Selective Internal Oxidation and Severe Plastic Deformation of Multiphase Fe-Y Alloys

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Abstract

Oxide dispersion strengthened (ODS) alloys are known for their desirable mechanical properties and unique microstructures. These alloys are characterized by an even dispersion of oxide phase throughout a metallic matrix, and exhibit high strength and enhanced creep properties at elevated temperatures. This makes them ideal candidate materials for use in many structural applications, such as coal-fired power plants or in next generation nuclear reactors. Currently most often produced by mechanical alloying, a powder metallurgy based process that utilizes high energy ball milling, these alloys are difficult and costly to produce. One proposed method for forming ODS alloys without high-energy ball milling is to internally oxidize a bulk alloy before subjecting it to severe plastic deformation to induce an even oxide distribution. This work examines such a processing scheme with a focus on the internal oxidation behavior.

Internal oxidation has been shown to occur orders of magnitude faster than expected in multi-phase alloys where a highly reactive oxidizable solute has negligible solubility and diffusivity in other, more-noble, phases. Commonly referred to as *in situ* oxidation, this accelerated oxidation process has potential for use in a processing scheme for ODS alloys. While *in situ* oxidation has been observed in many different alloy systems, a comprehensive study of alloy composition and microstructure has not been performed to describe the unusual oxidation rates. This work used Fe-Y binary alloys as model system to study effects of composition and microstructure. These alloys have been shown to exhibit in situ oxidation, and additionally, Y is typically introduced during mechanical alloying to form Y-rich oxides in Fe-based ODS alloys.

Alloys with Y content between 1.5 and 15 wt% were prepared using a laboratory scale arc-melting furnace. These alloys were two phase mixtures of Fe and $Fe_{17}Y_2$. First, samples were oxidized between 600 and 800 °C for 2 to 72 hours, using a Rhines pack to maintain low oxygen

partial pressures so that *in situ* oxidation could occur. Oxidation rates were accelerated when compared to traditional theory, and were not well described by a single parabolic rate constant throughout the duration of the experiment. While results agreed with Wagner theory that increased Y content should lead to decreased oxidation rates, this was attributed to a depletion of oxygen supply from the Rhines pack over time. Samples were also subjected to plastic deformation to observe how changes in microstructure influenced kinetics. Connectivity of the oxidizable phase was found to be critical to promoting the fastest rates of oxidation. Oxidation studies where then carried out using thermogravimetric analysis. A gaseous mixture of Ar-H₂ was passed through a dew point control unit to vary oxidant partial pressure between 10⁻²⁵ and 10⁻²⁰ atm. Flow rate of the gas parallel to the sample surface was also altered. Canonical correlation analysis was then used to analyze and simplify the relationships between input and output variables. This analysis pointed to the importance of quantifying the relationship between the size of formed oxides and changes in oxidation kinetics over time. Where sustained parabolic kinetics were observed, oxides were small throughout the depth of internal oxidation. The effects of oxide size on penetration depth were then numerically modeled and incorporated into existing oxidation theory to show that the observed kinetics could be qualitatively described.

After oxidation experiments, severe plastic deformation was applied to both oxidized and unoxidized microstructures using equal channel angular pressing. By manipulating pressing temperature and the number of passes, microstructures were altered to varying degrees of success. No oxide refinement was observed, but increasing temperatures and number of passes allowed for even dispersion of both oxides and $Fe_{17}Y_2$ intermetallic.

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Chapter 1

Introduction and Motivation

1.1 Oxide Dispersion Strengthened Alloys

Oxide dispersion strengthened (ODS) alloys have been developed for their unique capacity to withstand large stresses when exposed to severe, high-temperature environments. [1] ODS alloys are defined by, and owe their unique properties to, a high-density oxide dispersion throughout a base metallic matrix. These materials have shown promise for use as cutting tools, in advanced gas turbine chambers, high temperature heaters, diesel engines, and energy conversion systems. [1,2,3] Despite their potential, ODS alloys face limitations such as high degrees of anisotropy, large cost, and limited scalability due to the complex powder metallurgy processes typically used to form them. [4,5] Further widespread implementation of ODS alloys will require the development of alternatives processing routes to generate their unique microstructures.

1.1.1 History, Microstructure, and Properties of ODS Alloys

Coolidge performed the first examination of how inert additions can improve an alloy's mechanical behavior at elevated temperatures in 1910, using thoriated tungsten. [6] This work showed that minor "doping" additions drastically increase creep strength of the base alloy. Other work in the 1950's examined strengthening of an aluminum alloy through the addition of aluminum oxides, and the phrase "oxide dispersion strengthening" was first published in

1957. [7] Early development of ODS alloys also included studies on thoriated nickel in 1958. [8]

Currently, oxide dispersion strengthening is exhibited in a wide range of alloy types, often nickel or iron based. Other types of ODS alloys sometimes utilize a noble metal base, such as platinum. [3,9] Iron-based ODS alloys are currently widely studied, particularly as a replacement for 9Cr and 12Cr steels in structural applications. [10] Iron-based ODS alloys typically contain 12-20 wt% Cr, and smaller amounts of elements like Al, Ti, W, and Mo. The addition of Y₂O₃ occurs during processing, introducing oxygen into the alloy so that the dispersed oxide phase can form. [1] Oxides phases often include Y₂O₃, TiO₂, and Y₂Ti₂O₇. One subset of iron-based ODS alloys are nanostructured ferritic alloys (NFAs), which generally contain Ti-Y-O oxide clusters as small as 2-5 nm in diameter, and are promising candidate materials for nuclear applications. [10] Some typical compositions of iron-based ODS alloys are listed in Table 1.1, and representative microstructures are shown in Figure 1.1. [1]

In these alloys, oxide dispersions act as barriers to dislocation motion, providing increased strength and limiting high temperature creep. [11] Figure 1.2 shows a plot of creep rupture stress as a function of temperature for multiple high-temperature alloys to show how a typical ODS-FeCrAl alloy performs in comparison. [12] The favorable structure and properties of ODS alloys are a direct result of their microstructures and the mechanical alloying (MA) process used to form them.

	Composition (wt%)						
Alloy	Cr	Al	Ti	Мо	W	Y ₂ O ₃	Fe
MA957	14	-	1	0.3	-	0.3	Bal.
PM2000	20	5.5	0.5	-	-	0.5	Bal.
JW12YT	13	-	0.4	-	3	0.25	Bal.
U14YT	14	-	0.4	-	-	0.25	Bal.
U14YWT	14	-	0.4	-	3	0.25	Bal.

Table 1.1. Compositions of Fe-Based ODS Alloys [13]



Figure 1.1. Micrographs of commercial ODS alloys including A) MA956, B) MA957, and C) PM2000 [1]



Figure 1.2. Creep rupture strength as a function of temperature for an Fe-Based ODS alloy compared to other high-temperature alloys [12]

1.1.2 Mechanical Alloying

The production of ODS alloys via MA was studied in 1970 by Benjamin. [14] During the MA process, a powder mixture containing elements such as iron, tungsten, titanium, and chromium are milled together with an oxide component, often Y_2O_3 . Ball milling mixes the metal/ceramic powder, allowing oxygen to achieve supersaturation throughout the alloy. Oxygen then precipitates with yttrium and other elements during a hot consolidation and extrusion step, resulting in the dispersion of oxides throughout the material. From here the alloy is worked and heat-treated into a final product. A schematic of the process can be seen in Figure 1.3. [10] MA

introduces high degrees of anisotropy and texture to the microstructures of these alloys. For example, when extruded to form tubes, alloys typically have half the creep strength in the hoop direction when compared to the axial direction. They also have low toughness for cracks that propagate in the axial direction, further adding to the importance of post-MA heat treatments. Joining ODS alloys is also challenging because typical fusion welds alter their unique grain and oxide structures. The high cost and potentially difficult scalability of the mechanical alloying process are also unfavorable. [10] These concerns associated with the MA process make exploring alternate techniques for synthesizing ODS alloys an important precursor to their potential wide-spread implementation.



Fig 1.3. A schematic of the mechanical alloying process [10]

1.2 Potential Alternate Processing Routes

Synthesis of an ODS alloy equivalent to those formed via the MA process must both create and disperse similar oxides. The majority of the research associated with making ODS alloys has focused on post-processing schemes, though some current research has attempted to eliminate MA entirely. One attempt included introducing Y to the melt of an alloy before powder production, followed by a milling procedure with FeO, and another focused on adding reactive gasses to oxidize an alloy powder. [15] This reactive gas method has been utilized for a widely used ODS alloy, GlidCop copper. GlidCop is composed of 3 to 12 nm Al₂O₃ oxides dispersed throughout a copper matrix and is formed with no use of MA. Instead, a Cu-Al precursor powder undergoes internal oxidation to form the Al₂O₃ phase. [16] A similar process could potentially be applied to Fe-based alloys.

Theoretically, a bulk alloy could undergo internal oxidation, and then be subjected to severe plastic deformation to evenly spread the oxides and refine grain size. This would likely include a selective oxidation of the solute rich phases in a multi-phase alloy under low oxidant partial pressures to prevent the formation of an external scale. While traditional external oxidation kinetics are well-understood, as well as single-phase internal oxidation kinetics, current theory is inadequate to describe selective internal oxidation of multicomponent, multiphase alloys. Before bulk internal oxidation can be utilized as a step in forming ODS alloys, a better understanding of oxidation kinetics and post-oxidation microstructures must be established. These oxidized materials must also be subjected to severe plastic deformation processes to prove the capability of dispersing the oxide phase throughout the microstructure.

This work focused on gaining a better understanding of selective internal oxidation kinetics of multi-phase materials using Fe-Y as a model binary alloy system. This included an

examination of how alloy composition, alloy microstructure, and oxygen transport influence kinetics. After analyzing oxidation kinetics, an initial attempt was made to achieve an evenly dispersed microstructure. Equal channel angular pressing (ECAP) was used as a severe plastic deformation mechanism in order to manipulate the oxidized microstructures

Chapter 2

Technical Background

2.1 Internal Oxidation

2.1.1 Internal Oxidation of Single Phase Alloys

Traditional internal oxidation kinetics of single-phase alloys were established by Wagner and summarized by Rapp. [17,18] When considering a binary A-B alloy devoid of scale, with B being less noble, Wagner assumed that internal oxidation was a diffusion-controlled phenomenon, making penetration depth during oxidation a parabolic function of time. This is seen in Equation 2.1 with X representing the oxide penetration depth, t representing time, and k defined as the parabolic rate constant. Equation 2.1 can also be written to define penetration depth in terms of oxygen diffusivity (D_0) and a dimensionless proportionality constant (γ). This analysis also assumes that oxidant partial pressure is within the range of stability of the BO_v type oxide, but below that of the AO_v.

$$X = \sqrt{kt} = 2\gamma \sqrt{D_0 t} \tag{Eq. 2.1}$$

Solving Fick's second law for diffusion (Equation 2.2) with the boundary conditions in Equation 2.3, one can calculate concentration profiles for the solute (N_B) and oxidant (N_O) in the alloy and zone of internal oxidation. Equations 2.4 and 2.5 show the concentration profiles, where $\phi = D_O/D_B$. [19]

$$\frac{\partial N_O}{\partial t} = D_O \frac{\partial^2 N_O}{\partial x^2} \tag{Eq. 2.2}$$

$$N_B = N_B^0 \text{ for } x = 0, t = 0$$
 (Eq. 2.3a)

$$N_B = 0 \text{ for } x \le X_i, t > 0$$
(Eq. 2.3b)

$$N_L = N^S \text{ for } x = 0, t > 0$$
(Eq. 2.3c)

$$N_0 = N_0^\circ f or x = 0, t > 0$$
 (Eq. 2.3c)

$$N_0 = 0 \text{ for } x \ge X_i, t > 0$$
 (Eq. 2.3d)

$$N_O = N_O^S \left[1 - \frac{\operatorname{erf} \left(\frac{x_{2\sqrt{D_O t}}}{2} \right)}{\operatorname{erf}(\gamma)} \right]$$
(Eq. 2.4)

$$N_B = N_B^0 \left[1 - \frac{\text{erf}\left(\frac{x}{2\sqrt{D_B t}}\right)}{\text{erf}(\gamma \phi^{1/2})} \right]$$
(Eq. 2.5)

Using a flux balance of these profiles allows calculation of the depth of oxide penetration for any condition. The two most commonly studied limiting cases assume either negligible or significant solute counterdiffusion. Simplification of the flux balance leads to Equation 2.6.

$$\frac{N_O^S}{\nu N_B^O} = \gamma \sqrt{\pi} \exp{(\gamma^2)} \operatorname{erf}{(\gamma)}$$
(Eq. 2.6)

Assuming negligible solute counterdiffusion:

$$\frac{D_B}{D_O} \ll \frac{N_O^S}{N_B^O} \ll 1 \tag{Eq. 2.7}$$

$$\gamma \ll 1 \tag{Eq. 2.8}$$

$$\operatorname{erf}(\gamma) \cong \frac{2}{\sqrt{\pi}}\gamma$$
 (Eq. 2.9)

$$\exp\left(\gamma^2\right) \cong 1 \tag{Eq. 2.10}$$

Simplifying Equation 6 to:

$$\gamma \cong \sqrt{\frac{N_O^S}{2vN_B^O}} \tag{Eq. 2.11}$$

$$k = \frac{2N_O^S D_o}{\nu N_B^O}$$
(Eq. 2.12)

One can then arrive at the conclusion that penetration depth is dependent on the solubility $(N_O{}^S)$ and diffusion coefficient (D_O) of oxygen in the base metal alpha (A rich phase),

the concentration of B in alpha (N_B^O) , and the stoichiometric constant v of the formed oxide BO_v. Equation 2.13 connects these variables to the overall depth of penetration, *X*. [19]

$$X = \sqrt{\frac{2N_{O}^{S}D_{o}}{vN_{B}^{O}}t}$$
(Eq. 2.13)

Observing the other limiting case, significant counterdiffusion of solute, alters the previous derivation as follows:

$$\frac{N_O^S}{N_B^O} \ll \frac{D_B}{D_O} \ll 1 \tag{Eq. 2.14}$$

$$\gamma \phi^2 \ll 1 \tag{Eq. 2.15}$$

$$\gamma \cong \frac{\pi^{1/2} \phi^{1/2} N_O^S}{2\nu N_B^O}$$
(Eq. 2.16)

$$k = \frac{\pi (D_0 N_0^S)^2}{D_B (2\nu N_B^O)^2}$$
(Eq. 2.17)

It is also important to consider factors that influence external scale formation. Increasing the concentration of B will slow the rate of oxidation as the formation of an external BO_v scale becomes more favorable. The external scale is favored when a critical volume fraction (f_v^*) , typically estimated to be 0.3, of the internal oxide in the internal oxidation zone is surpassed. [17,18,20] A critical value of mole fraction of the internal oxide (f_{ox}^*) can be related to f_v^* via Equation 2.18, where $\rho = V_{ox}/V_{all}$ (the ratio between molar volumes of the oxide and the alloy). [21,22]

$$f_{\nu}^* = f_{ox}^* \frac{\rho}{1 + f_{ox}^*(\rho - 1)}$$
(Eq. 2.18)

Equation 2.19 further relates f_{ox}^{*} to a critical average concentration of B throughout the alloy $(N_B^{o^*})$:

$$N_B^{o*} = \frac{f_{ox}^*}{\varepsilon} = \frac{f_v^*}{\rho - f_v^*(\rho - 1)\varepsilon}$$
(Eq. 2.19)

In the equation, ε corresponds to the enrichment of B in the internal oxidation zone (f_{ox}/N_B^o) . [22] While these critical values may determine the transition from internal to external oxidation of B, another requirement, as stated earlier, is that oxidant partial pressure falls below the stability range for AO_v type oxides to prevent an external A-based scale.

2.1.2 Internal Oxidation of Multi-Phase Alloys

The formation of an external scale is typically more difficult in two-phase alloys compared to their single phase counterparts. [23] When predicting the formation of a protective scale, one must consider compositions and volume fractions of all present phases, oxide growth rates, and solute diffusivity/solubility.

Consider a two-phase alloy with phases α and β , with α rich in A and β rich in B (B is again the less noble component). With the limiting case of negligible solute counterdiffusion once again applied, the solubility and diffusivity of B in α are assumed to be insignificant. This makes the formation of an external BO_x scale unlikely, unless the matrix phase is primarily compromised of the β phase. B transport in the material does not occur, and the β phase transforms to oxide as the alloy internally oxidizes. The oxide phase therefore has the same location and morphology as the initial β phase, and the more noble α phase remains unoxidized. This specific circumstance has been called *in situ* or *diffusionless* internal oxidation. [21,23] This limiting case is theoretically described by traditional oxidation kinetics in Equation 2.12, and schematically illustrated in Figure 2.1. [21]



Figure 2.1. An example of in situ oxidation of an A-B binary alloy. β particles in an α matrix are oxidized and become BO particles near the surface while the matrix remains unoxidized. [21]

2.1.3 In Situ Oxidation

The *in situ* internal oxidation of many A-B binary systems, such as Fe-Cu, Ni-Zr-Y, Fe-Nb, Co-Nb, and Ni-Nb, has been studied, along with ternary systems like Ni-Zr-Y. [24–26] Past data shows that these alloy systems exhibit much faster kinetics compared to predictions of the traditional Wagner theory given in Equation 2.12. Experimental parabolic rate constants have been observed to be significantly larger than predicted, as summarized in Table 2.1.

Alloy (wt%)	Oxidation Temp. (°C)	k _{exp} (cm ² /s)	k_{theor} (cm ² /s)	k_{exp}/k_{theor}
Ni-15Nb	700	2.6 x 10 ⁻¹²	8.1 x 10 ⁻¹⁶	3210
Ni-30Nb	700	2.0 x 10 ⁻¹¹	3.8 x 10 ⁻¹⁶	52631
Co-15Nb	700	1.2 x 10 ⁻¹¹	4.1 x 10 ⁻¹⁴	293
Co-30Nb	700	1.8 x 10 ⁻¹²	1.9 x 10 ⁻¹⁴	95
Fe-15Nb	800	4.9 x 10 ⁻⁹	1.3 x 10 ⁻¹²	3769
Fe-30Nb	800	1.1 x 10 ⁻⁹	$6.0 \ge 10^{-13}$	1833
Fe-30Y	800	2.2 x 10 ⁻⁹	1.19 x 10 ⁻¹²	1849
Ni-0.5Zr-0.2Y	1000	2.54 x 10 ⁻⁸	5.87 x 10 ⁻¹¹	433
Ni-2Zr-0.2Y	1000	5.65x10 ⁻⁸	1.87 x 10 ⁻¹¹	3021

Table 2.1. Theoretical and experimental rate constants from studies of *in situ* oxidation [24,26,27]

While past work has shown that this phenomenon occurs in binary and ternary alloys, more work is needed to sufficiently model the kinetics. Concepts of "effective diffusivity" and "effective stoichiometry" have been utilized to correct theoretical predictions, but this does not fully describe the kinetic mechanisms. [27] Along with this, increased stress in the microstructure due to volume increases during oxidation have been proposed as causes of high diffusivity pathways such as dislocations, but nothing has presently confirmed this assertion. [20] Similarly an alternative to bulk diffusion would be oxygen transport along incoherent oxide-matrix interfaces. [26]

2.1.4 Oxygen Transport

Many of the above studies utilized Rhines packs, mixtures of the base metal and its oxide, to study internal oxidation. [28] These are also frequently used in the study of single phase alloy

internal oxidation. The assumption made is that the oxygen pressure at the metal surface is constant and equal to that for base metal/oxide equilibrium. The packs are typically evacuated, so oxygen is assumed to be the only gas present. The statement of a constant oxygen pressure implies no other processes affect supply of oxygen to the metal surface. Exceptions to this assumption in Rhines packs have been noted for refractory alloy systems at very high temperatures (approx. 1700 °C) where diffusion of oxygen in the alloy is very fast. [29] In this case the internal oxidation rate was controlled by the rate at which oxygen atoms struck the metal surface, which could be predicted by the kinetic theory of gases.

