease. Formation of differently oriented dislocation pits on different oxide grains is also clearly visible. It is interesting to note that dislocation growth-pits disappear in two different regions, in the area immediately underneath the gas pipe and in the area far away from the gas source. The growth-pit population in the area between these two extremes is maintained until the last minutes of the
Fig 28. Sequence of micrographs showing developments of growth-pits during wustite scale growth at 1050°C
A: after 10 min and 5 sec of oxidation,
B: 13 min and 30 sec,
Fig 28. (cont'd) after C: 16 min and 30 sec, D: 18 min and 30 sec, E: 21 min and 5 sec, F: 23 min and 15 sec,
Fig 28. (cont'd) G: 29 min and 20 sec, H: 38 min and 40 sec.
experiment. The overgrowth of the magnetite scale, which initiated directly beneath the leak pipe, is responsible for the disappearance of growth-pits in that area. The reason for the transition from growth-pits to planar scale in the area far away from the gas source, as shown in Fig. 28G and 28H, will be discussed later.

The most important effect associated with dislocation pits is their role in providing growth steps (or micro-ledges) at the gas/wustite interface, as previously reported by Jungling and Rapp (134). They showed that macroscopic growth ledges originated at the pit nadir and that those ledges traversed outward along the pit walls in their in-situ observations. As a consequence, a macroscopic layer of new oxide was formed. A sequence of micrographs revealing such growth steps is shown in Fig. 29. Two pits, marked by "a" and "b" in Fig. 29A, flattened out from their pit nadirs. During the process, the pit "a" disappeared, but three new pits nucleated in the pit "b". This process of flattening out and nucleation of new pits took place continuously throughout the period of the experiments, and ultimately the number of pits decreased and their orientation changed. The macroledges traversing the pit wall are indicated by an arrow in Fig. 29D.

According to the classification made by Jungling and Rapp (134), active growth-pits refer to dislocation pits which provide growth steps continuously at the pit nadir.
Fig 29. Sequence of activity/inactivity of growth-pits during wustite scale growth at 1050°C after:
A: 27 min and 35 sec,
B: 10 sec later,
C: 20 sec later,
D: 30 sec later.
Morphologically, active pits in a \{100\} surface have fourfold symmetry with an acute pit nadir, as shown by most of the growth-pits in Fig. 29. Inactive (or terminated) dislocation pits no longer provide such growth steps. These are characterized by the flattening of the pit beginning from the pit nadir; eventually, the pit is eliminated by this process. Flattening of the pit nadir was inferred to be caused by the displacement of the dislocation intersection at the gas/scale interface. Movement of this point of dislocation emergence by climb of a jog segment in the screw dislocation, suggested by Jungling and Rapp (134), can provide such a displacement. The same kind of repeated cycle of activity/inactivity/reactivity of a pit is also seen in the sequence of micrographs in Fig. 29.

The movement of macroscopic ledges along the surface of pit walls is associated with the cycle of activity/inactivity of the growth pits. Here, the word "macroscopic" is used to describe details which can be resolved at normal SEM magnifications during in-situ experiments at high temperatures. On the other hand, the word "microscopic" refers to the details which are not resolvable in the HSESEM because of their small size. Microscopic ledges are associated with active pits. Even though the migration of microscopic ledges is not resolved, their contribution to the overall growth of the new oxide should not be underestimated. The distinction between microscopic and
macroscopic ledges becomes clear from their observation by a two-stage TEM replication technique.

The crystallography of the growth-pits was studied by Matson et al (200). From a simple post-oxidation tilt experiment in the SEM, they showed that the pit walls were nominally \{110\} planes. But the planes of the pit walls are dissociated into microledges of \{100\} type planes as shown in a TEM replica of a pit in Fig. 30. The height of a microledge is approximately 100 nm and that of a macroledge shown in the Fig. 30A is about 1 um. Dissociation of a \{110\} plane into a set of \{100\} planes may result from the difference in surface energy between these two orientations. The \{100\} planes may be stable because the degree of anisotropy in surface energy between a \{100\} plane and any other crystallographic plane of wustite is so large the Gibbs–Wulff shape of the equilibrium crystal is composed of only \{100\} planes. There are no specific data available for the orientation-dependent surface energy of wustite to check this postulate. Similar results showing dissociation of a crystallographic plane into a combination of planes of low energy, because of high surface energy anisotropy, has been reported for evaporated surfaces of \{110\} NaCl (201), and \{111\} NaCl (202). For NaCl, both planes are bounded by a combination of \{100\} planes. Surface energy anisotropy in an NaCl crystal was discussed earlier, and illustrated in Fig. 7B.
Fig 30. TEM replica of a pit showing macro- and microledges (200).
2. Scale Growth by Microscopic Surface Ledges