Internal oxidation can also be studied by exposing samples to oxidants diluted by an inert gas. Oxidation in dilute gases is also of practical importance. Much attention has been devoted recently to the behavior of structural alloys for helium-cooled nuclear reactors, where contaminants in the helium can lead to internal oxidation, among other phenomena. [30] The dilution of oxidants by an inert gas creates the possibility of oxidation rate control by mass transfer in the gas phase. [31] While most internal oxidation studies rates will be controlled by solid state diffusion of oxygen, the presence a high density of interfaces or dislocations can increase the diffusivity of oxygen by orders of magnitude and other rate-controlling processes may be possible. Impacts of non-solid state diffusion control on internal oxidation have not been frequently discussed.

When oxidation is carried out in gas mixtures, such as H_2/H_2O or CO/CO_2 , the dissociation of the oxygen rich component at a sample's surface may control oxidation rates. Equation 2.20 defines the rate of increase in oxide thickness over time when oxidation is controlled by the dissociation of H_2O , where K_{H2O} is the rate constant for dissociation. [19]

$$\frac{dX}{dt} = k_l = K_{H2O} P_{H2O} \left(1 - \frac{a_0^{EQBM}}{a_0^{ambient}} \right) \left(a_0^{EQBM} \right)^{-2/3}$$
(Eq. 2.20)

Along with considering dissociation processes, supply of gas to the surface must also be considered. If oxidation rates are determined by diffusion of an oxidant, such as H₂O, through a gas phase boundary layer, the change in oxide thickness over time is described by Equation 2.21.

$$\frac{dX}{dt} = k_l = j_{H20} M W_{H20}$$
(Eq. 2.21)

The flux of the oxidant molecule can then be defined as:

$$j_{H20} = k_m (C_{H20}^o - C_{H20}^S)$$
(Eq. 2.22)

 P_{H2O}^{o} defines the bulk partial pressure of the gas, while P_{H2O}^{S} represents the pressure at the metal surface. The mass transfer coefficient k_m is defined as:

$$k_m = \left(\frac{0.68}{L}\right) D_{mix} Sc^{1/3} R e_L^{1/2}$$
(Eq. 2.23)

L represents the length of a sample's surface and D_{mix} is the diffusivity through the gas phase. D_{mix} is calculated using the Chapman-Enskog equation. *Sc* is the Schmidt number, and *Re* is the Reynolds number. These values depend on the kinematic viscosity of the gas mixture (*v*) and velocity of the gas (*u*).

$$Sc = v/D_{H20}$$
 (Eq. 2.24)

$$Re = uL/v \tag{Eq. 2.25}$$

This analysis helps to explain linear oxidation kinetics if observed during oxidation of samples in a multi-component gas atmosphere, though it is often ignored, as parabolic kinetics are often a controlling factor due to solid state mass transfer of oxygen. [19]

2.1.5 Deviations from Theory

Along with accelerated kinetics during *in situ* oxidation, studies on the internal oxidation of binary Ni-Al alloys illustrated other important deviations from predicted Wagner oxidation kinetics. Stott *et al.* examined the anticipated relationship, stated in Equation 2.13, that the depth

of internal oxidation should vary inversely with square root of solute content. [32,33] While confirming this relationship in multiple alloy systems, it was found that in Ni-Al binary alloys, depth of penetration was constant with varied Al content. Along with this, oxidation proceeded much faster than predicted. An examination of the post-oxidation microstructure showed a high density of Al₂O₃ oxides oriented perpendicular to the sample's surface. Enhanced kinetics were attributed to diffusion along the incoherent interfaces between these oxides and the nickel matrix. This was explained by defining an effective flux (J_{eff}) that considered flux through the metal matrix (J_l), through the oxide (J_{ox}), and through the interface between the two (J_i).

$$J_{eff} = J_l A_l + J_{ox} A_{ox} + J_i A_i$$
 (Eq. 2.26)

Assuming the flux of oxygen through the oxide to be negligible an effective diffusivity can then be defined as:

$$D_{eff} = D_0 A_l + D_{0i} A_i \tag{Eq. 2.27}$$

Assuming oxide rods of a fixed radius r, the total number of rods in a cross-sectional area Z can be calculated by considering the alloy's molar volume (V_{all}), the oxides molar volume (V_{ox}), and the mole fraction of oxide relative to that of the solute (N_{BOv}). [32,33]

$$\frac{N_{BOv}X}{V_{all}} = \frac{Z\pi 2X}{V_{ox}}$$
(Eq. 2.28)

From this equation the total interfacial area between oxide and matrix can be defined, with interface width noted as δ_i .

$$A_{l} = 1 - A_{i} - A_{ox} = 1 - 2\pi r Z \delta_{i} - Z\pi r^{2}$$
(Eq. 2.29)

These equations, along with the assumption that oxygen diffusivity along interfaces is much greater than lattice diffusion, showed that the effective diffusion coefficient through the internally oxidized zone was a linear function of rod density, and that permeability was a linear function of aluminum content. [32,33]

$$N_{O}^{S} D_{Oeff} = N_{O}^{S} D_{O} \left[1 + \frac{N_{BOv} V_{OX}}{V_{all}} \left(\frac{2\delta_{i} D_{Oi}}{r D_{O}} - 1 \right) \right]$$
(Eq. 2.30)

Wagner assumed that discrete spherical particles formed during internal oxidation when deriving traditional theory, but the work done by Stott shows that oxide morphology can have a dramatic impact on oxidation kinetics, and may help explain the accelerated kinetics observed during *in situ* oxidation.

At the front of internal oxidation, the nucleation of oxides, and the growth of existing particles compete with one another. During the initial stages of internal oxidation, the oxygen flux is high, promoting the nucleation of small particles, but over time as the front moves deeper into the alloy, fluxes will decrease and particle growth and elongation will be favored over nucleation. [32,33] As larger particles begin to predominate, the area fraction of interface will also decrease, reducing the available area for potential fast path diffusion of oxygen.

Bohm and Kahlweit defined how oxide sizes change through the depth of internal oxidation, assuming spherical oxides. Oxide number density (f_N) was calculated as a function of the spacing between successive nucleation events (ΔX), as indicated in Figure 2.2 and Equation 2.31. Number density was then computed as a function of a constant (k) and oxygen solubility according to Equation 2.32. [34]

$$f_N \approx \frac{1}{\Delta X^3} = \left(\frac{X_i}{\Delta X}\right)^3 \frac{1}{X_i^3}$$
 (Eq. 2.31)

$$f_N = \frac{k(N_O^s)^3}{X_i^3}$$
 (Eq. 2.32)



Figure 2.2. A depiction of oxide nucleation phenomena and regimes which are identified in the derivation of equations which identify the relationship between oxide size and penetration depth. [31]

Total area fraction is predicted to stay constant throughout the internally oxidized zone, so oxide radius (r) can be directly determined as a function of penetration depth. With the assumption of negligible solute enrichment and spherical oxides, Equation 2.33 relates number density of oxides to oxide size, where V_{OX} is the molar volume of the oxide. This is further reduced to Equation 2.34, which defines the proposed relationship between oxide radius and all considered variables. [34]

$$f_N \frac{4\pi r^3}{3} = V_{OX} N_B^o$$
(Eq. 2.33)

$$r = \left(\frac{V_{OX}N_B^0}{4\pi k}\right)^{1/3} \frac{X_i}{N_O^s}$$
(Eq. 2.34)

Equation 2.34 predicts a linear relationship between oxide size and penetration depth, along with increases as a function of solute content and a decrease as a function of increasing
oxygen solubility. Bohm and Kahlweit noted these relationships when oxidizing the Ag-Cd system, and Kahlweit and Bolsaitis observed them in Cu-Si alloys. [34,35]

While the traditional theory in Equation 2.34 is widely accepted, departures from the linear relationship between oxide size and penetration depth have been observed. Williams and Smith noted deviations from this relationship for the nucleation and growth of Cr oxides in Cu. In this instance oxide size was related to penetration depth to the power n, given that n fell between 0.5 and 1.0. [36] S. Wood identified a similar trend, noting n values close to 0.5 provided a superior fit to Bohm and Kahlweit's linear relationship, when examining the nucleation of Al oxide in Cu. [37] Works by Stott and Whittle both suggested also suggested deviations after the oxidation of Ni-Al alloys, where oxides formed in a more rod like shape oriented perpendicular to the sample surface. [32,33] Discontinuous precipitation has also been examined as a mechanism for internal oxidation, where lamellar oxides form, as opposed to spherical, as solute diffuses along incoherent boundaries between oxide and matrix. [31] These variations expose the error in the calculation by Bohm and Kahlweit of assuming the formation of spherical oxides.

These changes in oxide size and morphology over time were another component of internal oxidation left unaccounted for by initial derivations. Wagner also operated under the assumption of a single-phase alloy, with oxidizable solute dissolved evenly throughout, which would not be the case during *in situ* oxidation of multi-phase alloys. Better accounting of these assumptions would help to refine present theory.

2.2 The Fe-Y Binary System

One alloy system that would be of particular interest when attempting to recreate an Fe-based ODS alloys is Fe-Y, due to Y_2O_3 use during the mechanical alloying process and its presence in many oxides throughout their microstructures. [10] Additions of less than 1.0 - 15.8 wt% yttrium to iron will cause a second phase of Fe₁₇Y₂ intermetallic to disperse throughout an alpha-iron matrix. The phase diagram for the Fe-Y system can be seen in Figure 2.3. [38]



Figure 2.3. The Fe-Y binary phase diagram. [38]

Yttrium's high oxygen reactivity, low solubility, and low diffusivity in iron make it an example of an alloy that could undergo *in situ* internal oxidation. Fe-Y alloys have been shown to exhibit *in situ* oxidation in a past experiment by Niu and Gesmundo, though in alloys with

higher yttrium content (15.8-30 wt%). [27] When this binary allow undergoes *in situ* oxidation, the α -Fe remains unoxidized, while the Fe₁₇Y₂ becomes a mix of oxide and newly formed α -Fe, as illustrated in Figure 2.4. Oxide composition in these alloys has not been studied, though Schneibel suggested that oxides were likely spherical and rod-like Y₂O₃ and possibly a double oxide such as YFeO₃. [16]



Figure 2.4. Schematic of the *in situ* oxidation of a Fe-Y binary alloy.

Piekarcyk *et al.* examined the thermodynamic stability of oxides within the Y-Fe-O ternary system. Resulting definitions of 3-phase regions are shown in in Table 2.2. [39] These values were converted to atm and plotted in Figure 2.5. Figure 2.5 agrees that the most likely oxides to form include Y_2O_3 and YFeO₃. Examination of the diffusion path in this system during *in situ* oxidation suggests the same. Because of the limited solubility and diffusivity of Y in Fe, the diffusion path in this alloy is represented by a straight vertical line at a fixed Y-content, as illustrated in Figure 2.6. [27]

3-Phase Region		$Log(P_{O2})$ (Pa)	
Α	Fe-Y ₂ O ₃ -YFeO ₃	-29345/T + 13.00	
В	Fe-Y ₂ O ₃ -YFe ₂ O _{4-x'}	-28685/T + 12.53	
С	Fe-Fe _{1-y} 'O-YFeO ₃	-27855/T +12.03	
D	Fe-Fe _{1-y} 'O-YFeO _{4-x} ''	-27855/T +12.03	
Е	Y ₂ O ₃ -YFe ₂ O _{4-x} ···-YFeO ₃	-39375/T +20.43 (Above 1078 °C)	
F	Fe _{1-y} [,] O-YFe ₂ O ₄ -YFeO ₃	-45325/T + 25.64 (Above 1078 °C)	
G	Fe _{1-y} O-Fe ₃ O ₄ -YFeO ₃	-33245/T + 18.45	
Н	Fe ₃ O ₄ -YFeO ₃ -Y ₃ Fe ₅ O ₁₂	-26365/T + 17.13	

Table 2.2. Three phase regions in the Y-Fe-O ternary system with corresponding equilibrium oxygen partial pressures. [39]



Figure 2.5. Equilibrium partial pressures for three phase regions in the Fe-Y-O system corresponding to Table 2.2.



Figure 2.6. Isothermal phase diagram of the Fe-rich corner of the Fe-Y-O alloy system. The vertical dotted line indicates a theoretical diffusion path for *in situ* oxidation occurring at a pressure P_{g} . [27]

Fe-Y alloys show the same sort of accelerated oxidation seen in previously mentioned alloys. [27] Gaining a better understanding of the alloy's microstructure both pre- and post-oxidation may lead a stronger explanation of the observed kinetics. While oxide structure in powder metallurgy processed ODS alloys has been studied via three-dimensional atom probe and transmission electron microscopy (TEM), this has not been the case in internally oxidized Fe-Y alloys. [3,5,40,41] Previously mentioned work by Schneibel, utilizing scanning electron microscopy (SEM), has established a correlation between oxidation temperature and oxide

size. [16] When oxidizing a mostly $Fe_{17}Y_2$ sample (15.8 wt% Y) for 3 days at 700 °C, lamellar and spherical oxides about 20-40 nm in diameter/width were visible. Under the same conditions but at 600 °C no oxides were visible via SEM, despite evidence of an internally oxidized layer in the alloy. These smaller oxides could potentially be similar in size to oxide clusters in ODS alloys. In the same study, nanohardness measurements showed that the sample oxidized at 600 °C had higher hardness than that of the 700 °C sample. This implies more strengthening due to smaller oxides particles forming at 600 °C are indeed present, and that manipulation of oxidation conditions could lead to oxides more similar to those seen in powder metallurgy processed ODS alloys. [16]

The above-mentioned work by Schneibel on internally oxidized Fe-Y alloys also examined coarsening during post-oxidation anneals. Significant coarsening was observed after annealing at 1000 °C for 24 hours. Oxides particle sizes reached about 200 nm in diameter, making them visible at low magnifications with SEM. [16] In contrast, annealing many ODS alloys such as 12YWT, 14YWT, and MA957 at temperatures as high as 1300 °C for 24 hours have resulted in minimal coarsening. [13,41,42] It has been hypothesized that the Y-Ti-O nano-oxides that form resist coarsening due to high solute-oxygen affinity inhibiting the solute elements from diffusing through the ferritic matrix. A proposed explanation for the lack of stability in internally oxidized alloys is that higher oxide volume fractions shorten oxide-oxide distance, which promotes faster coarsening in internally oxidized alloys. [16]

The previously discussed studies show clear evidence that one step in an alternate processing route to ODS alloys could be internal oxidation of bulk alloys. *In* situ internal oxidation in Fe-Y alloys has been studied, but only in alloys with between 15.8 and 30 wt% Y. Examination of this behavior in alloys with lower Y content will allow continued progress

toward developing a precursor material which could be used in conjunction with severe plastic deformation to achieve even oxide dispersion.

2.3 Severe Plastic Deformation

2.3.1 History

The need for improved mechanical behavior of metals and alloys has continuously spurred the exploration of grain size refinement. The basic theory behind the mechanical behavior as a function of grain size is stated by the Hall-Petch relation (Equation 2.35), which defines yield stress (σ_y) as a function of grain size (d), where σ_0 is the friction stress and K is a material constant. [43] The increase in strength with decreasing grain size described by the Hall-Petch relation is an easily exploitable way to alter material properties.

$$\sigma_y = \sigma_0 + K/\sqrt{d} \tag{Eq. 2.35}$$

Gleiter initially presented the idea of nanocrystalline (grain sizes less than 100 nm) materials formed by inert-gas condensation in 1981, and the development of ultrafine-grained (UFG) materials remains a major area of research today. [44] UFG materials have recently been given the more exact definition of "polycrystals having very small grains with average grain sizes less than ~1 μ m". Bulk UFG materials also require reasonably equiaxed microstructures and a large fraction of grain boundaries with high angles of misorientation. One subset of UFG materials are "bulk nanostructured materials", which typically consist of grains less than 100 nm. [45]

Early attempts at grain size refinement included powder metallurgy based processes, wire drawing, surface modification, and optimized heat treatments concurrent with hot working. More recent developments have identified severe plastic deformation (SPD) as a tool for achieving ultrafine-grained microstructures. [43] The core ideas behind SPD were formally developed as a result of studies of superplasticity between 1930-1960. These studies examined the unusually high ductility of materials at elevated temperatures and drew connections between fine grain sizes, large grain boundary volume fractions, and superplastic deformation behavior. Bridgman was responsible for pioneering work examining how high hydrostatic pressures and shear deformation, two important aspects of SPD, can be utilized in materials processing. Bridgman also first suggested the SPD process currently known as high-pressure torsion (HPT). [46,47]

Work published in 1992 first used the phrase "severe plastic deformation" to describe how an Al-Cu-Zr alloy deformed during HPT, and the phrase continued to gain traction through the 1990s. [48] The formal modern definition of SPD is "any method of metal forming under an extensive hydrostatic pressure that may be used to impose a very high strain on a bulk solid without the introduction of any significant change in the overall dimensions of the sample and having the ability to produce exceptional grain refinement". Of particular note is the minimal change in sample dimensions, which generates hydrostatic pressure and allows the material to achieve the desirable high strains and high defect density necessary to produce grain refinement. Examples of modern SPD processes include equal-channel angular pressing (ECAP), highpressure torsion (HPT), accumulative roll bonding (ARB), multi-axial forging, and twist extrusion (TE). [45]