Occasionally, instead of pits, rather highly faceted surface morphologies develop under nominally identical experimental conditions. As shown in Fig. 31, the initial stages of oxidation are almost identical to the previous case shown in Fig. 23 where dislocation growth-pits developed later. However, soon after equiaxed wustite grains were formed, massive movement of surface ledges took place as shown in Fig. 31D through 31H. During a period of 15 seconds, between the times represented in Fig. 31G and Fig. 31H, the macroscopic surface ledges migrated an appreciable distance. Because of such massive surface ledge migration, morphologies at the gas/scale interface changed rapidly. Figure 32A shows changes in oxide grain morphologies at a low magnification. In comparing Figs. 31A through 31D, there is a big change in oxide grain size. Several equiaxed wustite grains of size 10 to 20 μm in Fig. 31A grew into one big flat grain of a size well over 100 μm in a period of less than 10 minutes. It is very difficult to observe whether grain coalescence also takes place in this case because dislocation growth-pits do not appear at the gas/scale interface. Because the normal mode of interface-energy-driven grain growth, characterized by migration of boundaries of a larger grain toward a smaller grains, does not always occur, there is again the possibility that grain coalescence takes place.
Fig 31. Sequence of micrographs showing development of surface ledges during wustite scale growth at 1050°C after A: 4 min, B: 8 min, C: 10 min, D: 12 min.
Fig 31. (continued) E: 14 min,  
F: 30 sec later,  
G: 1 min, 30 sec later,  
H: 1 min, 45 sec later.
Fig 32. Sequence showing massive movement of surface ledges during wustite scale growth at 1050°C after 
A: 20 min and 10 sec,  B: 5 sec later, 
C: 30 sec later,  D: 35 sec later.
The crystallography of the surface ledges is not clear until the ledges grow to an appreciable size, as in the later stages of oxidation shown in Figs. 33 and 34. The area, which was a flat scale with few initial small surface ledges in Fig. 32A, is covered by a high density of the large macroledges in Fig. 33A. The surfaces of those macroledges are composed of crystallographically well defined planes of low energy. From the results of the previous section, the surface orientation of the ledges is believed to be \{100\}. The nominal surface orientation of the oxide scale is expected to depend on the relative heights and spacings of the different \{100\} ledges. For example, the nominal surface orientation will be \{110\} if the surface is composed of an equal number of (100) and (010) planes of constant height, as shown previously for the surface orientation of a pit wall. In this context, a more general, irrational type of nominal surface orientation is also possible, such as \{hk1\} or \{hk0\}; this is believed to be the case for the surfaces shown in Fig. 33 and Fig. 34, respectively. When discrete smaller surface ledges are formed rather than massive surface ledges as shown in Figs. 33 and 34, it is easier to estimate the surface orientation. Figure 35 shows a typical example of such discrete surface ledges on nominal \{111\} planes. This morphology was observed very rarely. The geometry of this particular morphology was confirmed using SEM tilt experiment.
Fig 33. Movement of macroledges during wustite scale growth at 1050°C after, A: 33 min and 40 sec, B: 30 sec later, C: 1 min and 5 sec later, D: 1 min and 40 sec later.
Fig 34. Movement of macroledges during wustite scale growth at 1050°C after A: 41 min and 15 sec, B: 43 min, C: 43 min and 30 sec, D: 43 min and 45 sec.
There are various sources of surface ledges in the pit-free grains. However, it seems reasonable that grain boundaries and dislocations in the oxide phase are two major sources. In practice, it is difficult to pinpoint the origin of the continuously supplied surface ledges merely from the study of surface morphologies of the scale. In the initial stages of oxidation, oxide grain boundaries are believed to be the major source because the length of the surface ledges are the same as the width of the oxide grains. Any microstructural defect, most notably dislocations, in the oxide grain interior will disturb the continuity of these surface ledges. With further oxidation, the oxide grain boundary area decreases because of grain growth and hence the importance of grain boundaries in initiating surface steps also decreases. Then, the role of dislocations in providing a continuing supply of surface ledges should become important, as will be shown in the next section.