A focus of SPD research has been modeling the grain refinement process. Early work described grain refinement through dislocation wall formation, which has led to disclinationbased refinement models. In this process, incomplete disclinations form and produce misorientation between grains. [49] Current models assume that a dislocation cell structure forms in the early stages of SPD, and this inevitably becomes the final grain structure. This allows deformation behavior to be described by a material's dislocation density. One important assumption of these models is that dislocation cell size (*d*) scales inversely with dislocation density (ρ). This is seen in Equation 2.36, where *K* represents a proportionality constant. [43]

$$d = K/\sqrt{\rho} \tag{Eq. 2.36}$$

Total dislocation densities in a material can be calculated as a weighted sum of dislocations in both cell walls and interiors. The fraction of cell walls decreases during SPD until reaching a saturation point due to thinning. From these observations the changes in dislocation density can be described by coupled differential equations, which show that cell size, and therefore grain size, both decrease until asymptotically reaching a saturation point despite continued deformation. The smallest possible grain size achievable via SPD (d_s) can be estimated using Equation 2.37 in terms of applied stress as follows, where M is the Taylor factor, G is the shear modulus, α is a numerical constant, σ_m is the highest achievable stress, and b is the magnitude of the Burgers vector. [43]

$$\frac{d_s}{b} \approx KM\alpha \frac{G}{\sigma_m} \tag{Eq. 2.37}$$

Typical values of the shear modulus are about 0.5, K is about 10, and M is roughly 3. These approximations estimate that grain sizes below about 100 nm can not be achieved based on this cell formation mechanism, which contradicts experiments that have achieved much smaller grain sizes. Another indication that this model is not complete, is that as grain sizes decrease, strain hardening does not occur as dislocation diffusion along walls dominates. Newer modeling techniques have identified factors such as lattice curvature within individual grains and nanotwinning as possible mechanisms for grain fragmentation. [43]

2.3.2 Equal Channel Angular Pressing

Equal channel angular pressing (alternately referred to as equal channel angular extrusion) has been one of the most studied methods of SPD. Segal proposed ECAP as a method for synthesizing UFG alloys in 1981, and defined it as "a deformation technique to impart intensive, uniform and oriented simple shear for materials processing". [50] Valiev, Horita, Azushima, and others popularized the method throughout the 1990s. [51] During ECAP, a bulk ingot is pressed in a die, through two connected channels of equal cross sectional area which intersect at an angle, traditionally 90°. After being pressed through the die, the process is repeated, continuing for *n* cycles, with the ingot typically rotated 90 or 180° between each pass. Segal's philosophies were applied to describe how ECAP can be made more effective by reducing friction between the billet and die, keeping the intersection angle close to 90°, and keeping all regions within the die as filled with material as possible. [52]

Recently, changes have been made to some typical ECAP processing schemes so that larger billets can be pressed and more difficult to deform alloys can undergo SPD. These alterations include improved lubricants, the use of back-pressure to ensure complete filling of the die, and utilizing channel intersection angles that are larger than 90°. [53] Other variables that can be manipulated are pressing temperature and rate. Along with bulk alloys, metallic powders can also undergo, and be consolidated through ECAP. [54] One typical schematic of ECAP can be seen in Figure 2.7. [55]



Figure 2.7. A Schematic of a representative scheme for equal channel angular pressing [55]

The Von Mises strain of a sample after undergoing ECAP is defined as follows, where ϕ is the angle of intersection between channels in the die and ψ is the angle subtended by the arc of curvature at the point of intersection:

$$\varepsilon = \frac{1}{\sqrt{3}} \left[2 \cot\left(\frac{\phi}{2} + \frac{\psi}{2}\right) + \psi cosec\left(\frac{\phi}{2} + \frac{\psi}{2}\right) \right]$$
(Eq. 2.38)

Typically used values ($\psi = 0^{\circ}, \phi = 90^{\circ}$) give a strain of 1.15 after 1 pass, and the total strain after *n* passes is 1.15 multiplied by *n*. The saturation point for grain refinement typically occurs at strains between 5 and 30. [55] The schematic in Figure 2.8 shows how an ingot will shear in the X, Y, and Z planes after 1 pressing, as depicted in Figure 2.7. After the first pressing occurs,

different processing routes can be followed depending on how the sample is rotated. In Route A, the sample is not rotated, in route B_A the sample is rotated 90° in alternating directions, route B_C utilizes a counter-clockwise rotation of 90° after each pass, and route C uses a 180° rotation. The shearing characteristics of the X, Y, and Z planes in each processing scheme are shown in Figure 2.9. [55] Typical lab-scale ECAP is performed on samples with cross-sectional dimensions between 10 and 20 mm, but through both modeling and laboratory experiments that have studied friction during ECAP and contact stresses, industry-scale ECAP has been performed on billets 500 mm in length with 50 x 50 mm cross-sections. [52]



Figure 2.8. Shear of an ingot during equal channel angular processing [55]



Figure 2.9. Observes deformation of the X, Y, and Z, planes of a billet during ECAP subjected to different processing schemes [55]

Most early research on ECAP focused on aluminum and copper based alloys, but presently the scope of this work has expanded to examine how ECAP alters microstructures of both pure iron and various steels. In one example of such work, ECAP of low carbon steel (Fe-0.15wt%C-0.25%Si-1.1%Mn) occurred at 350 °C for up to twelve passes. After two passes, ferrite grain size reduced from initial values of 30 µm down to 0.4 µm. Subsequent passes yielded dimensions reductions, with the smallest grain size of 0.2 µm reached after twelve passes. These grain size reductions were paired with TEM observation of poorly defined grain boundaries and a high density of dislocations. Cementite particles precipitated during pressing and were observed in ferrite grains near pearlitic regions. These particles also became more prevalent as the number of passes increased. Annealing for 1 hour at about 500 °C resulted in varying degrees of microstructural recovery. This did not result in grain growth or recrystallization in any sample, but dislocation density did generally decrease. The samples pressed for eight and twelve passes showed limited amounts of recovery, even after the time of annealing was raised to 24 hours. [56] The generally exhibited microstructural stability in this instance would be a necessary trait in an ODS alloy if employed at elevated temperatures.

Commercially pure Fe was also pressed at room temperature to gain a better understanding of microstructural development during ECAP. Tensile testing showed that the sample's yield strength increased from about 80 to 700 MPa after four passes, and to about 800 MPa after eight passes. While undeformed Fe showed clear signs of work hardening, none was observed in the pressed samples, indicating that necking occurred at the onset of yielding. Grain sizes reached about 0.2 µm, as observed in previous studies. It was found that after initial pressings, low-energy dislocation structures form, but the subsequent passes cause high-energy dislocation structures to form, limiting ductility. Subsequent annealing treatments (200 °C for 1 hour) caused the high-energy structures to revert back to low-energy, with no observed grain growth. This showed that ECAP of Fe-alloys can be combined with a post processing heat treatment in order to cause strengthening in the alloy, but also recover some ductility. [57]

Temperature has also been found to be an important variable during processing, even when comparing samples that have undergone ECAP to the same amount of strain. Altering processing temperature during ECAP has been shown to alter the disclination based model in Equation 2.37, changing the minimum achievable grain size of a material. [58] This is illustrated in Figure 2.10, which shows a variation of grain size on the Y-axis as a function of Temperature for various face and body centered metals. [58] The temperature dependence on intragrain strain rate has also been noted, and the effects of recrystallization must also be considered. Further

evidence of this was examined in Al-Cu alloys, where increasing pressing temperature at constant strain resulted in increased grain sizes and decreased the average misorientation angles between grains. [59] These factors all illustrate that even at constant strains, sample-to-sample microstructures can vary depending on ECAP processing temperature.



Figure 2.10. Minimum achievable grain size in a material after ECAP as a function of melting point divided by deformation temperature [58]

SPD processes such as ECAP have been previously utilized in an attempt to synthesize nanocomposite materials. Studies have shown that the ECAP of metal-metal composites allows for increased grain refinement when compared to ECAP of the individual elements that comprise it. Grain sizes of 10-20 nm have been achieved in W-25wt%Cu, Cu-Cr, and Fe-Cu composites through HPT. [60–64] During the SPD of Cu-Cr and Fe-Cu, supersaturation was achieved between the components, despite traditionally showing negligible solubility. HPT of Cu-28wt%Ag demonstrated how a eutectic phase can be dispersed throughout a microstructure via SPD. Individual particles within a matrix can also be formed, refined, and distributed throughout a microstructure by SPD. [65–67] Suehiro was particularly successful at refining micrometer

sized Co particles in Cu-Co alloys to nanometers. [68,69] Nanometer sized particles were also observed after the SPD of Al-11wt%Fe alloys. [70]

Metal-Ceramic composites have also been subjected to SPD. These composites typically exhibit high strength, stiffness, and wear-resistance, which should be improved by increasing the distribution and refinement of second phase particles, as in ODS alloys. Cu alloys with 0.5wt% Al₂O₃ saw reductions in grain size to 80 nm, and particle size to 20 nm after HPT, but ARB of a Cu-15vol%Al₂O₃ did not refine particle size. [71,72] ECAP refined the grains of an Al6061 alloy with 10 vol% Al₂O₃ particles, but left particle size unchanged. [73–75] Sabirov was able to improve the uniformity of particle size distribution after ECAP at elevated temperatures in Al6061-20vol%Al₂O₃. [76] These works illustrate that processing conditions can be altered to achieve desired microstructural features in composite alloys. Grain refinement is typically easy to achieve, but refining second phase particles often proves more difficult.

2.4 Canonical Correlation Analysis

Canonical correlation analysis (CCA) is a multivariate statistical method for reducing the dimensionality within a data set and identifying cross-correlations between a set of dependent and independent variables. [77,78] During CCA, variables are first separated into groups of independent and dependent variables that are subsequently defined as vectors (\vec{X} and \vec{Y} respectively) according to Equations 2.39. Examples of currently examined independent variables include time, oxidant partial pressure, Y content, and flow rate. Examples of dependent variables include parabolic rate constants, oxide penetration depth, and oxide size. CCA will then identify the linear combinations between these vectors, known as canonical variates, which maximize cross correlation. [77,78]

$$\vec{X} = \{X_{i=1}, X_2, \dots, X_n\} = \{t, P_{O2}, wt \ \% Y, flow, \dots\}$$

$$\vec{Y} = \{Y_{i=1}, Y_2, \dots, Y_m\} = \{k, X, d_{OX}, \dots\}$$

(Eq. 2.39)

A covariance matrix (*C*) is then constructed according to Equation 2.40 and an eigenvalue analysis is performed using Equation 2.41. Taking the square root of the eigenvalues (\mathbb{R}^2) yields a value for the canonical correlation (\mathbb{R}), and canonical weights (α and β) are selected to maximize this value. The maximum number of solutions to Equation 2.41 is equal to the size of the smallest vector used to construct the covariance matrix. [77,78]

$$C = \begin{bmatrix} C_{\vec{X}\vec{X}} & C_{\vec{X}\vec{Y}} \\ C_{\vec{Y}\vec{X}} & C_{\vec{Y}\vec{Y}} \end{bmatrix}$$
(Eq. 2.40)

$$C_{\vec{X}\vec{X}}^{-1}C_{\vec{X}\vec{Y}}C_{\vec{Y}\vec{Y}}^{-1}C_{\vec{Y}\vec{X}}\alpha = R^{2}\alpha$$

$$C_{\vec{Y}\vec{Y}}^{-1}C_{\vec{Y}\vec{X}}C_{\vec{X}\vec{X}}^{-1}C_{\vec{X}\vec{Y}}\beta = R^{2}\beta$$
(Eq. 2.41)

Canonical variates for the input variables (Var_X) and output variables (Var_Y) are then defined by Equation 2.42. The first solution (canonical variate one) maximizes all correlation, and the proceeding variates establish the highest cross correlation possible from the residual variance after the first solution has been removed. This process repeats until either no residual variance remains, or the total number of canonical variates reaches the number of components in the smallest vector from Equation 2.39. Canonical loadings, which define the contribution of an individual variable to a chosen canonical variate, are also calculated. Analysis of the canonical weights and loadings simplifies analysis of a data set and allows easier examination of trends due to the reduction of dimensionality. [77,78]

$$Var_X = \sum_i X_i \alpha_i$$

$$Var_Y = \sum_i Y_i \beta_i$$
(Eq. 2.42)

Chapter 3 Objectives and Hypothesis

The overall objective of this research was to investigate the feasibility of alternate processing routes for iron-based ODS alloys so that they can be produced at lower costs, with increasing degrees of scalability, and with less inherent anisotropy. The central difficulty associated with this concept is achieving a dispersed oxide phase while avoiding the use of high-energy ball milling, which occurs in the widely used mechanical alloying processes. One proposed approach includes internally oxidizing a bulk precursor material, before subjecting it to severe plastic deformation in order to achieve this high density oxide dispersion throughout the microstructure.

Two distinct phases of work were important for exploring an internal oxidation based alternate processing route. First, a more comprehensive study of the internal oxidation kinetics of two-phase binary alloys was necessary. The selective internal oxidation of solute-rich phases in multi-component alloys has shown promise for its inclusion in such a processing scheme due to inherently fast kinetics that have been exhibited in numerous alloy systems. Traditional Wagner oxidation kinetics do not adequately explain this unique limiting case, and recent work in the field has not fully studied compositional and microstructural effects on kinetics. Increased knowledge of the variables controlling these oxidation rates will allow for easier and more accurate planning and implementation of a new processing route. Such a study was performed using Fe-Y as a model alloy system due to the prevalence of Y-rich oxides in Fe-based ODS alloys. This was coupled with an analysis of pre- and post-oxidation microstructures to find relationships between the two. Specific factors of interest included alloy composition, distribution of intermetallic phase, and oxide size/morphology. Atmospheric conditions during oxidation were also be manipulated with the use of both Rhines packs and Ar-H₂ gas mixtures in an attempt to observe the effects of transport phenomena on oxidation kinetics. This included both varied oxygen partial pressures and gas flow rates perpendicular to sample surfaces.

After oxidation, SPD was applied using ECAP in an attempt to promote refinement in oxide size and even distribution throughout sample microstructures. Both oxidized and unoxidized Fe-Y microstructures underwent the deformation, for varied numbers of passes at varied temperatures.

The principal hypotheses of this work are as follows:

1) Deviations from traditional Wagner oxidation kinetics during *in situ* oxidation of binary, two-phase, Fe-Y alloys are due to the distribution and connectivity of the intermetallic phase. The shape, size, and distribution of formed oxides determines the extent of enhanced solid state diffusion.

2) Manipulation of oxidizing atmospheres and gas flow rates can be utilized to control oxidation behavior. In the presence of accelerated solid state diffusion, gas phase mass transfer can emerge as the rate controlling factor for *in situ* oxidation.

3) Severe plastic deformation, applied through ECAP, can be used to refine and homogenize the microstructures of oxidized Fe-Y alloys, producing a material with both better mechanical performance and thermal stability than that of pure Fe.

Chapter 4

Synthesis and Characterization of Fe-Y Alloys

Partially adapted from: S.J. Kachur and B.A. Webler: Oxid. Met., 85, 343-55 (2016)

4.1 Introduction

The Fe-Y alloy system emerged as an ideal candidate to study in situ oxidation due to the limited solubility and diffusivity of Y in Fe, the high degree of Y reactivity with oxygen, and the ability to create two-phase microstructure with varying amount of Y-rich second phase. The presence of Y in ODS alloys was also beneficial for connecting the work to real world engineering applications. Before performing oxidation experiments it was necessary to form and characterize Fe-Y alloys of varying Y content and microstructure. Microstructures were also assessed using theoretical solidification calculations to explain observed deviations from more traditional eutectic solidification of binary alloys.

4.2 Technical Approach

4.2.1 Alloy Preparation

Fe-Y alloys were produced in a laboratory-scale electric arc button remelt furnace. Starting materials were 99.97+% pure Fe pieces and 99.9% 40 mesh Y powder. Alloys were arc melted in a Cu crucible, which was evacuated using a vacuum pump, and then filled with ultra high purity Ar gas. This evacuation and subsequent filling with Ar was repeated three times prior to melting. After solidification, buttons were flipped and remelted two more times to ensure

uniformity of composition. The resulting alloy buttons were approximately 6 mm thick and 30 mm in diameter. Five alloys were made with nominal Y contents of 1.5, 3, 6, 12, and 15 wt%.

4.2.2 Characterization

Samples were ground to a 1200 grit finish with SiC paper, and polished to 1 µm using colloidal silica. Scanning electron microscopy (SEM) was performed using both a Phillips XL-30 and an FEI Quanta 600 field emission gun-SEM in backscattered electron (BSE) imaging modes to enhance mass contrast. Energy dispersive x-ray spectroscopy further identified phase compositions. A Rigaku MiniFlex diffractometer was then used to perform x-ray diffraction (XRD) to confirm phase identities within the microstructure.

4.3 Results

The as-melted microstructures in Figure 4.1 exhibited distinct changes with varying Y content. Since backscattered image contrast results from differences in atomic number, the lighter regions were concluded to be $Fe_{17}Y_2$ and the darker regions Fe. EDS further confirmed the presence of both Fe and Y in the lighter regions and the absence of Y in the darker regions. Higher magnification micrographs in Figure 4.2 show the eutectic structure of the higher Y-content alloys compared to those of a low Y-content alloy. 15 wt% Y alloys were synthesized on two separate occasions, and a comparison of their microstructures is depicted in Figure 4.3. The area fraction of the Fe₁₇Y₂ phase were measured for all alloys and these quantities are listed in Table 4.1. For these measurements, regions of eutectic were estimated to be pure $Fe_{17}Y_2$. XRD confirmed the presence of body-centered cubic Fe and $Fe_{17}Y_2$ in the microstructures. XRD results, plotted in Figure 4.4 also showed the amount of $Fe_{17}Y_2$ increased as Y content increased.

Figure 4.5 shows a theoretical diffraction pattern for $Fe_{17}Y_2$, generated with CrystalMaker and CrystalDiffract software. [79]



Figure 4.1. BSE images of as-cast, unoxidized, Fe-1.5 (A), -3 (B), -6 (C), -12 (D) and -15 wt% Y (E). Phases include α -Fe (dark grey) and Fe₁₇Y₂ (light grey).



Figure 4.2. High magnification BSE images of the eutectic microstructure present in both the 12 and 15 wt% Y alloys, and the 3 wt% Y microstructure as a comparison showing the absence of a fine eutectic component. Apparently porous areas are highlighted with circles.



Figure 4.3. BSE images of the eutectic composition of two different melts of a 15 wt% Y alloy.



Figure 4.4. Intensity as a function of 20 for a 3, 12, and 15 wt% Y alloy. α -Fe peaks are identified.



Figure 4.5. Simulated XRD scan of $Fe_{17}Y_2$ created with CrystalMaker and CrystalDiffract software, plotted as intensity as a function of 2 θ , with peaks labeled when their relative intensity is greater than 10%. [79]

Table 4.1.	Nominal	Y content,	average	area fra	action (2	4 _f), ranges	of area	fraction	observed,	and
measured	Y content	(from ED	S) of the	$Fe_{17}Y_2$	phase 1	measured	from mi	crograph	s of as-me	elted
material.										