In the later stages of oxidation, the mobility of macroscopic surface ledges decreased drastically. The arrival of cations by diffusion through the oxide layer on the surface to the microledges at the gas/scale interfaces contributed to the rate control for further scale growth. At about the same time, the transformation of the wustite scale to magnetite started in the area directly beneath the gas pipe. The magnetite then grew laterally. The dark area
Fig 35. Migration of surface ledges during wustite scale growth at 1050°C after
A: 35 min,  B: 10 sec later
at the top left part of the Figs. 33D and 33D is the area where magnetite scale has formed. The height of the steps on wustite at this stage appears to be very uniform and is about a few micrometers.

3. Transition of Morphologies from Growth-Pits to Surface Ledges

Since Jungling and Rapp (134) first reported two apparently different morphologies of a wustite scale under the almost identical experimental conditions, namely growth-pits and microledges, an effort has been made to distinguish these two features. It was thought that the mechanism of the wustite scale growth by dislocation growth-pits and by surface ledges is basically the same because lattice extension of the oxide phase takes place at the surface steps provided by those two different morphological features. The study of these two features is possible because of the common in-situ observation of the transition from growth-pits to growth ledges in a HSESEM. From this study, other important physical constants, such as the ratio of surface energy to shear modulus, could be estimated.

Crystallographically, two types of transitions from growth-pits to microledges were observed as shown in Figs. 36, 37 and 38. Figure 36 shows the transition of pits along a pit edge, which is {111} zone axis. Growth-pits shown in Fig. 36A rotate their axes of growth toward the gas pipe and
thereby generate the same morphologies shown previously in Fig. 33, viz. a high density of macroledges on the surface of the scale. The sequence of micrographs in Figs. 36B and 36C shows migration of the surface ledges. The second type of transition of pits takes place along \{110\} pit walls, as shown in Figs. 37 and 38. A sequence of micrographs in Fig. 37 shows such a transition. Two growth-pits at the bottom of the picture of Figs. 37A and 37B disappeared, one after the other, in Figs. 37C and 37D, respectively. Macroledges on the \{110\} pit wall are not revealed in this sequence of micrographs, but are clearly shown in the sequence of pictures in Fig. 38.

These two special cases, where growth-pits changed their orientation along simple crystallographic orientations, do not seem to represent any preference in the direction of rotation. It is rather believed that growth-pits of any orientation will turn toward the direction where oxygen is being supplied. In other words, the main reason for the transition in the morphological features is believed to be caused by the geometrical arrangement imposed by the HSESEM. As shown in a schematic diagram in Fig. 39, growth of the new oxide is influenced increasingly by the directionality of the incoming oxygen as the oxide scale thickens. As shown in the first figure, the distance from the gas pipe to the surface of the specimen is fixed. Therefore the spacing between the gas/scale interface and
Fig 36. Sequence of micrographs showing transition of growth pits to facetted macroledges along pit edges. A: 32 min, B: 10 sec later, C: 30 sec later.
Fig 37. Sequence of micrographs showing transition of growth pits to microledges along {110} pit wall. A: 20 min, B: 10 sec later, C: 25 sec later, D: 1 min later.
Fig 38. Transition of growth-pits to macroledges along \{110\} pit wall A: 22 min and 55 sec, B: 20 sec later, C: 30 sec later.
the tip of the gas pipe decreases as the thickness of the oxide scale increases. As the distance decreases, the angle \( \theta \) shown in Fig. 39 also decreases and hence the area where the oxygen gas arrives relatively uniformly also decreases. The area far from the gas pipe, where changes in morphology are generally monitored, is then exposed to the highly directional oxygen supply. For thick oxide scales, this geometry-dependent oxygen availability is an important factor for the experimental arrangement of this current HSESEM. Because the geometric factor itself is not believed to be a sufficient condition for the transition in morphology, the kinetic factor should be considered. For example, the conditions for morphological transition is more critical when cations are readily available at the gas/scale interface. In this case, the directional availability of oxygen gas becomes very important. Wustite growth is known to satisfy both these conditions because of the rapid diffusion of cations in wustite.