Alloy	wt% Y	at% Y	<i>A_f</i> Fe ₁₇ Y ₂ Average	A _f Fe ₁₇ Y ₂ Range	wt % Y (EDS)
1	1.5	1.0	0.060 ± 0.020	0.024 - 0.099	1.77
2	3.0	1.9	0.240 ± 0.076	0.135 - 0.390	3.67
3	6.0	3.8	0.330 ± 0.044	0.249 - 0.370	5.64
4	12.0	7.9	0.782 ± 0.098	0.603 - 0.880	12.97
5	15.0	10.0	1.00 ± 0.00	1.00	14.0

4.4 Discussion

4.4.1 Observed Microstructures

Based on the Fe-Y binary phase diagram (Figure 2.3), samples were expected to contain a mix of primary α -Fe or primary Fe₁₇Y₂ intermetallic and eutectic constituent depending on Y content. This was generally confirmed with EDS and XRD. While EDS could identify phase compositions, XRD was necessary for verification that α -Fe and Fe₁₇Y₂ were the actual phases present. High-intensity peaks in Figure 4.4 at approximately 45° and 65° correspond to the (110) and (200) peaks of α -Fe, respectively, and were observed in all alloy compositions. In the 3 wt% Y sample pattern, these peaks represent the strongest signal. Increasing to 12 and 15 wt% Y leads to a reduction in their intensity, accompanied by an increase in signal from other planes. To confirm that these peaks corresponded to Fe₁₇Y₂, XRD of the phase was simulated using CrystalDiffract software. Peaks with a relative intensity greater than 10% were then cross-referenced between the simulation and theory, and are recorded in Table 4.2. In the 3 wt% Y alloy, only the most intense theoretical peaks were observed. The majority of the peaks were present in both the 12 and 15 wt% Y samples. Omissions of peaks from experimental data are easily explained, as the XRD was performed on bulk samples. The high degree of directionality

in the solidified microstructures likely caused the omission of peaks from certain samples and the variations of intensity of others. Performing a scan after the samples were made into a powder would resolve this issue, but the correlations between experimental and simulated XRD were enough to confirm the presence of $Fe_{17}Y_2$ in the microstructure.

Table 4.2. Simulated peaks for the XRD of $Fe_{17}Y_2$ with their corresponding 2 θ and relative intensity values, along with confirmation of their experimental presence.

	Simula	tion Values	Peak Present Experimentally?			
Peak	2θ (°)	Relative Intensity (%)	3 wt% Y	12 wt% Y	15 wt% Y	
(113)	30.2	11	No	Yes	Yes	
(030)	36.8	32	Yes	No	Yes	
(220)	42.7	39	Yes	Yes	Yes	
(033)	43.0	42	Yes	Yes	Yes	
(226)	62.8	10	No	Yes	Yes	
(333)	70.5	17	No	Yes	Yes	
(060)	78.2	19	No	Yes	No	

Primary Fe dendrites were observed in all cases except the 15 wt% Y alloy. This was somewhat unexpected in the near-eutectic 12 wt% Y alloy. The Fe + Fe₁₇Y₂ eutectic constituent was present in the 12 and 15 wt% Y samples. Fe within the eutectic appeared circular or rod-like, as opposed to faceted. Regions containing Y in the 1.5, 3, and 6 wt% alloys appeared as single phase Fe₁₇Y₂. All regions containing Y, whether as a single phase intermetallic or within the eutectic, were easily distinguished.

Differences between the two solidified 15 wt% Y samples were observed in Figure 4.3. In the second melted button the amount of eutectic in the microstructure is reduced, in favor of larger bulk regions of primary $Fe_{17}Y_2$. While the composition of the alloy prior to melting was measured to be exactly the same as the first button, it is clear that the nominal alloy composition shifted closer to that of the line compound on the phase diagram.

Small, circular, dark regions, highlighted in Figure 4.2, were also present throughout the microstructures. These were likely inclusions that formed during solidification, as minor oxygen impurities present in the Ar oxidized a small amount of the solute prematurely. These large Y oxides were likely pulled from the microstructure during sample preparation, resulting in the apparent dark porous regions. Other residual dissolved gasses in the liquid or general solidification shrinkage may also explain these regions.

Solidification of the alloys likely occurred rapidly, promoting some of the discrepancies observed in the alloys, such as the formation of primary Fe dendrites in near eutectic, 12 wt% Y microstructure and the low amount of primary intermetallic in the 15 wt% Y alloy. This was similar to microstructures observed in Al-Si alloys, where the presence of a skewed eutectic alters what phases are anticipated for a given alloy composition. [80,81] Calculations were performed in order to assess the feasibility of this occurrence in Fe-Y alloys.

4.4.2 Theoretical Solidification Calculations

Traditional solidification theory was applied to quantitatively explain observed Fe-Y microstructures. To assess how microstructures developed in these alloys, it was first necessary to estimate the solidification time for each alloy using Chvorinov's Rule (Equation 4.1). Variables and constants used are outlined in Table 4.3. [82] Alloy volume was calculated assuming a cylindrical button, and the surface area in contact with the mold was calculated assuming the entire alloy contacted the mold except for the round top surface. Other thermodynamic values were taken as averages, weighted by bulk alloy Y content and volume fraction Fe₁₇Y₂ where applicable. Calculated solidification times ranged from about 0.018 s for

cases with high Y content (12 and 15 wt%) to 0.016 s when Y content was reduced. This corresponds to a solidification velocity between 0.7 and 0.8 m/s respectively.

$$t_f = \frac{\pi}{4k_m \rho_m c_{pm}} \left(\frac{\rho_s L_f}{T_f - T_0}\right)^2 \left(\frac{V}{A}\right)^2$$
(Eq. 4.1)

	Variable	Value	Source
t_f	Solidification Time	-	-
k _m	Mold Thermal Conductivity	$401 \text{ Wm}^{-1}\text{K}^{-1}$	[83]
$ ho_m$	Mold Material Density	8960 kg m ⁻³	[83]
c_{pm}	Mold Material Specific Heat	385 J kg ⁻¹ K ⁻¹	[84]
$ ho_s$	Solid Alloy Density	7300 - 7870 kg m ⁻³	[83]
L_{f}	Alloy Latent Heat of Fusion	250 - 286 kJ kg ⁻¹	[85]
T_f	Alloy Equilibrium Freezing Temp.	1623 K	[38]
T_{θ}	Initial Mold Temp.	293 K	NA
V	Solid Alloy Volume	$4.25 \text{ x } 10^{-6} \text{ m}^3$	NA
A	Solid Alloy Surface Area in Contact With Mold	$1.18 \ge 10^{-3} = m^2$	NA

Table 4.3. Definitions and values for all symbols used in Equation 4.1.

Following this calculation, an analysis of competitive growth between primary phases (Fe and $Fe_{17}Y_2$) and the eutectic was considered. Assuming an alloy contains only non-faceted phases, the coupled zone, which defines where the solidification of a regular eutectic microstructure will occur on a phase diagram, is wide and symmetric about the eutectic point. In the case where one of the components is faceted, growth of this phase will lag, and the coupled zone will skew towards it. This skewed coupled zone is responsible for the unique microstructures observed in Al-Si alloys, as it allows the primary phase at lower compositions (in this case Fe) to nucleate in hypereutectic alloys at high velocities. [80,81] This likely explains observed Fe-Y microstructures due to the anisotropy in the $Fe_{17}Y_2$ phase.

Kurz and Fisher analyzed multiple alloy systems to define equations that analyze the growth kinetics of alloys containing a faceted phase, a non-faceted face, and their eutectic. [86] These are summarized by undercooling Equations 4.2 - 4.4, where *G* is the temperature gradient in the liquid (K/mm), D_L is diffusivity in the liquid (mm²/s), and *v* is the solidification rate (mm/s).

$$\Delta T^{Fe} = \frac{GD_l}{\nu} + A^{Fe} \sqrt{\nu} \tag{Eq. 4.2}$$

$$\Delta T^{Fe17Y2} = \frac{GD_l}{v} + A^{Fe17Y2} \sqrt{v}$$
 (Eq. 4.3)

$$\Delta T^{eut} = A^{eut} \sqrt{\frac{\nu}{G}}$$
(Eq. 4.4)

Constants (A^x) in Equations 4.2 - 4.4 were calculated for multiple alloy systems by Kurz and Fisher. [86] Using their methods, the constant for each present component was estimated as a range of values to determine the spread of possible microstructures as a result of the skewed eutectic. These values were $10 - 20 \text{ °Cs}^{1/2} \text{mm}^{-1/2}$ for α -Fe, $20 - 40 \text{ °Cs}^{1/2} \text{mm}^{-1/2}$ for Fe₁₇Y₂, and $80 - 100 \text{ °C}^{3/2} \text{s}^{1/2} \text{mm}^{-1}$ for the eutectic. The temperature gradient was estimated to be 20 K/mm and the diffusivity was considered to be 0.005 mm²/s. Using these estimates to calculate undercooling values for each components with Equation 4.2 - 4.4, plots of temperature vs. solidification velocity can be created to describe which phases solidify at different velocities. Figure 4.6 shows plotted results for 6, 12, and 15 wt% Y alloys, assuming the lowest estimated constant (A) values for each.



Figure 4.6. Solidification temperature as a function of solidification velocity for 6, 12, and 15 wt% Y alloys. Curves are for each possible component in the microstructure, primary Fe, primary $Fe_{17}Y_2$, and the eutectic. Values were calculated using the lowest estimated A values.

The curves for the 6 wt% Y alloy are characteristic of calculations performed for all low Y content alloys. Curves are clearly separated from one another and over the entire range of velocities primary Fe dendrites will form first. As Y-content is increased, the curves begin to converge at low velocities, but are still relatively spread apart at higher values. Further increasing to a hypereutectic, 15 wt% Y composition, shows that at lower velocities, the formation of primary Fe₁₇Y₂ can be promoted, but at the presently examined velocities (0.7 to 0.8 m/s) Fe dendrites are still favored.

Increasing to the upper bounds of estimated constant values alters the curves as shown in Figure 4.7. There is a clear shift in the curves for all alloys. Low wt% Y alloys still remain safely within the regime where primary Fe formation is encouraged, despite some convergence with the curve for the eutectic at elevated solidification rates. This convergence continues as Y-content is increases, as observed in the 12 wt% Y alloy. Despite this, the plot still predicts initial formation of primary Fe dendrites. At the hypereutectic composition the eutectic and Fe lines essentially overlap in the relevant velocity range.



Figure 4.7. Solidification temperature as a function of solidification velocity for 6, 12, and 15 wt% Y alloys. Curves are for each possible component in the microstructure, primary Fe, primary $Fe_{17}Y_2$, and the eutectic. Values were calculated using the highest estimated A values.

While some estimation was involved in the above calculations, results matched well with observed microstructures. In the hypoeutectic 1.5, 3, and 6 wt% Y alloys, the bulk of the microstructure consists of primary Fe with increasing amounts of Y-rich phase, in agreement with the calculations. High magnification examination of the Y-rich phase confirmed that this was not a eutectic microstructure, but single phase $Fe_{17}Y_2$. Upon formation of Fe, the metastable extension of the intermetallic is likely crossed, resulting in this formation. Elevating Y content to the near eutectic 12 wt% composition still results in the formation of a large amount of primary Fe. This again provided a theoretical basis explaining the as-melted microstructures, implying the presence of a skewed eutectic. This held true within the entire range of constant values examined. While not shown on the current figures, decreasing solidification rates further shows that a manipulating casting conditions could result in the formation of a eutectic microstructure.

The range of outcomes in hypereutectic alloys is somewhat more ambiguous. Compositions of 15 wt% Y fall approximately 0.5 wt% Y below the line compound $Fe_{17}Y_2$. The observed microstructures are clearly dominated by a eutectic that looks similar to those found in hypereutectic Al-Si alloys solidified at fast velocities, though one melted sample did include an increased amount of primary intermetallic. Calculations did not predict the formation of primary $Fe_{17}Y_2$, but it is possible that the degree to which the composition sits near that of the line compound for that individual sample, along with errors in estimating constant values, lead to this difference. The formation of primary intermetallic is clearly sensitive to small changes in this regime, and it is clear that in hypereutectic alloys at higher solidification rates, the formation of eutectic occurs to a greater degree than anticipated.

4.5 Conclusions

- Microstructures are composed of primary Fe and Fe₁₇Y₂ at low Y contents (1, 3, and 6 wt% Y) with the amount of intermetallic increasing as a function of Y content.
- The 12 wt% Y, near-eutectic composition contained a large fraction of primary Fe dendrites along with a fine eutectic structure. This was unexpected but was shown to be plausible in the presence of a skewed eutectic zone via the method of Kurz and Fisher.
- 15 wt% Y alloys, which were theoretically predicted as line compounds of the intermetallic phase were mostly composed of a eutectic microstructure. The analysis by Kurz and Fisher again showed that this is within the real of possible outcomes due to the skewed eutectic. Some loss of Y to premature oxidation during melting of the alloy could further explain why a more single phase intermetallic microstructure is not observed.
- While some degree of estimation was necessary the calculations performed match observed microstructures well. This estimation was taken into account by presenting constants as a range of possible values and computing the outcome for each potential circumstance. The presence of a skewed eutectic in Fe-Y alloys is highly likely.

Chapter 5

Effects of Microstructure on Oxidation Behavior

Chapter adapted from: S.J. Kachur and B.A. Webler: Oxid. Met., 85, 343-55 (2016)

5.1 Introduction

This work demonstrated the role of microstructure on the *in situ* internal oxidation rate of twophase alloys. Fe–Y alloys with Y contents between 1.5 and 15 wt% were employed as a model system. Alloys were prepared by arc-melting and their starting structures were as-solidified, twophase mixtures of Fe and Fe₁₇Y₂ intermetallic. An alloy with 1.5 wt% Y was cold-rolled to further alter the intermetallic morphology. Oxidation was conducted in an Fe–FeO Rhines pack at 600, 700, and 800 °C for up to 72 hours. Pre- and post-oxidation microstructures were characterized with electron microscopy. Consistent with other studies, only the Fe₁₇Y₂ phase internally oxidized and no external scale was formed. Transmission electron microscopy showed that the Fe₁₇Y₂ transformed into rod-like nanometer-scale oxides. Oxidation rates were always greater than those predicted by Wagner theory. Parabolic kinetics were obeyed for about the first 10 hours of oxidation. During this time the parabolic rate constants decreased with wt% Y. The effect of alloy microstructure on oxidation kinetics was attributed to connectivity of the Fe₁₇Y₂ phase.

5.2 Technical Approach

5.2.1 Alloy Preparation

Fe-Y alloys with Y-content between 1.5 and 15 wt% were synthesized according to the methods outlined in Chapter 4. One button of 1.5 wt% Y alloy was plastically deformed by rolling to alter microstructure while holding composition stable. The sample was heated to 300 °C and immediately rolled, reducing thickness approximately 0.5 mm at a time. This heating and rolling process was repeated until an 80-85% reduction in thickness was reached.

5.2.2 Oxidation

Approximately cubic, 1 x 1 x 1 cm samples of each alloy were cut and ground to a 600 grit finish on all sides with SiC abrasive paper. Samples were cleaned in ethanol and dried. Oxidation occurred at 600, 700, and 800 °C inside a horizontal tube furnace with ultra high purity argon flowing through at 0.25 L/min. During the process the furnace was heated and cooled at a rate of 2 °C/min and isothermal hold times ranged from 2-72 hours.

Oxygen partial pressure was established at the surface of each sample utilizing a Rhines pack. [28] The Rhines pack consisted of a 1:1 mixture, by mass, of Fe:Fe₂O₃. This resulted in an oxygen partial pressure equal to that for Fe/FeO equilibrium. Since the Rhines pack mixture was static, oxygen pressures varied with temperature. Oxygen pressures were calculated based on the reaction in Equation 5.1, using the standard Gibbs free energy change in Equation 5.2, and assuming the activities of Fe and FeO were equal to 1. [70] This was a safe assumption for Fe, but because FeO is not stoichiometric it can have varied activities. FactSage was used to compute the activity of FeO for the three temperatures examined. [85] At 600 °C FeO remains stoichiometric so it's activity remains 1. At 700 °C activity reduces to 0.991, and at 800 °C the

phase continues to become metal deficient and activity decreases to 0.981. These values cause negligible changes to the calculated oxygen partial pressures. The combinations of sample composition and oxidation conditions are given in Table 5.1. This methodology varied from traditional experiments utilizing Rhines packs as the powder mixture and samples were not sealed in an evacuated quartz tube.

$$Fe(s) + \frac{1}{2}O_2(g) = FeO(s)$$
 (Eq. 5.1)

$$\Delta G^0 = -263,700 + 64.35 T [J/mol]$$
(Eq. 5.2)

T, p ₀₂ wt% Y	$600 \ ^{\circ}C$ $p_{O_2} = 10^{-25} atm$	$700 \ ^{\circ}C$ $p_{O_2} = 10^{-22} atm$	$800 \ ^{\circ}C$ $p_{O_2} = 10^{-19} atm$
1.5	5, 10, 24, 48, 72 hr	5, 10, 24, 48, 72 hr	2, 5, 10, 24, 48, 72 hr
3	5, 10, 24, 48, 72 hr	5, 10, 24, 48, 72 hr	2, 5, 10, 24, 48, 72 hr
6			2, 5, 10, 24, 48, 72 hr
12			2, 5, 10, 24, 48, 72 hr
15	5, 10, 24, 48, 72 hr	5, 10, 24, 48, 72 hr	2, 5, 10, 24, 48, 72 hr
1.5 rolled	5, 10, 24, 48, 72 hr	5, 10, 24, 48, 72 hr	2, 5, 10, 24, 48, 72 hr

Table 5.1. Summary of alloy compositions and oxidation conditions.

5.2.3 Sample Analysis

After oxidation, samples were sectioned and mounted so that the oxidation front would be visible via microscopy. They were then prepared for microscopy by grinding to a 1200 grit finish with SiC abrasive paper, and further polished using 1 µm colloidal silica. A Phillips XL-30 scanning electron microscope (SEM) equipped with a field emission gun was used in backscattered electron (BSE) imaging mode to observe microstructures and determine the depth of internal

oxidation. Energy dispersive x-ray spectroscopy (EDS) was used to qualitatively analyze composition. The image analysis program ImageJ was used to measure microstructural features from the images. [88] At higher magnifications, a JEOL2000EX transmission electron microscope (TEM) was used to examine oxide shape and size. Further TEM analysis was carried out using a Technai F20 field emission TEM in scanning (STEM) mode. The use of a high angle annular dark field (HAADF) detector enabled samples to be imaged with mass contrast, as opposed to diffraction contrast.

5.3 Results

5.3.1 Unoxidized Microstructures

Characteristics of as-melted microstructures are detailed in Chapter 4. Discrete regions of primary Fe were observed in the majority of samples, and a fine eutectic was identified at higher Y contents. Backscattered SEM images of the rolled and unrolled 1.5 wt% Y alloys are seen in Figure 5.1. Other samples were too brittle to be subjected to the rolling procedure.



Figure 5.1. BSE images of unoxidized, unrolled (A) and rolled (B) 1.5wt% Y samples. Light grey phases represent Fe₁₇Y₂, while dark grey regions are Fe.
5.3.2 Oxidized Microstructures

Typical internal oxidation behavior was illustrated in Figure 5.2 for the 12 wt% Y alloy. A reaction front was clearly visible. EDS confirmed the presence of O, Fe, and Y in the region marked "Oxidized $Fe_{17}Y_2$." Only Fe was detected in the region marked "Unoxidized Fe". Only Fe and Y (no O) were detected in the region labeled "Unoxidized $Fe_{17}Y_2$ ".



Figure 5.2. Near-surface BSE image of a 12 wt% Y sample oxidized for 72 hr at 800 °C. This image illustrates the relevant oxidized and unoxidized regions.

The internal oxidation penetration depth was easily identifiable using SEM for all alloys. Example images are given in Figure 5.3. At low magnifications oxidized phases appear to be one new phase, though at higher magnifications using SEM (Figure 5.4) and TEM (Figure 5.5), at least two phases were visible. After oxidation at 800 °C, oxides were rod-like with diameters

approximately 80 nm. The rod-like morphology was again observed after oxidation at 600 °C, but the sizes were smaller, approx. 5-10 nm. These oxides could only be resolved in the TEM. The orientation of the rods appeared to be random. STEM images captured using the HAADF detector showed the oxides in the microstructure with the removal of noise from diffraction contrast in Figure 5.6. A series of STEM images were also recorded at varying tilts to confirm the presence of oxides in Figure 5.7.



Figure 5.3. Fe-1.5 (A), -3 (B), -6 (C), -12 (D), and -15 (E) wt% Y samples after oxidation at 800 °C and various times showing the front of internal oxidation.



Figure 5.4. SEM images of oxides in a 12 wt% Y sample after oxidation at 800 °C for 72 hours.



Figure 5.5. TEM images of 3 wt% Y samples oxidized for longer than 24 hours at both 600 °C (A) and 800 °C (B).



Figure 5.6. STEM-HAADF micrographs of samples oxidized at 600 and 800 °C. Oxidized regions are noted and dark grey networks are oxides. Oxides are circled in the 800 °C sample, but were too fine to note in the 600 °C case



Figure 5.7. STEM micrographs from samples oxidized at 800 °C at 0° of tile, +5°, and -5°.

5.3.3 Oxidation Kinetics

Penetration depth of the internal oxidation front was plotted as a function of time in Figure 5.8 for all compositions, temperatures, and times. Penetration depths were measured on at least 3 images. Standard deviations were less than $5 \,\mu$ m.



Figure 5.8. Penetration depth of the oxidation front as a function of time for 600, 700, and 800 $^{\circ}\mathrm{C}$

5.3.4 Effect of Rolling

Oxidized microstructures of rolled alloys are illustrated in Figure 5.9, with their as-cast counterpart for comparison. Penetration depth of the two samples was plotted as a function of time in Figure 5.10. Standard deviations were again less than 5 μ m.



Figure 5.9. Oxidized unrolled (A) and rolled (B) 1.5wt% Y Samples.



Figure 5.10. Penetration depth as a function of time comparing rolled and unrolled 1.5 wt% Y samples.

5.4 Discussion

5.4.1 Microstructure

As shown in Figure 5.1, rolling effectively broke down the $Fe_{17}Y_2$ from a connected network to isolated areas of approximately 10 µm in diameter. After oxidation, no external oxide layers were detected in any sample. This suggests the environment was sufficiently controlled and the partial pressure of oxygen at the oxide/metal interface was defined by the Rhines pack and was equal to that for Fe/FeO equilibrium (Equations 5.1 and 5.2).

The contrast between the oxidized and unoxidized regions was easily observed in SEM images. EDS verified the presence of oxygen in regions that were previously $Fe_{17}Y_2$, while no oxygen was detected in Fe. The oxidized regions had the same distribution as the $Fe_{17}Y_2$. This was consistent with *in situ* oxidation. [21] The oxides formed have not yet been identified, but other work in this system suggested they could be Y_2O_3 , YFeO₃, or $Y_3Fe_5O_{12}$. [16,27] Theory

presented in Chapter 3 indicated that they were most likely Y_2O_3 with some potential for YFeO₃. Because oxidation was performed in Rhines packs, identification of the oxides using XRD was not possible.

TEM better showed that oxides were randomly oriented rods with approximate diameters of about 80 nm when samples were oxidized at 800 °C (Figures 5.5 and 5.6). At 600 °C oxides were similarly shaped but size was reduced to approximately 5-10 nm. These results were consistent with previous observations on an oxidized Fe-Y intermetallic. [16] STEM further confirmed these assertions. The matrix phase and oxides were clearly visible with diffraction contrast removed. Varying the tilt during imaging resulted in no observed changes to the micrographs, confirming the rods were oxides, and not an artifact of microstructural features such as grain boundaries.

5.4.2 Kinetics

Oxidation kinetics were analyzed by producing parabolic plots (square of penetration depth with time) as seen in Figure 5.11. The R^2 values for linear trendlines averaged 0.921 ± 0.097 with one value below 0.875. These fitting parameters suggested a single parabolic rate constant could not describe behavior over the entire time period. This was consistent with thermogravimetric measurements on Fe – 15 wt% Y alloy performed by Niu et al. [27]



Figure 5.11. Penetration depth squared as a function of time for all oxidized samples accompanied by linear trend lines which define parabolic rate constants.

The initial period of oxidation was better described by a single parabolic rate constant. Since the kinetics were not continuously measured in this study, the point where rates began to deviate was not discretely determined. An approximate transition point was found at 10 hours. While based on fewer data points than when considering the entire 72 hour oxidation period, the rate constants utilizing the first 10 hours of data were adequate for identifying trends in the data and clearly identified the transition in behavior at extended times. As discussed below, rate constant magnitudes were much higher than expected assuming rate control by bulk diffusion of oxygen. This was attributed to fast-path diffusion of oxygen at the large interfacial area formed between the metal and the large number of small oxides that form in the regions that contained $Fe_{17}Y_2$.

A transition point was expected because oxide size should increase as a function of penetration depth, blocking the fast oxygen diffusion paths. The extent to which rates changed at longer times was dependent on microstructure (which was determined by yttrium content). The

1.5 wt% Y alloy oxidized much more slowly at longer times, which could be attributed to coarsened oxides more quickly blocking the regions for oxygen diffusion. This would explain why, over time, the 3 wt% Y alloy starts to show penetration depths greater than that of the 1.5 wt% Y alloy. While additional work is necessary to more precisely describe behavior over the entire time period, the discussion below focuses on oxidation times less than 10 hours (when kinetics described by a single parabolic rate constant) to examine trends in temperature, wt% Y, and $Fe_{17}Y_2$ morphology.

For times less than 10 hours, rate constants were calculated with average R^2 values of 0.97 on parabolic plots for all temperatures and wt% Y. These rate constants are plotted in Figure 5.12 and listed in Table 5.2. For comparison, values calculated from the classical Wagner theory (Equation 2.12) are also listed in Table 5.2. This calculation assumes the yttrium was present in solution rather than as a discrete phase and further assumes bulk diffusion of oxygen controls the overall internal oxidation rate. Diffusivity data from Takada et al. was used (Equation 5.3), and the surface oxygen content was taken to be the solubility limit in Fe (Equation 5.4), also reported by Takada et al. [89]

$$D_0 = 1.79 x \, 10^{-3} \exp\left(-85.7 k J/mol / RT\right) [cm^2 s^{-1}]$$
 (Eq. 5.3)

$$N_o^{(s)} = 0.381 \exp(-104 \, kJ/mol/RT)$$
 (Eq. 5.4)



Figure 5.12. Parabolic rate constant as a function of wt% Y for times less than 10 hr.

Table 5.2. Experimental (k_{exp}) and theoretical (k_{th}) rate constants calculated from the classical Wagner theory of internal oxidation.

	800) °C	700 °C		600 °C		
wt% Y	k_{th} [µm ² /hr]	k_{exp} [µm ² /hr]	k_{th} [µm ² /hr]	k_{exp} [µm ² /hr]	k_{th} [µm ² /hr]	k_{exp} [µm ² /hr]	
1.5	20.2	394.8	2.25	178.6	0.2	24.8	
3	9.5	246.3	1.07	86.3	0.1	23.4	
6	5.0	170.65	-	-	-	-	
12	2.4	181.0	-	-	-	-	
15	1.8	152.4	0.2	48.2	0.01	15.2	
1.5 rolled	20.2	133.2	2.25	62.6	0.2	19.7	

The results in Table 5.2 and Figure 5.12 showed experimental rate constants decreased with increasing yttrium content and decreasing temperature. Oxidation of the 6 and 12 wt% Y

samples at 600 and 700 °C was not carried out because the trends were qualitatively the same as those at 800 °C as shown in Figure 5.12. Examination of the 600 °C data in Table 5 shows oxidation rate is still a function of Y content at lower temperatures. All measured rates were substantially faster than their theoretical counterparts. This increase in rate was consistent with other work on two-phase alloy internal oxidation. Figures 5.5 and 5.6 showed the high density of rod-like, nanometer scale oxides, which provided a high interfacial area for rapid oxygen diffusion. Oxide precipitates with orientations both normal to and parallel to the metal surface were observed. Previous studies on two-phase alloy oxidation attributed the enhanced kinetics in part to fast diffusion of oxygen down oxide/metal interfaces. Enhanced diffusion of oxygen at interfaces has also been observed during oxidation of single phase alloys, e.g Ni-Al system, where rod-like internal Al₂O₃ form. [32,33]

The well-connected $Fe_{17}Y_2$ regions were found to be critical for rapid penetration. Comparison of the rolled and unrolled samples showed that (1) rolling broke up the connected $Fe_{17}Y_2$ phase and (2) kinetics were much slower and closer to (but still greater than) Wagner theory predictions. This finding supported the hypothesis that diffusion along interfaces in the oxidizable $Fe_{17}Y_2$ regions was largely responsible for the accelerated oxidation rate. When these regions became isolated from one another, as in the rolled samples, diffusion through the Fe matrix must occur, slowing the oxidation rate.

It was also possible transformation stresses played a role, as the amount of transforming material was smaller as wt% Y decreased and this transforming material was constrained by the surrounding Fe. This possibility was not examined in detail, however extruded pure Fe regions at the original interface were observed in samples with high Y content (12+%). Regions of pure

solvent metal extruded above the oxide/metal interface have been suggested to occur due to high stress in the internally oxidized region. [20]

The dependency of oxidation rate with alloy Y content is more complex than predicted by Equation 2.12, which predicts that the rate constant will be inversely proportional to the concentration of solute present in the oxidizable phase. In Equation 2.12, the solute is assumed to be dissolved in solution, while in this study the concentration of solute $(N_v^{(o)})$ stays constant and equal to 0.105 within regions of $Fe_{17}Y_2$. Therefore if the oxidation rate was solely controlled by oxygen diffusion normal to the surface, the rate should be independent of bulk alloy yttrium content. The decrease in rate with bulk yttrium content was attributed to oxygen supply. The amount of oxygen required to create an internally oxidized layer of a certain depth increases as the bulk yttrium content increases. Since layer growth is so fast, the supply of oxygen from the Rhines pack may be insufficient to maintain a rate controlled by solid state oxygen diffusion. This possibility was raised in analysis of enhanced diffusion in Ni-Al alloys. [32,33] Limitations on oxygen supply would lead to the lower rates in alloys of 12 wt% and 15 wt% yttrium. At lower yttrium levels, rates would be higher because sufficient oxygen would initially be present but as time increased a transition to oxygen supply-limited behavior could occur. This may also be an effect of utilizing a non-traditional Rhines pack methodology. These considerations in addition to the possibility of oxide coarsening raised illustrate several complications to analyzing kinetics of two-phase alloy oxidation.

5.4.3 Variations in Rhines Pack Methodology

The utilized Rhines packs were atypical, as the pack and sample were not sealed together an evacuated quartz tube. This necessitated consideration of oxygen transport to the surface of the

samples in both the current and traditional circumstances. In a near vacuum, as would be the case in the traditional Rhines pack methodology, the flux of oxygen molecules colliding with the sample surface (in mol/m²/s) is defined by the Hertz-Knudsen-Langmuir equation, where α is the adherence coefficient, p_{O2} is in Pa, and M_{O2} is in kg/mol. [90]

$$j_{02} = \alpha \frac{p_{02}}{(2\pi M_{02}RT)^{.5}}$$
(Eq. 5.5)

Assuming oxidation at 800 °C in a traditional Fe/FeO Rhines pack, estimating a partial pressure of 1 x 10^{-15} Pa (1 x 10^{-20} atm), the flux of oxygen molecules striking a sample surface is calculated to be about 2.4 x 10^{-17} mol/m²/s.

In the presently examined case diffusion of oxidant molecules occurs through the Rhines pack itself, and Argon carrier gas is also utilized. At 800 °C and 1 x 10^{-20} atm, the diffusivity of O₂ molecules in Argon gas (D_{O2-Ar}) was calculated to be about 2.4 cm²/s using the Chapman-Enskog equation, which took into account molecular collisions between Ar and O₂. In this equation σ is the effective collision diameter and Ω is the collision integral. [90]

$$D_{O2-Ar} = \frac{0.001858T^{3/2}}{P\sigma_{O2-Ar}^2 \Omega_D} \left[\frac{M_{O2} + M_{Ar}}{M_{O2}M_{Ar}} \right]^{1/2}$$
(Eq. 5.6)

This was then compared to the Knudsen diffusivity of oxygen, where there is an absence of molecular collisions and collisions with pore walls dominate ($D_{O2,K}$). In this equation d_p is the size of the pores in the Rhines pack. This was taken to be about 8 µm, calculated by assuming a powder diameter of approximately 5 µm and a porosity of 0.4. The Knudsen diffusivity was calculated to be 22.3 cm²/s. This values is about 10 times larger than that of the diffusivity considering molecular collisions. While this is initially counterintuitive, the large pore sizes likely minimize collisions.

$$D_{O2,K} = \frac{d_p}{3} \sqrt{\frac{8RT}{\pi M_{O2}}}$$
(Eq. 5.7)

The two diffusivity values can be estimated to combine as a series of resistances according to Equation 5.8. This new diffusivity is then manipulated to consider the tortuosity (τ) and porosity (ϕ) of the Rhines pack. Tortuosity was estimated to be 2, and porosity was again estimated to be 0.4. This leads to an effective diffusivity of about 0.43 cm²/s, which is then converted to a flux of 4.9 x 10⁻²¹ mol/m²/s. [90]

$$\frac{1}{D_{O2,T}} \cong \frac{1}{D_{O2-Ar}} + \frac{1}{D_{O2,K}}$$
(Eq. 5.8)

$$D_{O2,EFF} = \frac{\phi}{\tau} D_{O2,T}$$
 (Eq. 5.9)

This flux is lower than that of oxidation with a Rhines pack in an evacuated quartz tube by four orders of magnitude, indicating a clear difference in the mass transfer of oxygen to the sample surfaces when comparing the two methods.

Some sources of error remain in this calculation, making it difficult to exactly quantify the difference in behavior between the evacuated/sealed Rhines pack and the presently examined atypical case. One complicating factor is the fact that the Ar carrier gas is only 99.999% pure. The oxygen impurity in the gas was not great enough to promote the formation of an external Fescale, but this additional oxygen may contribute to increase the flux of O₂ through the Rhines pack. Along with this the regions of the pack in close contact with the specimen surface may be the main contributor to establishing oxygen partial pressure at the Fe/FeO equilibrium value. These factors make it difficult to calculate exact mass transfer conditions during oxidation in the atypical Rhines pack set up that was used. Experimentally, oxidizing in an evacuated and sealed pack could yield a more direct comparison. As opposed to repeating the oxidation process in sealed packs it was decided that oxidizing under a continuous flow of reactive dilute gasses would also provide easy manipulation of oxidant partial pressure and correct for any effects of oxidant depletion from the pack over time. This would simplify relevant mass transfer processes to solid-state diffusion through the internally oxidized zone and gas phase mass transfer.

5.5 Conclusions

- Binary Fe-Y alloys with Y content between 1.5 and 15.8 wt% Y undergo diffusionless, or *in situ* internal oxidation when subjected to low oxidant partial pressures between 600 and 800 °C. This was consistent with behavior in other two-phase alloys.
- Oxidation kinetics, measured by O penetration depth, were initially parabolic. Rates deviated from parabolic behavior at longer times (approximately > 10 hours). For all wt% Y and temperatures, rates were significantly faster than predicted by the Wagner theory of internal oxidation. The increase was attributed to rapid O diffusion along metal/oxide interfaces. A high density of nano-scale oxides formed, leading to a large interfacial area available for O diffusion.
- Penetration rate increased as wt% Y decreased. This was attributed partially to limited oxygen supply from the Rhines pack. Penetration depths decreased and oxide particles were smaller at lower oxidation temperatures. More work is necessary to quantify microstructures and explain kinetics at long oxidation times.
- The connectivity of the oxidizable intermetallic phase was critical to achieving the fastest oxidation rates.

Chapter 6

Effects of Oxidant Pressure on Kinetics and Microstructure *Chapter partially adapted from: S.J. Kachur and B.A. Webler: Met. Trans. E, (2016)*

6.1 Introduction

Internal oxidation can also be studied by exposing samples to oxidants diluted by an inert gas. Oxidation in dilute gases is also of practical importance. Much attention has been devoted recently to the behavior of structural alloys for helium-cooled nuclear reactors, where oxidizing contaminants in the helium can lead to internal oxidation, among other phenomena. [30] The dilution of oxidants by an inert gas creates the possibility of oxidation rate control by mass transfer in the gas phase. [31] While most internal oxidation studies rates will be controlled by solid state diffusion of oxygen, the presence a high density of interfaces or dislocations can increase the diffusivity of oxygen by orders of magnitude and other rate-controlling processes may be possible.

Studies in Chapter 5 examined the effects of microstructure and solute content on *in situ* oxidation kinetics in Fe-Y alloys containing 1-15 wt% Y oxidized between 600 and 800 °C for 2 – 72 hours in an Fe/FeO Rhines pack to establish low oxygen partial pressures. [91] As expected, all alloys exhibited in-situ oxidation with penetration rates much higher than predicted assuming rate control by bulk diffusion of oxygen in iron. The penetration rates were not purely parabolic, with deviations noted after approximately 10 hours exposure. These deviations were

suggested to be caused by the nucleation of larger oxides as oxygen was depleted at the front of internal oxidation. In addition, oxidation rates decreased as overall alloy yttrium content increased. This should not have been the case for two-phase alloys because the concentration of yttrium in the oxidizable phase (the $Fe_{17}Y_2$) is independent of alloy yttrium content. This is in contrast to single phase alloys, where the solute is evenly distributed, and rates should be inversely proportional to solute content as shown by Equation 2.12. However, it is still true that more oxygen is needed to create IOZs of equivalent depth in a higher yttrium alloy than in a lower yttrium alloy. Calculations of the flux of oxygen to the sample surface were somewhat ambiguous, as traditional Rhines pack methodology was not followed, making it difficult to form a complete estimate of the mass transfer conditions and oxidation kinetics.

To continue studying these effects in a more fixed environment and observe how *in situ* oxidation rates changed over time with variations in oxygen supply, thermogravimetric analysis (TGA) was used to measure weight gain during oxidation. Experiments occurred at 800 °C, at varied oxidant partial pressures and oxidant flow rates. This allowed for the study of potential mass transfer and microstructural effects on *in situ* oxidation behavior. Additional microstructural evaluation was carried out with scanning electron microscopy and canonical correlation analysis (CCA) was used to examine the relationships between the numerous variables examined.