Once the wustite scale grows to a certain thickness by the migration of microledges along the faces of dislocation growth-pits, a small difference in oxygen availability in the two opposite pit walls is generated. The pit wall facing the gas pipe grows faster than the pit wall shadowed on the opposite side. Later, the difference in oxygen availability between the two opposite pit walls becomes larger because one side has grown preferentially. This
Fig 39. Schematic diagram showing geometric constraints in oxygen availability during wustite scale growth.
situation continues until the pit morphologies change as previously shown. This explanation, based on the geometric and kinetic factors, is consistent with the following experimental observations: 1) The transition from growth-pits to microledges occurs at a late stage of oxidation and not in the initial stages, 2) The transition from microledges to growth-pits has not been observed at a late stage of oxidation, 3) As shown previously, dislocation growth-pits of an oxide grain far from the gas pipe disappeared preferentially compared to those on an oxide grain closer to the gas pipe. It would be interesting to demonstrate that one could transform the microledges, at a later stage, to growth-pits by merely changing the position of the gas pipe, but this would require a difficult revision of the experimental arrangement.

As the change in growth direction continues, the angle between the nominal orientation of the free surface and dislocation line decreases as shown in Fig. 40. Figure 40 depicts a configuration of a growth-pit and a dislocation in the oxide scale, where the dislocation line vector makes an angle $\theta$ with the free surface of the oxide scale. When the intersection angle $\theta$ in Fig. 40 between the dislocation line vector and the free surface exceeds a critical value, the dislocation does not exert enough line tension to stabilize the pit. The dislocation growth-pits are then no longer stable thermodynamically and the dislocation will merely
provide surface steps for further lattice growth. This angle could not be determined experimentally. However, from the geometrical relationships in the NaCl structure, the pit morphology becomes stable when the angle $\phi$ reaches 45 degrees. Figure 29A shows the pit morphology (marked by an arrow) when the intersection angle of the dislocation to the free surface is 45 degrees.

The thermodynamic criterion discussed thus far is important as long as a steady-state condition is maintained in the growing oxide scale. In this case, the steady-state condition refers specifically to the situation where cations are readily available at the reaction front at near the local equilibrium concentration at the scale/metal interface. As the oxide scale thickness increases, this steady-state condition may no longer be satisfied because of the reduced cation flux. For a constant oxygen supply, the reduced cation flux leads to changes in the degree of supersaturation. There is a possibility then that some kinetic factors, controlled by the degree of supersaturation, may contribute to the transition of morphology from growth-pits to microledges. According to Cabrera and Levine (206), the average spacing of ledges, $\lambda$, shown in Fig. 41, increases as the degree of supersaturation is decreased. Qualitatively, the distance between ledges will keep increasing since the degree of supersaturation is expected to decrease drastically once the steady-state
Fig 40. Schematic diagram of the force balance between the surface energy and line tension of a dislocation.

$L = 2\pi b \gamma \cos \theta$ (After McLean & Hirth)
condition is not met. Morphologically, it might be very difficult to distinguish between growth-pits and microledges when the distance, $\lambda$, becomes extremely large. This could lead to the development of a planar wustite scale. However, this process has not been experimentally confirmed in the work presented here, because such a long-term experiment required to study this phenomenon would always lead to the development of magnetite.

Figure 40 provides a way to estimate the surface energy for wustite (110) planes. The equation was derived originally by McLean and Hirth (203) for the evaluation of the equilibrium shape of a dislocation etch-pit. A mathematical derivation was attempted based on the etch-pit shape being that of a catenoid and not of square symmetry. However, the final formula, given in Fig. 40, does not have any significance on the shape of the pit. The formula states that some characteristic length, $2\pi b$, times the surface energy balances the force exerted by the line tension of a dislocation. From the equation, the estimation of surface energy is possible if the line tension of a dislocation (or shear modulus) in the wustite phase were known. Otherwise, from information about the surface energy and shear modulus of wustite, the critical angle above which the pit morphology is no longer stable can be calculated. Unfortunately, there are no data available to confirm these points. From the equation, however, the ratio of surface
Fig 41. Schematic diagram showing growth ledges of the spacing, $\lambda$, and a dislocation associated with it.
energy to shear modulus was calculated. According to Frank (204), shear moduli and surface energies of materials tend to vary empirically in a parallel manner so that the ratio \( \gamma/\mu \) is roughly a constant value, a typical value being about 2.5 nm. The calculated value for wustite is compared with other materials in Table 2, which includes a metal, ionic crystal, and two oxides. Values for other materials are also reported by Frank (204). The calculated value of 3.4 nm for wustite is quite reasonable. The estimated value for the surface energy of \{110\} wustite was not reasonable because of the extremely low value of the reported shear modulus (205).

Table 2. Shear Moduli and Surface Energy of Solids

<table>
<thead>
<tr>
<th>Substance</th>
<th>Shear Modulus ( \mu ) (10(^{11}) erg cm(^{-3}))</th>
<th>Surface Energy ( \gamma ) (erg cm(^{-2}))</th>
<th>Ratio* ( \gamma/\mu ) (10(^{-8}) cm)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>4.4</td>
<td>1400</td>
<td>0.32</td>
<td>(204)</td>
</tr>
<tr>
<td>NaCl</td>
<td>1.5</td>
<td>155</td>
<td>0.10</td>
<td>(204)</td>
</tr>
<tr>
<td>MgO</td>
<td>9.3</td>
<td>1150</td>
<td>0.12</td>
<td>(205)</td>
</tr>
<tr>
<td>FeO</td>
<td>0.04</td>
<td>(?)</td>
<td>0.34</td>
<td>(205)</td>
</tr>
</tbody>
</table>

* \( \mu b^2/2 = 2 \pi b \cos \theta \); \( \gamma/\mu = b/4 \pi \cos \theta \)
In summary, two distinctively different morphologies were developed during wustite scale growth in a HSESEM at 1050°C and partial pressure of oxygen at $10^{-4}$ atm, depending on the intersection angle between the dislocation line vector and the free surface. A morphological transition from growth-pits to microledges was explained on this basis. The geometric and kinetic factors of the wustite scale growth were discussed as a possible causes for the transition. It is important to realize that the two distinctively different morphologies can be formed from the same microstructural defect. The analysis of the line tension of dislocations and the surface energy of wustite results in a reasonable value for the ratio of surface energy to shear modulus.
C. Development of Columnar Grains in Wustite Scale Growth

The importance of the microstructure of oxide grains on the oxidation kinetics have been emphasized in the previous chapters. A change in the extent of the short-circuit diffusion paths in the oxide produces corresponding changes in the rate of oxidation. A direct relation between the extent and efficiency of the short-circuit diffusion paths for different crystallographic orientations and oxidation anisotropies shown in oxidation of nickel (48) is a good example. However, little attempt has been made to study similar phenomena for iron oxidation, probably because of complexities arising from the formation of three different product phases. Formation of single phase oxide wustite in this study made it possible to study the grain structure of the oxide scale. This chapter describes the results obtained in this study and discusses the consequences of such microstructures.

Transverse sections of the oxide grains indicated that mono-crystalline columnar oxide grains were formed. Figures 42 and 43 show post-oxidation SEM micrographs taken from the both sides of the wustite scale, which had been mechanically detached in liquid nitrogen. These figures are composed of a montage of photomicrographs over extensive areas of the interfaces. Morphological evidence of oxide grain
Fig 42. Montages of the oxygen/wustite interface of the wustite scale formed at 1050°C for 20 min.
Fig 43. Montages of the wustite side of the wustite/iron interface. The area with pits in Fig. 42 are covered with oxide nodules in this figure.
boundaries at the gas/scale interface (Fig. 42) and at the oxide surface of the scale/metal interface (Fig. 43) is clearly shown. The grain morphologies at these two interfaces indicate the presence of a columnar structure of the wustite scale, in preference to duplex structure frequently reported in many other oxide scales. The columnar structure was confirmed from a transverse sectional view of the fractured surface of the wustite scale as shown in Fig. 44. Small equiaxed oxide grains near the scale/metal interface, a structure which is characteristic of the duplex structure, were not seen in either case.

As pointed out previously, the exact cause for the development of oxide grain morphologies for these two cases, columnar and duplex structure, are not known. The grain growth characteristics of a wustite scale, grain coalescence, are suggested to be responsible for the development of columnar grains. Small equiaxed oxide grains were shown to grow immediately after nuclei are formed. Three types of grain growth are possible at this stage. Firstly, interface-energy-driven grain growth takes place such that grain boundaries of big grains migrate toward surrounding small grains; this mode of growth was rarely observed during wustite scale growth. Secondly, predominant lateral growth of one grain over other grains is also possible. This appears as grain growth when one observes this process from above the oxide scale, as in the case of in-situ observation.
Fig 44. Cross-sectional view of the cleaved wustite scale showing the columnar structure. Specimen was tilted by 30 degrees.
performed here. Small grains just overgrown by surrounding grains would be left behind underneath the larger grains; this mode of grain growth has been observed occasionally in this experiment. Both of these growth processes involve the apparent migration of grain boundaries. Therefore, a clear distinction between these two processes in not possible during in-situ observation. A transverse sectional view of the oxide scale does reveal which growth mechanism was predominant during scale growth. The second grain growth mechanism favors the formation of a duplex structure. Lastly, grain coalescence as described earlier is also possible. This process is considered to be major mode of grain growth in wustite because very little grain boundary migration was observed during scale growth. When grain growth of the oxide takes place predominantly by grain coalescence, a single crystalline columnar structure is expected to form.