6.2 Technical Approach

6.2.1 Alloy Preparation

Fe-Y alloy buttons approximately 6 mm thick and 30 mm diameter were made in a laboratoryscale electric arc button remelt furnace using 40-50 grams of 99.97+% pure Fe pieces and 99.9% 40 mesh Y powder. Samples had nominal Y contents of 1.5, 3, 6, 12, and 15 wt%. Arc melting occurred in a Cu crucible under inert Ar gas. Complete alloy preparation details are outlined in Chapter 4.

6.2.2 Sample and Furnace Parameters

Oxidation was performed using a Setaram SETSYS Evolution thermogravimetric analysis (TGA) furnace, which measured continuous weight gain during oxidation of Fe-1.5, -3, -6, 12 and -15- wt% Y alloys. Samples were approximately 1.25 x 0.75 x 0.1 cm rectangular pieces with a 1 mm diameter hole drilled near an edge. Samples with 15wt%Y were too brittle to properly drill, so they were hung with wrapped high purity platinum wire during oxidation. Surfaces were ground to a 600 grit finish on all sides with SiC abrasive paper and then cleaned with ethanol. The surface area of each sample was measured with the software ImageJ after imaging with a stereomicroscope. [88] The furnace heated and cooled at 99°C/min, and an isothermal hold occurred at 800°C for 5 to 24 hours.

6.2.3 Atmosphere Control

A dry gas mixture of 5% H_2 and 95% Ar gas was utilized during oxidation. The gas contained a small amount of oxygen impurity (approximately 1 ppm) which equilibrated with the hydrogen at 800°C. The oxygen pressure after equilibration was measured to be 10^{-25} atm using a zirconia oxygen sensor. To examine potential effects of gas phase mass transfer, experiments were conducted at varied flow rates. The volumetric flow rate of the gas was either 80 or 230 mL/min (linear flow rates of 0.5 and 1.5 cm/s).

After oxidation experiments occurred at 10^{-25} atm, a DewGen high accuracy dew point generator, seen in Figure 6.1, was installed prior to the gas inlet of the furnace. Gas flowed through the DewGen, which allowed for dew points to be generated between +15 and -80°C. Equations 6.1 and 6.2 were used to estimate the required dew point to establish a specific oxygen partial pressure during oxidation. [92] Using these equations a dew point of 3.7°C was estimated to approach the oxygen partial pressure (~10⁻²⁰ atm) provided by the Fe/FeO equilibrium of Rhines packs used in prior experiments at 800°C. An intermediate pressure (5 x 10⁻²³ atm) was also achieved at the dew point of -26.6°C. At 10⁻²⁰ atm oxidation lasted 10 hours, and at 5 x 10⁻²³ atm time was reduced to 5 hours.

$$log_{10}p_{satH20} = \begin{cases} 9.80 \frac{DP}{273.8+DP} - 2.22 & if DP \le 0^{\circ}C \\ 7.58 \frac{DP}{240+DP} - 2.22 & if DP > 0^{\circ}C \end{cases}$$
(Eq. 6.1)

$$\frac{1}{2}\log_{10}p_{02} = 3.00 - \frac{13088}{T} + \log_{10}\left(\frac{p_{satH20}}{p_{H2}}\right)$$
(Eq. 6.2)

Since fine changes in the settings of the DewGen could produce large changes in dew point, a DewMaster hygrometer (Figure 6.2) was also installed before the inlet to ensure proper atmospheric conditions were maintained throughout the duration of the experiment. All samples oxidized are summarized with their oxidation conditions in Table 6.1.



Figure 6.1. DewMaster dew point control unit. [93]



Figure 6.2. DewMaster dew point monitor. [93]

P _{O2} (atm)	Dew Point (°C)	Temperature (°C)	Gas Flow Rate (mL/min)	Time (hr)	S	ampl (es Oz wt%Y	xidize ()	ed
1 x 10 ⁻²⁰	3.7	800	80	10	1	3	-	-	15
1 x 10 ⁻²⁰	3.7	800	230	10	1	3	-	-	15
5 x 10 ⁻²³	-26.6	800	80	5	1	3	-	-	15
5 x 10 ⁻²³	-26.6	800	230	5	1	3	-	-	15
1 x 10 ⁻²⁵	-40	800	80	24	1	3	6	12	15
1 x 10 ⁻²⁵	-40	800	230	10	1	3	6	12	15

Table 6.1. Sample, furnace, and atmospheric parameters for all experiments.

6.2.4 Characterization

Following oxidation samples were sectioned, ground, and polished to a 1- μ m finish before imaging using an FEI Quanta 600 field emission gun-SEM and XRD analysis with a Rigaku MiniFlex diffractometer. To correct for microstructural variation sample to sample, the area fraction of Fe₁₇Y₂ was measured near the surface of each sample from 3 different regions and an average value was recorded using ImageJ software. The depth of internal oxidation was also measured at each region and averaged. At higher magnifications, oxides were imaged in 3 locations: (1) the surface of the sample, (2) half the penetration depth of internal oxidation, and (3) the front of internal oxidation.

6.2.5 Canonical Correlation Analysis

Due to the large number of input and output variables associated with present experiments, CCA, a form of linear subspace analysis, was implemented to better quantify and visualize relationships between variables. More information about CCA is found in Chapter 2. Oxidation data from all trials was separated into input/independent variables and output/dependent

variables according to Equation 6.3. Input variables were oxidation time (t), partial pressure (P₀₂), Y-content (wt% Y), and flow rate (flow). Output variables were the parabolic rate constants for both regimes of oxidation (k_i and k_i), penetration depth (X), the percent change in oxide size from sample surface to the oxidation front ($\%\Delta d_{OX}$), and the percent change in rate constant from region I to II ($\%\Delta k$). Calculations were performed and plotted using R software, version 3.3.2, along with packages *car* and *yacca*. These results were combined with physical theory to cohesively explain observed kinetics and microstructure. [94,95]

$$\vec{X} = \{t, P_{02}, wt \%Y, flow\}$$

$$\vec{Y} = \{k_i, k_{ii}, X, \%\Delta d_{0X}, \%\Delta k\}$$
(Eq. 6.3)

6.3 Results

There were three main sets of results generated from the above tests:

- Section 6.3.1 Oxidation kinetics as mass change per unit area vs. time, measured continuously during oxidation
- Section 6.3.2 Penetration depths of the internally oxidized zone, measured from low magnification SEM images of the oxidized microstructures
- Section 6.3.3 Post oxidation microstructures, including oxide particle sizes, measured from high magnification SEM images

6.3.1 Oxidation Kinetics

Weight gain data was recorded as a total sample mass gain as a function of time. Typically this data is normalized to the sample surface area. In the Fe-Y system, however, only the $Fe_{17}Y_2$ phase oxidizes. Therefore the mass change data was normalized to the following quantity (sample surface area)*(area fraction $Fe_{17}Y_2$). The area fraction of $Fe_{17}Y_2$ phase was measured

from BSE-SEM images and was reported in Table 6.2. For the purpose of these measurements eutectic regions in the 12 wt% Y alloys were estimated to consist of only $Fe_{17}Y_2$, and 15 wt% Y alloys were assumed to be single phase $Fe_{17}Y_2$ (area fraction = 1). The mass change per unit area $Fe_{17}Y_2$ was plotted in Figures 6.3 – 6.5 for all Y-contents oxidized at all three partial pressures and both flow rates examined.

	Area Fraction Fe ₁₇ Y ₂									
Sample (wt%Y)	1	.5		3	(6	1	2	1	5
Flow Rate (mL/min)	80	230	80	230	80	230	80	230	80	230
10^{-20} (atm)	0.076	0.072	0.211	0.238	-	-	-	-	1	1
5×10^{-23} (atm)	0.070	0.067	0.147	0.193	-	-	-	-	1	1
10^{-25} (atm)	0.034	0.056	0.204	0.363	0.309	0.315	0.763	0.703	1	1

Table 6.2. Area fraction $Fe_{17}Y_2$ of each oxidized sample



Figure 6.3. Mass change per unit area, adjusted for area fraction of $Fe_{17}Y_2$ as a function of time for 1.5 wt% Y alloys. Curves are included for all atmospheres and flow rates examined.



Figure 6.4. Mass change per unit area, adjusted for area fraction of $Fe_{17}Y_2$ as a function of time for 3 wt% Y alloys. Curves are included for all atmospheres and flow rates examined.



Figure 6.5. Mass change per unit area, adjusted for area fraction of $Fe_{17}Y_2$ as a function of time for 15 wt% Y alloys. Curves are included for all atmospheres and flow rates examined.

Parabolic rate constants (*k*) were calculated as summarized by Equation 6.4, by performing a linear regression on these plots after squaring the y-axis. Rate constants were calculated for the initial period of oxidation (hours 0-1.5, k_i) and a second region following a transition in behavior (hour 3.5 – end, k_{ii}). All curves were divided into 2 regions, but there were cases (samples oxidized at 10^{-20} atm) where a single rate constant did an adequate job describing the data for the duration of oxidation. These values are recorded in Table 6.3, and an example plot of the curves used to calculate these constants is shown in Figure 6.6. Figures A1 – A3 in Appendix A show all curves. These are presented as weight gain per unit area Fe₁₇Y₂ squared, as a function of time.

$$k = \left(\frac{\Delta m}{area * f_{Fe17Y2}}\right)^2 * \frac{1}{t}$$
(Eq. 6.4)



Figure 6.6. Representative mass change curves used to calculate parabolic rate constants for all oxidized 1.5 wt% Y alloys. Regions are separated by dotted red lines which mark transitions in oxidation behavior.

$P_{O2} = 10^{-25}$	80 m	L/ min	230 m	L/min	
wt% Y	$k_i (mg^2/cm^4/s)$	k_{ii} (mg ² /cm ⁴ /s)	$k_i (mg^2/cm^4/s)$	k_{ii} (mg ² /cm ⁴ /s)	
1.5	7.68 x 10 ⁻³	1.09 x 10 ⁻⁵	2.42×10^{-3}	6.44 x 10 ⁻⁵	
3	4.73 x 10 ⁻⁴	3.90 x 10 ⁻⁶	1.39 x 10 ⁻⁵	4.13 x 10 ⁻⁶	
6	8.24 x 10 ⁻⁴	2.10 x 10 ⁻⁵	3.64 x 10 ⁻⁵	2.46 x 10 ⁻⁵	
12	3.97 x 10 ⁻⁵	2.64 x 10 ⁻⁶	2.35 x 10 ⁻⁵	4.83 x 10 ⁻⁵	
15	8.50 x 10 ⁻⁵	1.16 x 10 ⁻⁶	1.76 x 10 ⁻⁵	3.37 x 10 ⁻⁵	
$P_{O2} = 5 \times 10^{-23}$	80 mL/min		230 mL/min		
wt% Y	$k_i (mg^2/cm^4/s)$	k_{ii} (mg ² /cm ⁴ /s)	$k_i (mg^2/cm^4/s)$	k_{ii} (mg ² /cm ⁴ /s)	
1.5	4.75 x 10 ⁻³	7.48 x 10 ⁻⁴	3.48 x 10 ⁻³	1.04 x 10 ⁻³	
3	8.54 x 10 ⁻⁴	1.41 x 10 ⁻⁴	4.58×10^{-4}	1.20×10^{-4}	
15	4.56 x 10 ⁻⁵	1.60 x 10 ⁻⁵	7.82 x 10 ⁻⁵	4.61 x 10 ⁻⁵	
$P_{O2} = 10^{-20}$	$P_{O2} = 10^{-20}$ 80 mL/min		230 mL/min		
wt% Y	$k_i (mg^2/cm^4/s)$	k_{ii} (mg ² /cm ⁴ /s)	$k_i (mg^2/cm^4/s)$	k_{ii} (mg ² /cm ⁴ /s)	
1.5	9.02 x 10 ⁻⁴	6.62 x 10 ⁻⁴	2.02×10^{-3}	1.01×10^{-3}	
3	1.12×10^{-4}	9.89 x 10 ⁻⁵	2.15×10^{-4}	1.28 x 10 ⁻⁴	
15	8.68 x 10 ⁻⁵	5.86 x 10 ⁻⁵	1.43×10^{-4}	9.04 x 10 ⁻⁵	

Table 6.3. Parabolic rate constants for region I (k_i) and II (k_{ii}) for all oxidized samples.

6.3.2 Internally Oxidized Zone Penetration Depth Measurements

Low-magnification micrographs of the microstructures oxidized at 10^{-20} atm, taken with backscattered SEM are shown in Figure 6.7. These micrographs are representative of microstructures observed for all samples, and dotted lines note the internal oxidation front. Penetration depths for all samples are listen in Table 6.4.



Figure 6.7. Backscattered electron images of oxidized 1.5-, 3-, and 15-wt%Y alloys, oxidized under high and low flow conditions at 800°C at 10^{-20} atm for 10 hours.

	Penetration Depth (µm)									
Sample (wt%Y)	1	.5		3	(6	1	2	1	5
Flow Rate (mL/min)	80	230	80	230	80	230	80	230	80	230
10 ⁻²⁰ (atm)	74.2	71.3	73.0	70.3	-	-	-	-	35.3	39.1
5×10^{-23} (atm)	19.3	23.4	16.5	16.5	-	-	-	-	9.3	10.0
10 ⁻²⁵ (atm)	32.7	26.4	22.9	26.7	19.7	29.7	14.7	32.7	13.4	37.6
Standard deviations typically less than 5.0 µm										

Table 6.4. Penetration depths of internal oxidation for all oxidized samples

6.3.3 Sample Surfaces, Oxide Identification, and Size Measurements

Oxidizing with the dilute gas mixtures, as opposed to Rhines packs, yielded samples with clean surfaces. This allowed for both SEM and XRD analysis that was not possible previously due to signal from the Fe/FeO mixture. First SEM showed protruded nodules on the surfaces of 1.5 and

3 wt% Y alloys in Figure 6.8. XRD results from a 3 wt% Y alloy, with Fe and Y_2O_3 peaks identified, are shown in Figure 6.9.



Figure 6.8. Backscattered electron images of the surfaces of a 1.5- and 3-wt%Y alloy immediately following oxidation. Nodules are Fe (blue X's) and regions immediately near these nodules also contain O and Y (red X's). Regions far from nodules are pure Fe (blue X's).



Figure 6.9. XRD results from a 3wt% Y alloy following oxidation.

Characteristic micrographs of oxides from 15 wt% Y samples oxidized at 5 x 10^{-23} atm are shown in Figure 6.10. Oxide particle sizes were imaged and measured at three locations: (1) near the sample surface, (2) halfway through the internally oxidized zone, and (3) at the boundary separating oxidized and unoxidized material. Measurements were performed manually on 15 discrete oxides per micrograph. Oxides were randomly selected for measurement, and values were then averaged. Figure 6.11 shows plots of oxide size as a function of penetration depth for all samples examined. Graphs of oxide size with corresponding standard deviations are shown in Figure 6.12. Where oxides were unresolvable (all samples oxidized at 10⁻²⁰ atm and near surface regions in 1.5 and 3 wt% Y alloys at $10^{-23}/10^{-25}$ atm), they were estimated to be 10 nm in diameter. This value was selected based on both SEM and TEM images. The smallest resolvable and measurable oxides using SEM were 16.0 nm, establishing an upper boundary of the possible sizes of these unresolvable oxides. In other samples where oxides were unresolvable with SEM (those oxidized in Rhines packs at 600 °C) oxides were shown to be between 5 and 10 nm with TEM. This presents a realistic floor of potential oxide diameter, establishing a potential range between 5 and 16 nm. Because of this 10 nm was considered to be a good estimate for the average oxide size. Figures B1 – B6 in Appendix B show oxides at the surface, mid-point, and front for each sample oxidized at 5 x 10^{-23} and 10^{-25} .



Figure 6.10. Representative micrographs of a 15 wt% Y alloy, oxidized at 5 x 10^{-23} atm P₀₂, illustrating how oxide size changes as a function of penetration depth within the alloy. Similar images for all alloys are found in Appendix B, Figures B1 – B6.



Figure 6.11. Oxide size measurements and standard deviations for samples oxidized at 10^{-23} and 10^{-25} atm



Figure 6.12. Plots of oxide size as a function of penetration depth for samples oxidized at 10^{-23} and 10^{-25} atm at low and high flow rates. When oxidized at 10^{-20} atm oxides were unresolvable and estimated to be 10 nm.

6.4 Discussion

Discussion was divided into three main areas

- Section 6.4.1 Pre-oxidation microstructures were analyzed. While the majority of microstructures were identical to those observed in previous chapters, some variation was seen when comparing 15 wt% Y alloys because samples came from two different solidified alloy buttons.
- Section 6.4.2 An analysis of potential weight gain due to the permeability of Fe was performed in order to justify normalizing rate constants by area fraction of Fe₁₇Y₂. General relationships between rate constants and oxidation conditions were qualitatively identified
- Section 6.4.3 Canonical correlation analysis was used to further quantify the relationships between input and output variables. Flow rate was found to minimally alter kinetics, while oxide size was identified as a critical factor for determining oxidation rates.

6.4.1 Microstructure

Microstructures presented in Figure 6.7, paired with EDS, again showed clear indication that *in situ* oxidation of $Fe_{17}Y_2$ intermetallic occurred in the absence of an external scale, and the depth of internal oxidation was clearly visible. Unoxidized microstructures of the 15 wt% Y alloys varied slightly, as a new alloy button needed to be made after the original was fully used in previous experiments. The differences between these microstructures were discussed in Chapter 4, and their micrographs are shown again in Figure 6.13. Alloys oxidized at 10^{-25} atm were from the original alloy button, while at elevated pressures the second button was used. Alloys were

still deemed adequate for comparisons of oxidation kinetics, as a large amount of eutectic was still present in the alloy, and compositions likely only differed by about 1 wt%. Along with this, no noticeable perturbations in the movement of the internal oxidation front were noticed when comparing oxidized regions of primary intermetallic and the eutectic in these alloys.



Figure 6.13. BSE images of the eutectic composition of two 15 wt% Y alloys, with oxidation conditions that samples were used for noted.

Surface images from the 1.5 and 3 wt%Y alloys in Figure 6.8 showed nodular extrusions characteristic with volume expansion resulting from internal oxidation. These surface features followed a distribution identical to the $Fe_{17}Y_2$ morphology observed in sample cross sections. This was easier to observe in the 3 wt%Y alloy, likely due to the increased volume fraction of intermetallic phase resulting in more densely populated networks of nodes at the surface. EDS identified the extrusions as pure Fe, which was anticipated. Regions immediately next to the nodes contained Fe along with traces of Y and O, indicating that underneath, Y-rich intermetallic had oxidized resulting in the transformation stresses necessary to form the Fe extrusions. Moving further away from the nodes, pure Fe is the only element present in the smooth surface regions. This lends further substantiation to the theory that volume expansion during *in situ* oxidation can

cause residual stresses and dislocation formation, partially promoting accelerated oxidation kinetics, along with diffusion along oxide/matrix interfaces.