The nature of the oxide grain boundaries, when they first form from nuclei, is also believed to be important in establishing the final appearance of the grain morphology. Grain coalescence does not occur for oxide grains that form high angle grain boundaries, where only the first two types of grain growth are possible. As shown previously, wustite nuclei on the same metal grain are separated by low angle grain boundaries. The probable explanation is that there exists one most favorable epitaxial relationship between the
gamma iron and wustite nuclei, as reported for the case of alpha iron and wustite (190). Therefore, oxide nuclei formed on the same metal grain would form only one type of oxide orientation. For the oxides which have several competitive epitaxial relationships, as is the case of nickel oxide (207) and copper oxide (50), there is a possibility that two adjacent nuclei exhibit a high angle of misorientation. These two metal oxides are also well known for the development of duplex structure. More extensive study is needed to clarify the contribution of grain growth characteristic to the development of oxide grain structure.
V. Summary and Conclusions

An in-situ study of wustite scale growth in the hot stage environmental scanning electron microscope (HSESEM) at 1050°C and $P_{O_2}$ of $10^{-4}$ atm revealed several distinctive morphological features at the gas/scale interface. These morphological features were caused by microstructural defects, such as grain boundaries and dislocations. From the observation of these morphological features and their evolution, the following conclusions are made.

In the initial stages of oxidation, discrete wustite nuclei were epitaxially developed on the austenite grains. Rapid dissolution of oxygen at the grain boundaries of the iron substrate during nucleation was indicated by the absence of the oxide nuclei in the vicinity of the boundaries. The above two experimental findings strongly suggest that dislocations in the metallic phase are not favorable nucleation sites under the experimental conditions of the present work. Once the oxide nuclei grew laterally and formed oxide grains, very rapid grain growth took place. Grain coalescence by annihilation of grain boundary dislocations was believed to be the major mode of grain growth. This led to the development of a columnar oxide grain structure at a later stage of oxidation, in preference
to the duplex structure frequently reported in many other studies of oxide scales.

Two distinctively different morphologies, namely growth-pits and microledges, developed during steady-state scale growth. The crystallographic orientations of the pit walls were found to be those of nominally \{110\} planes. These \{110\} planes are dissociated into microledges of \{100\} type planes. The large degree of anisotropy in surface energy of wustite results in only one crystallographic plane, \{100\}, as a free surface. The nominal surface orientation of microledges depends on the way the \{100\} planes are arranged.

A morphological transition from growth-pits to microledges was explained based on the thermodynamic criterion of the minimum free energy configuration involving a balance between surface energy and the line tension of the dislocation. When the intersection angle between the dislocation line vector and the free surface exceeds the critical value, the dislocation does not exert enough line tension to stabilize a pit. The dislocation will, then, merely provide surface steps for further growth. As a possible causes for the critical intersection angle at the transition, the geometrical factors in the HSESEM and kinetic factors associated with the wustite scale growth were discussed. The thermodynamic analysis of the line tension of dislocations and the surface energy of wustite
results in a reasonable value for the ratio of surface energy to shear modulus. It seems very important to realize that under the same experimental conditions two distinctively different morphologies can be formed from the same microstructural defect.
VI. References


16. L. Peralta, Y. Berthier, and J. Oudar, 14e Colloque de Physique et Chimie des Surfaces Solides, Antibes (1978), No. 83 de la Revue "La Vide" (1980).


70. A. Atkinson, R. I. Taylor and A. E. Hughes, Phil. Mag., A45, 823 (1982).


171. S. Amelinckx, Solid State Physics, Suppl. 6 (1964).


175. E. Metcalfe and A. Charalambous, Central Electricity Research Laboratories, VH102 (1981).


206. N. Cabrera and M. M. Levine, Phil. Mag., 1, 450 (1956).