XRD shown in Figure 6.9 identified the presence of multiple peaks corresponding to Y_2O_3 , matching predictions from theory and work by other authors. While it was still possible that double oxides such as YFeO₃ formed, they were not identified, and Y_2O_3 is likely found to predominate. Using an SEM with improved resolution, oxides were resolvable in most samples, as illustrated in Figure 6.10, and Appendix B Figures B1 – B6. Oxides were unresolvable throughout the entire depth of penetration when oxidized at 10^{-20} atm and at near surface regions when oxidized at 10^{-23} and 10^{-25} atm. Other samples showed the clear trend, as predicted by theory and outlined in Chapter 2, that larger oxides nucleated as penetration depth increased. The formation of larger oxides at lower pressure was also expected, due to the fact that in oxygen lean environments, supersaturation at the oxidation front is difficult to maintain.

6.4.2 Oxidation Kinetics

During thermogravimetric analysis, it is possible that a fraction of the recorded mass change was a direct result of dissolved oxygen in the unoxidized iron matrix. An attempt was made to quantitatively estimate this effect using traditional diffusion-based analysis. Surface oxygen contents were estimated for each case examined, according to the methods used by Huin et, al. in Equation 6.5 and are listed in Table 6.5. [92]

$$log_{10}C_0^{surf} = 1.00 + \frac{9398}{T} + \frac{1}{2}log_{10}p_{02}$$
(Eq. 6.5)

PO_2 (atm)	Dew Point (°C)	C _o ^{surf} (ppm)
1 x 10 ⁻²⁵	-40	0.00181
5 x 10 ⁻²³	-26.2	0.0406
1 x 10 ⁻²⁰	3.7	0.574

Table 6.5. Calculated atmospheric conditions during thermogravimetric analysis

Assuming a semi-infinite planar specimen, with surface oxygen content (C_S) held constant throughout the duration of the experiment, the inward diffusion of oxygen is described by Equation 6.6. [96]

$$\frac{C(x,t)-C_S}{C_0-C_S} = \operatorname{erf}\left(\frac{x}{2\sqrt{Dt}}\right)$$
(Eq. 6.6)

Under the assumption that the initial concentration of oxygen in the sample (C_0) is equal to zero, the equation can be manipulated to calculate the amount of oxygen (M) that has entered the alloy after a given time. This equation is further altered to account for oxygen pickup from both faces of the sample. [96]

$$\left(D\frac{\partial C}{\partial x}\right) = \frac{DC_S}{\sqrt{\pi Dt}}$$
(Eq. 6.7)

$$M = 2C_S \left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} s$$
 (Eq. 6.8)

Applying these calculations to the most oxygen rich environment, and assuming a 24 hour-long experiment, provides an upper boundary for the greatest amount of weight gain of a sample observed that is not related to sample oxidation, but rather the permeability of the iron matrix. Figure 6.14 shows concentration profiles for various experiment durations calculated using Equation 6.6.



Figure 6.14. Concentration of oxygen in an Fe sample as a function of penetration depth for 1 - 72 hours of oxidation at 10^{-20} atm

After 24 hours of oxidation, Equation 6.8 was used to show that 661 ppm O entered the sample. This value was also confirmed by performing a numerical integration of the curve plotted in Figure 6.14. The number was then estimated as the concentration of oxygen throughout the entire sample and converted to a value of 0.0189 wt% O. Assuming a typical sample size (about 1 cm² surface area and about 1 mm thick sample) this concentration was then converted to expected mass gain per unit area. This final value was 0.075 mg/cm² for a partial; pressure of 10^{-20} atm. A similar calculation at the lowest oxygen partial pressure yielded 2.36 x 10^{-4} mg/cm². Therefore these calculations indicated that the measured weight gain in each experiment performed can be attributed solely to the internal oxidation of Fe₁₇Y₂, and not to dissolved oxygen in the Fe matrix, indicating that normalizing weight gain data to the area fraction of intermetallic was the proper step to take when analyzing data.

Figure 6.5 qualitatively showed that in single phase Fe₁₇Y₂ (15 wt% Y samples) increasing oxidant partial pressure led to higher rate constants. Figures 6.3 – 6.5 and Table 6.3 show that total mass change per unit area was greatest in the 1.5 wt% Y alloys after accounting for area and the fraction of Fe₁₇Y₂, while the 15 wt% Y alloys showed the least mass gain. This was true for all three pressures examined regardless of flow rate. The effects of varying flow rate and partial pressure were unclear for the low wt% Y alloys, where microstructure and distribution of Fe₁₇Y₂ likely played larger roles. Oxidation at 10⁻²⁵ atm was not necessarily fixed at this exact partial pressure for all trials, as it is possible that the amount of oxygen impurities in the H₂-Ar gas mixture varied experiment to experiment. This was not an issue at elevated partial pressures, as the dewpoint control system was utilized to control the atmosphere. This would lead to randomness when comparing samples oxidized at 10⁻²⁵ atm to samples oxidized at other pressures, and also complicate analyzing the effects of changing flow rates after oxidation at 10² atm. The minimal differences in flow rates at elevated partial pressures indicated this to be the most likely scenario, along with the aforementioned variability of microstructure.

In order to simplify this analysis, the percent decrease in rate constant from region one to region two was calculated and listed in Table 6.6. The percent increase in oxide size from the alloy's surface to the oxidation front was also added to Table 6.6. Increasing partial pressure yielded smaller changes in rate constant over time, signaling better description by traditional parabolic oxidation kinetics, and flow rate effects were again ambiguous. This was further substantiated by the calculated changes in oxide diameter, as the most drastic decreases in rate constant throughout the depth of penetration (10^{-20} atm trials), changes in oxidation rate were minimized.
This helped confirm the idea that fast path oxygen diffusion is occurring along the oxide/matrix interfaces in the internally oxidized zone.

Table 6.6. The percent change in parabolic rate constant from region I to region II along with the percent change in oxide size from the sample surface to the oxidation front for all Y-contents, partial pressures, and flow rates examined.

$P = 10^{-25}$	% Ch	ange <i>k</i>	% Change <i>d_{OX}</i>		
$P_{02} - 10$	(Region	I to II)	(Surface to Oxidation Front)		
wt% Y	80 mL/min 230 mL/min		80 mL/min	230 mL/min	
1.5	-99.9	-97.8	503.2	26.8	
3	-99.2	-60.0	896.0	64.7	
6	-97.5	-50.0	896.0	64.7	
12	-92.5	150	326.1	52.1	
15	-98.9	50	326.1	52.1	
D 5 10-23	% Change k		% Change <i>d_{OX}</i>		
$P_{02} = 5 \times 10$	(Region I to II)		(Surface to Oxidation Front)		
wt% Y	80 mL/min	230 mL/min	80 mL/min	230 mL/min	
1.5	-85.4	-71.4	978.6	226.2	
3	-88.9	-80.0	114.9	269.9	
15	-60.0	-37.5	92.4	8.6	
$P_{O2} = 10^{-20}$	% Change k		% Change <i>d_{OX}</i>		
	(Region I to II)		(Surface to Oxidation Front)		
wt% Y	80 mL/min	230 mL/min	80 mL/min	230 mL/min	
1.5	-22.2	-50	0	0	
3	0.0	-50	0	0	
15	-33.3	-10	0	0	

6.4.3 Canonical Correlation Analysis

In order to better visualize and analyze the relationships between all considered input and output variables, data was subjected to a canonical correlation analysis (CCA). The first results of this analysis were 3 separate cross correlation matrices for all input and output variables. In these matrices, red squares indicate strong, positive correlation between variables (R = 1), and dark blue squares represent strong negative correlations (R = -1). Green squares specify that no correlation exists between variables (R = 0). Matrices are shown in Figures 6.15 – 6.17. First input variables are compared to other input variables (Figure 6.15), followed by a comparison of output variables (Figure 6.16), and lastly an analysis between the two (Figure 6.17). Certain areas have been outlined and numerically labeled to correspond to the following analysis.



Figure 6.15. Correlation plot showing the direct correlations between input variables. Dark red boxes imply a strong positive correlation, while dark blue imply a strong negative correlation. Green boxes suggest no correlation. Boxes relevant to analysis have been outlined and numbered for reference.



Figure 6.16. Correlation plot showing the direct correlations between output variables. Dark red boxes imply a strong positive correlation, while dark blue imply a strong negative correlation. Green boxes suggest no correlation. Boxes relevant to analysis have been outlined and numbered for reference.



Figure 6.17. Correlation plot showing the direct correlations between input and output variables. Dark red boxes imply a strong positive correlation, while dark blue imply a strong negative correlation. Green boxes suggest no correlation. Boxes relevant to analysis have been outlined and numbered for reference.

As anticipated, little correlation existed between input variables after examination of Figure 6.15. The negative correlation between time and P_{O2} (area 1, Figure 6.15) was consequence as shorter experiments were necessitated at elevated P_{O2} to conserve gas. This was because generating higher P_{O2} levels required higher flow rates through the DewGen system, prior to a reduction in flow rate as the gas entered the furnace. Shorter experiments were deemed to be of sufficient length for a direct comparison to the data presented in Chapter 5, as the transition in oxidation behavior occurred within the first two hours of the experiment.

Correlations between output variables in Figure 6.16 were evident, as larger rate constants in one region, predict larger rate constants in the other (area 2, Figure 6.16). This was anticipated, but was not a perfect correlation, as the samples that did not follow good parabolic behavior sometimes had drastic decreases in rate. This is observed in the 1.5 wt% Y samples oxidized at 10^{-25} atm. Penetration depth of the oxidation front was shown to have little correlation with the initial oxidation rate, yet had a strong positive correlation with k_{ii} values (area 3, Figure 6.16). Despite typically larger k_i values, this was likely explained by the extended amount of time spent in the k_{ii} regime. The other key relationship between output variables was that large increases in oxide size were accompanied by decreases in penetration depth and large decreases in rate from region one to region two (area 4, Figure 6.16). This added more quantitative evidence supporting observations from Table 6.6 and is explained in further detail in Chapter 7.

The correlations between input and output variables were largely as expected, with factors like k_i , k_{ii} , and X negatively correlated with yttrium content (area 5, Figure 6.17). Increased flow rate was slightly correlated with minimized changes in both oxide size and rate constant, but surprisingly did little to vary raw rate constant values (area 6, Figure 6.17). The fact

that the actual rate constants did not change with flow rate point to this being an anomaly within the results, likely caused by variations in the amount of oxygen impurity in the gas during the 10⁻²⁵ atm trials. These experiments actually showed a decrease in oxidation rate when increasing gas flow. This runs counterintuitive to theory, as changing gas flow should only have an effect if it acts as the rate-limiting step during oxidation, and if this were the case linear oxidation kinetics would be observed. Along with this increasing flow would increase the flux of oxidant to the surface, increasing rate constant values. Also unexpectedly, increases in partial pressure seemed to have no effect on k_i , but positively correlated with k_{ii} and X (area 7, Figure 6.17). The only variable having a strong influence on k_i was yttrium content, suggesting that a microstructure could again be influencing kinetics.

This analysis showed simple correlations between two chosen variables, but CCA results further showed how combinations of variables interacted with one another. The canonical correlations for four computed canonical variates are found in Table 6.7, while the canonical weights and loadings for each input and output parameter are listed in Table 6.8. Plots of the four canonical variates are shown in Figure 6.18.

	CV1	CV2	CV3	CV4
R	0.93	0.80	0.48	0.21
\mathbb{R}^2	0.87	0.64	0.23	0.05

Table 6.7. Canonical correlations for the four calculated canonical variants

	Weights			Loadings				
Parameters	CV1	CV2	CV3	CV4	CV1	CV2	CV3	CV4
Time	0.071	-0.033	0.128	-0.071	0.180	-0.736	0.568	-0.321
P _{O2}	0.367	0.280	0.297	0.089	0.564	0.696	0.109	0.430
Wt%Y	-0.111	0.042	0.116	0.048	-0.716	0.207	0.605	0.280
Flow Rate	-0.0003	0.007	0.003	-0.012	-0.208	0.639	-0.127	-0.730
k i	53.587	-133.408	-176.620	-567.419	0.353	-0.423	-0.619	-0.541
k _{ii}	65.258	1510.737	-2714.453	1828.231	0.458	0.366	-0.781	0.211
X	0.048	-0.0003	0.029	0.002	0.738	0.526	0.219	-0.029
%Δd _{ox}	0.001	-0.002	0.0001	0.002	0.078	-0.868	-0.284	0.350
%Δk	-0.010	0.004	-0.003	-0.001	-0.353	0.598	0.156	-0.042

Table 6.8. Canonical weight and loadings for each parameter and each canonical variate. Values noted in analysis have been highlighted



Figure 6.18. Plots of the weighted data defining the 4 calculated canonical variates (CV1 - CV4)

Of the four canonical variates, CV1 and CV2 explain the majority of the correlation found in the data set. The third and fourth variates still explain some of the residual correlation, but Figure 6.18 shows that they do not follow linear relationships. Examination of the loadings listed in Table 6.8 provide a summary of which variables contribute most to each variate, with relevant values in bold print and highlighted. Loadings are used, as opposed to weights, due to the likely presence of multicollinearity within the data set.

The input variables that most heavily influence variate 1 are oxygen partial pressure and alloy composition, and they most directly affected penetration depth, and to a lesser extent individual rate constant values. Variate 2 was heavily dependent on time and pressure, and to a lesser extent flow rate, while change in oxide size and change in rate constant were the output variables most affected. The individual rate constant variables were also heavily influenced by variate 3, indicating fairly weak relationships. This matches well with the qualitative examination that an obvious trend was not present in their values. This analysis identified relevant correlations within the data set but, but required further analysis to connect these experimentally observed trends to physical theory.

6.5 Conclusions

• *In situ* oxidation was carried out in Fe-Y alloys over a range of oxygen partial pressures at varied oxidant flow rates. Kinetics were not typically well described by a single parabolic rate constant, with a transition in behavior occurring after about 1.5 hours of oxidation.

- Oxide size increased as a function of penetration depth in agreement with theory. The largest increases in oxide size were found to correlate with the largest decreases in rate constant in samples over time.
- CCA identified sample decreased solute content and increased oxidant partial pressure as the factors most responsible for increased oxidation rates. The calculated rate constant in region II was more strongly correlated with penetration depths than the constant corresponding to region I.
- Flow rate had a minimal effect on rate constant values, indicating gas phase mass transfer effects are limited. Effects of changing flow rate are likely an artifact of the variability of results at 10⁻²⁵ atm due to limited control of the levels of oxygen impurity in the absence of the dewpoint generation system.
- CCA both confirmed earlier examined trends and identified the importance of considering the effect of oxide size on kinetics in the present system. More work was needed to connect these statistical results to physical descriptions.

Chapter 7

Modeling Oxide Size Effects on Oxidation Kinetics

7.1 Introduction

While CCA confirmed some trends discussed in previous chapters, and identified others, further physical explanations are still necessary to connect parts of this analysis to mass transfer and oxidation theory. One of the most prominent correlations identified was that lower pressures and flow rates resulted in the formation of larger oxides over time and a decreases in rate constant from region 1 to 2. The definition of two rate constants from the experimental data was done to simplify the analysis. In principle the rate constant was a continuous function of the internally oxidized zone depth because oxide size increased with penetration depth. The approach of Stott et al in Chapter 2 was used here to connect oxygen diffusivity to oxide size and oxide size to penetration depth, thereby enabling a depth-dependent rate constant to be defined. The goal of this analysis was to determine:

(1) if fast path diffusion along oxide/matrix interfaces can increase oxidation rates to the magnitudes experimentally observed and

(2) if increasing oxide size as a function of penetration depth could cause oxidation kinetics to deviate from traditional parabolic behavior in a manner similar to recorded data.

7.2 Defining Effective Diffusivities and Effective Rate Constants

The approach of Stott/Whittle., as outlined in Chapter 2, determined the effect of changing the diameter (*d*) of a rod-like oxide on the effective diffusivity of oxygen. [32,33] There were two parts to this analysis: the first was defining how the oxygen diffusivity changed with oxide size and second was defining how the oxide size changed with depth. Assuming negligible flux of oxygen occurs through formed oxides, the effective diffusivity (D_{eff}) of oxygen is estimated to be a function of the oxygen diffusivity (D_o) through the fraction of metal lattice (f_L) and the interface diffusivity of oxygen (D_{Oi}) along the fraction of oxide-metal interface (f_i).

$$D_{eff} = D_0 f_L + D_{0i} f_i \tag{Eq. 7.1}$$

First the estimated fractions of interface and metal lattice were made. The relationship between the relevant constituents in the microstructure was:

$$f_L + f_{int} + f_{OX} = 1$$
 (Eq. 7.2)

The total oxide fraction was theoretically constant (f_{OX}) regardless of oxide size or shape within an oxidized region of formerly Fe₁₇Y₂. Using Appendix images B1 – B6 and the thresholding capabilities of ImageJ software, the average value of f_{OX} was measured to be 0.338. [88] Equation 7.3 defines the total volume of an individual oxide with a given diameter and length (*L*). Equation 7.4 can then be used to determine the total number of oxides (n_{OX}) present in a given volume of intermetallic (V_{tot}).

$$v_{OX} = \pi \left(\frac{d}{2}\right)^2 L \tag{Eq. 7.3}$$

$$n_{OX} = \frac{v_{tot} f_{OX}}{v_{OX}}$$
(Eq. 7.4)

The volume of interface between matrix and one oxide can then be calculated, in nanometers, assuming the interface to be a 1 nm thick cylindrical shell surrounding a cylindrical oxide, according to Equation 7.5. This was consistent with the initial derivation. [32, 33]

$$v_{int} = \pi L(wd + w^2) \tag{Eq. 7.5}$$

After this, the total volume of interface (V_{int}) is found using Equation 7.6, while the total volume of oxides (V_{OX}) is calculated with Equation 7.7. The fraction of interface and lattice are then found with the relationships shown in Equation 7.8 and 7.9.

$$n_{OX}v_{int} = V_{int} \tag{Eq. 7.6}$$

$$n_{OX}v_{OX} = V_{OX} \tag{Eq. 7.7}$$

$$V_{int}/V_{tot} = f_{int}$$
 (Eq. 7.8)

$$1 - f_{int} - f_{OX} = f_L (Eq. 7.9)$$

Simplifying equations 7.6 - 7.9 leads to formulas that define the fraction of interface and lattice as functions of the variable oxide diameter, and the constant oxide fraction (Equations 7.10 and 7.11). These are then used to calculate an effective diffusivity in Equation 7.12 and consequently an effective rate constant in Equation 7.13. The final assumption made in this equation is that interface diffusivity of oxygen is about 1000 times that of lattice diffusivity, an intermediate value estimated in the work from which this derivation is based. [32,33] Effective diffusivity values, which range from 7 to 150 times greater than lattice diffusivity values, are plotted as a function of oxide diameter in Figure 7.1.

$$f_{int} = \frac{4f_{OX}(d+1)}{d^2}$$
(Eq. 7.10)

$$f_L = 1 - f_{OX} - \frac{4f_{OX}(d+1)}{d^2}$$
 (Eq. 7.11)

$$D_{eff} = D_0 \left[1 - f_{OX} - \frac{4f_{OX}(d+1)}{d^2} \right] + (1000D_0) \frac{4f_{OX}(d+1)}{d^2}$$
(Eq. 7.12)

$$k_{eff} = \frac{2N_0^S D_{eff}}{\nu N_B^O}$$
(Eq. 7.13)



Figure 7.1. Effective diffusivity of oxygen, as calculated according to Equation 7.12, as a function of oxide diameter

Calculating solubility values based on surface oxygen content, according to the methods of Swisher et al. then allows the conversion of effective diffusivity values to effective parabolic rate constants, which were plotted as a function of oxide diameter in Figure 7.2. This plot shows three distinct regions, each corresponding to a different oxygen partial pressure. At 10⁻²⁰ atm, effective rate constants converge onto one value, as oxide size was estimated as constant

throughout these alloys. With the exception of one outlier point at 10-23 atm, the largest spread in effective rate constants occurred at 10-25 atm. The increasing spread with lower oxygen partial pressure was attributed to the inability to precisely control oxidant pressure control at 10⁻²⁵ atm, as outlined in Chapter 6.



Figure 7.2. Effective parabolic rate constants for all samples, plotted as a function of oxide diameter. Values at $10^{-20} P_{O2}$ are overlaid on one another due to constant oxide size. Dark grey circles indicate low flow, and black circles indicate high flow. Regions are color coded according to P_{O2}

7.3 Estimating Effective Oxide Penetration Depth

Experimental penetration depths, measured after oxidizing in both Rhines packs (Chapter 5) and thermogravimetric analysis (Chapter 6), clearly deviated from traditional Wagner theory. Effective rate constants calculated based on oxide diameter in the previous section show the general magnitude of effect that this variable can have locally, but do not take into account the fact that oxide sizes change as a function penetration depth in the alloy and therefore time. In order to asses this effect, the following three step approach was taken to compare experimentally measured penetration depths results to predicted penetration depths based on modifications of increasing complexity:

- (1) A single rate constant described internal oxidation. The rate constant was calculated using the lattice diffusion of oxygen in iron. This was a reference case for comparisons.
- (2) A single rate constant described internal oxidation. The rate constant was calculated using an effective oxygen diffusivity were estimated by multiplying the lattice diffusivity by a constant.
- (3) Effective diffusivities are defined according to Equation 7.12, and change throughout the depth of oxidation as oxide sizes increase. This is accomplished by integrating the parabolic rate law equation utilizing an effective rate constant which changes as a function of penetration depth. Three selected rates of oxide diameter (d) change as a function of time were selected

a.
$$d = zX + b$$

b. $d = zX^{1/2} + b$
c. $d = zX^3 + b$



Figure 7.3 shows the summary of these results and the calculation details are given in the subsections below.

Figure 7.3. Plots of experimentally measured penetration depth as a function of predicted penetration depth based on; traditional Wagner theory (black circles), lattice diffusivity multiplied by a factor of 1,000 (green circles) or 10,000 (red circles), or calculated assuming linear oxide growth (blue circles), $X^{1/2}$ oxide growth (grey circles), or X^3 oxide growth (orange circles). The dotted line represents a theoretical 1:1 match between the values

7.3.1 Traditional Rate Constant Estimation

Equation 2.13 was used to calculate the theoretical penetration depths for all alloys after thermogravimetric analysis. These were compared to experimental values and are plotted in black in Figure 7.3. Measured values ranged from about 10 to 150 times larger than theory predicted.

7.3.2 Traditional Rate Constant with Enhanced Diffusivity

Calculations from section 6.3.1 were repeated twice, but theoretical lattice diffusivity was multiplied by factors of 1,000 and 10,000 to account for the interfacial area of oxides. This was the estimated range proposed in past work. [32,33] These results are also plotted in green and red respectively in Figure 7.3. Multiplying diffusivity by 1,000 produced some estimations near the measured experimental values, but the majority were overestimated, as indicated by the slope of 0.32. Multiplying by 10,000 further overestimated values, reducing the slope of the plot to 0.10.

7.3.3 Variable Effective Diffusivity

While multiplying lattice diffusivity by 1,000 yielded improved predicted penetration depths, this methodology was overly simplistic and had minimal physical grounding. Instead of settling on one number it was better to consider how effective diffusivities changed over time. Calculating an effective penetration depth, assuming diffusivity changes as a function of time, and parabolic kinetics, required integration of Equation 7.14. In this equation, D_{eff} was defined as Equation 7.12, with the diameter term being a function of penetration depth.

$$\frac{dX}{dt} = \frac{k_{eff}}{X} = \frac{\frac{k_0}{D_{lattice}}}{X} D_{eff}$$
(Eq. 7.14)

This calculation is highly dependent on how the change in oxide size as a function of penetration depth and effective diffusivity values are defined. Because of this variability, the calculation was repeated three times, each time assuming different relationships between oxide size and penetration depth and changing the magnitudes of constants used to calculate effective diffusivity values.

7.3.3.1 Linear Oxide Growth

Initially, a linear regression was performed on the plots of oxide size vs penetration depth (Figure 6.12) to estimate how oxide size changed as a function of penetration depth. Linear growth of oxides provided fair estimation for all samples with the exception of 1.5 wt%Y alloys oxidized at 10⁻²³ atm under low flow. This was a clear outlier in the data, as oxide sizes varied within the sample to a much greater extent than in other samples. Equation 7.14 was then integrated, taking into account varying effective rate constant values, for each sample, to determine a new theoretical depth of internal oxidation. This integration is carried out in detail in Appendix C.

Figure 7.3 shows that for this effective diffusivity model (blue points), experimental values are only 1.5 to 10 times greater than theory. These results show an improvement over simply multiplying effective diffusivity by 1,000, as the slope in Figure 7.3 rose to 0.82, and took into account growth of oxides over time. Results of the integration expressed as penetration depth as a function of time are plotted in Figure 7.4. Points on the plot correspond to measured values in each sample after a discrete oxidation time, and are color-coded to correspond to each theoretical curve. In the majority of the cases, this modified theory still falls below measured outcomes, but there is a distinct improvement when compared to the original theoretical method.

One assumption made within this effective diffusivity model remained unexamined. The exact value of boundary diffusivity was still in question. In order to identify the degree to which changing this value alters results, calculations were repeated with a new value 10,000. Increasing this value improved the fits of the model at lower partial pressures, but exaggerated effects at 10⁻²⁰ atm. A value between the two is likely the most accurate, but this identified that the general

range of boundary diffusivity being between 1,000 and 10,000 times greater than lattice diffusivity to be accurate.



Figure 7.4. Plots of predicted penetrations depth of internal oxidation, based on varying oxygen diffusivity as oxide sizes increase, for each examined sample, as a function of time. Each curve has corresponding experimental values plotted as discrete points.

7.3.3.2 Oxide Growth as X^{1/2}

The approximation of linear oxide growth was not exact, and does not necessarily agree with theory. As discussed in Chapter 2, theory by Bohm et al. proposed a linear relationship between oxide size and penetration depth, but multiple sources indicate deviations form this ideal behavior. [34] Notably, Wood observed exponential relationships to the power n, with n falling between 0.5 and unity. [37] Altering this behavior to this square root relationship would cause changes in the shape of the curves plotted in Figure 7.4.

Measuring oxide sizes at more penetration depths would theoretically improve this error, but the lack of precise movement of the stage of the SEM at high magnifications made this impractical. As an alternative, the integration of Equation 7.14 can be easily repeated assuming different rates of change in oxide size. First a square root relationship was examined as suggested by Wood, according to Equation 7.15 where X is the penetration depth, d is the oxide diameter, Z is a constant, and b is the initial oxide size at the surface. [37]

$$d = z\sqrt{X} + b \tag{Eq. 7.15}$$

Figure 7.5 shows oxide size as a function of penetration depth with these trend lines estimated and plotted for each sample. Fits are relatively poor at 10⁻²⁵ atm and low flow, but the rest of the trial fit fairly well. These curves were used to estimate constants *z*, while b was estimated to be 10 nm. The full integration is found in Appendix D, and plotted for 3 wt% Y alloys under low flow in Figure 7.6. Figure 7.6 shows more of a transition in behavior than the one observed in the linear plots, but the shape of the curves still does not completely capture the effects observed in the experimental data. As seen in Figure 7.3 at the beginning of this section, using this relationship yielded superior results for predicting penetration depths than the linear model as the slope further increased from 0.82 to 0.88.



Figure 7.5. Oxide size as a function of penetration depth with trend lines indicating the square root relationship defined by Equation 7.15.



Figure 7.6. Curves of predicted penetration depth as a function of time for 3 wt% Y alloys oxidized at low flow. Curves were calculated assuming a square root relationship for the growth of oxides according to Equation 7.15.

7.3.3.3 Oxide Growth as X³

This process was repeated again assuming the cubic relationship shown in Equation 7.16. A cubic relationship has not previously been proposed, but fit the current data fairly well. In many samples oxide sizes do not start to increase until deep into the internally oxidized zone, where size increases rapidly, resembling cubic growth. The full integration is found in Appendix E, plots of oxide size as a function of penetration depth with this relationship are contained in Figure 7.7, and results of the integration for 3 wt% Y alloys at low flow are plotted in Figure 7.8.

$$d = zX^3 + b \tag{Eq. 7.16}$$



Figure 7.7. Oxide size as a function of penetration depth with trend lines indicating the cubic relationship defined by Equation 7.16.



Figure 7.8. Curves of predicted penetration depth as a function of time independent of alloy composition. Curves were calculated assuming cubic growth of oxides according to Equation 7.16. Constant values were estimated to match the relative scale of observed oxide sizes.

Observation of Figure 7.8 shows a slightly more abrupt change in oxidation behavior compared to the $X^{1/2}$ model, and similar effective penetration depths. An initial rapid period of oxidation is followed by a transition at approximately hour 1, followed by a prolonged, slow oxidation region. This curve shape is a not a perfect match for the experimentally acquired curves, but represents a notable improvement over both the linear model and theory.

Increasing the number of sites where oxide sizes were measured, and observing different planes of the sample through milling with a FIB to identify the 3-dimensional nature of the oxide rods should help to better identify the exact relationship between oxide size and penetration depth to further adapt these models. Despite these potential sources of error, and room for improvement, all models illustrated that accounting for changing oxide size throughout the depth of internal oxidation can increase the predictability of the magnitude of *in situ* oxidation kinetics in Fe-Y alloys. Assuming non-linear relationships between oxide sizes and penetration depths adapts the shapes of oxidation curves to better fit those observed experimentally.

7.4 Comparison to Rhines Pack Data

Integration was repeated utilizing oxide sizes measured with STEM in samples oxidized at 800 for 3 days in a Rhines pack from Chapter 5. STEM samples were taken from the front of internal oxidation, so based on final oxide size, constants were fit to reach this final value at the penetration depths of both a 1.5 and 15 wt% Y alloy. This was performed twice, once using the $X^{1/2}$ relationship, and a second time with the X^3 relationship. These are shown in Figures 7.9 and 7.10 respectively, with measured penetration depths from Rhines pack samples also plotted.



Figure 7.9. Plot of predicted penetration depth based on the $X^{1/2}$ relationship for a 1.5 and 15 wt% Y alloy. Corresponding penetration depth data from Rhines pack experiments is also plotted.



Figure 7.10. Plot of predicted penetration depth based on the X^3 relationship for a 1.5 and 15 wt% Y alloy. Corresponding penetration depth data from Rhines pack experiments is also plotted.

The X³ oxide growth model (Figure 7.10) shows good agreement between measured and predicted penetration depth in the 1.5 wt% Y sample, while over-predicting penetration for the 15 wt% Y sample by a factor of about 1.10. The X^{1/2} based model showed improved agreement for the 15 wt% Y alloy at the expense of the 1.5 wt% Y sample, as variations in oxide size had less of an effect on penetration depth. Ideally further measurements could be taken with STEM to determine constants for each sample, but it is evident regardless that the two extreme relationships identified based on integration of Equation 7.14 match well with the Rhines pack data acquired in Chapter 5. Rhines pack penetration depth data was also compared to the most comparable TGA data (10^{-20} atm) in Figure 7.11. Negligible difference was observed in the penetration depths of the 15 wt% Y alloys. The 1.5 and 3 wt% Y alloys both saw slight reductions in penetration depth when oxidized in Rhines packs. The magnitude of variation can explained by a secondary effect of local variations in Fe₁₇Y₂ (Table 6.2) and atypically sized oxides. This is further described in the following section.



Figure 7.11. Penetration depths of the internal oxidation front after 10 hours with oxidation conditions identified on the X-axis.

7.5 Atypically Sized Oxides

After quantifying the effects of oxide size on oxidation behavior over time, some variables were still left unexplained. Further evidence of microstructural effects were present when considering oxide size. While average oxide sizes were measured and calculated for each sample, noticeable outliers existed in the 1.5 wt% Y samples. In particular, when a region of intermetallic narrowed in width, thicker oxides appeared to form. This is seen in Figure 7.12, where one region of $Fe_{17}Y_2$ immediately next to another showed larger oxides as it constricted. Evidence was of a similar effect was also found in 12 wt% Y alloys (Figure 7.13), where the regions of intermetallic immediately surrounding α -Fe dendrites had larger oxides than the surrounding area. One possible explanation is that the oxides are oriented in a different direction, influencing their apparent size. Assuming this is not the case, these bottlenecking effects in low Y content alloys could further explain the magnitude of the decline in rate constant in certain 1.5 wt%Y alloys from region 1 to 2. If orientation is changing, further microstructural analysis via FIB could reveal this information, and be used to alter and improve the effective diffusivity model, as previously discussed.



Figure 7.12. A 1.5 wt% Y alloy oxidized at 10^{-25} atm and 230 mL/min showing both a narrow and wide region of oxidized intermetallic.



Figure 7.13. A near-front region of a 12 wt% Y alloy showing larger oxides surrounding an unoxidized Fe dendrite

7.6 Conclusions

- Post-oxidation microstructures were found to be a critical factor in explaining transitions in oxidation behavior over time
- Taking oxide size into account, an effective diffusivity of oxygen along the oxide/matrix interfaces could be calculated, and used to better predict penetration depth of oxidation than traditional Wagner theory. While this model, assuming linear growth of oxides, improved upon theoretical calculations, the shape of predicted oxidation curves did not match experimental data.
- Estimating the change in oxide size as a function of penetration depth as either cubic with relation to, or as the square of penetration depth, predicts an oxidation curve that better matches the shape of those observed experimentally. These represent extreme cases, where intermediate situations still adequately describe experimental behavior.
- At higher partial pressures, as expected, oxides were typically smaller. This allowed for the most rapid, and the most parabolic in shape, oxidation to occur. In oxygen lean environments a greater degree of randomness was observed in the data, as atmospheres were potentially not as well controlled and fluxes of oxygen to the surface were reduced.

Chapter 8

Equal Channel Angular Pressing of Oxidized Fe-Y Alloys

8.1 Introduction

Severe plastic deformation mechanisms would likely be necessary for recreating a Fe-based oxide dispersion strengthened alloy in the absence of the mechanical alloying process. Past research on the severe plastic deformation of alloys with second phase particles has yielded mixed success at both refining and distributing these particles. Oxidized Fe-1.5wt% Y microstructures, having a large density of nanometer scale oxides unevenly distributed throughout, provide reasonable starting points for an investigation of severe plastic deformation as it may apply to generating an ODS alloy.

Equal channel angular pressing was selected as the method for applying SPD to oxidized Fe-1.5 wt% Y microstructures. Unoxidized microstructures were also deformed to generate a baseline comparison. How both Y-rich oxides and unoxidized intermetallic deformed were of interest. Fe-Y samples were formed into rods and canned within the center of pure Fe billets so that the deformation process could occur. Pressing temperature and the number of passes were altered to study the extent of deformation behavior. Samples underwent annealing treatments at a two different temperatures post-ECAP to observe any oxide coarsening behavior and changes in microstructure. Vickers microhardness indentation was used to obtain general hardness data for each sample, and nanohardness indentation was used when greater precision was necessary. *In*

situ oxidation studies were also performed using a Rhines pack at 800 °C and kinetics were compared to previous work on the oxidation behavior of Fe-1.5wt% Y alloys with varied microstructures, as presented in Chapter 5.

8.2 Technical Approach

8.2.1 ECAP Preparation

Fe-1.5 wt% Y buttons were arc-melted as outlined earlier. Cylindrical rods were then cut out of the buttons using electrical discharge machining (EDM). Rods were approximately 2.5 cm long with a diameter of 0.6 cm. Each rod was surface treated with 600 grit SiC paper to remove oxide that formed during the cutting process. After removing all surface oxide, multiple samples were internally oxidized in a tube furnace at 800 °C for 5 days. *In situ* oxidation was again promoted using a Fe/Fe₂O₃ Rhines pack while UHP Ar gas flowed at 0.25 L/min.

Holes about 4 cm deep and 0.6 cm in diameter were then drilled at the ends of 99.9% pure Fe billets with dimensions $1.9 \times 1.9 \times 12$ cm and the Fe-Y rods were inserted, before being capped with an Fe plug. This is illustrated in Figure 8.1.



Figure 8.1. Schematic of Fe billets that held the Fe-Y alloy rods during ECAP.

8.2.2 ECAP

Seven different samples were prepared to undergo ECAP. Samples were either oxidized or unoxidized, and underwent four or eight passes at 25 or 350 °C. Samples and their designations are listed in Table 8.1. Room temperature pressing occurred at a displacement rate of 0.254 cm/s, and 0.635 cm/s at 350 °C. Samples were wrapped in Teflon during processing, and sliver grade anti-seize lubricant was applied to the die plates. Processing route B_C was used, meaning the samples were rotated 90° counterclockwise between each pass, and an equiaxed microstructure should be achieved. [55]

Temperature Alloy	25 °C	350 °C
1.5 wt% Y Oxidized	4 Passes (A) 8 Passes (B)	4 Passes (C) 8 Passes (D)
1.5 wt% Y Unoxidized	4 Passes (E) 8 Passes (F)	8 Passes (G)

Table 8.1. ECAP sample specifications and each sample's corresponding designation (A-G)

8.2.3 Post-ECAP Oxidation and Annealing

After ECAP billets were cross-sectioned, starting at the center, and moving outward, until the regions containing the Fe-Y rods were reached. Cuts were taken from each sample (A-G) and subjected to a high temperature anneal at 1000 °C for 10 hours. After analysis a low temperature treatment was also performed on samples A-D at 250 °C for 2 hours. Both annealing treatments were carried out in a tube furnace under flowing UHP Ar. Sections were also taken from unoxidized ECAP samples (E, F, and G) and then oxidized at 800 °C in a tube furnace, using an Fe/Fe₂O₃ Rhines pack, for 24 hours.

8.2.4 Analysis Methods

Samples were imaged with SEM after ECAP, and also after the separate oxidation and annealing treatments. Grain sizes were measured using the linear intercept method (ASTM E112) after imaging utilizing channeling contrast. [97] Vickers microhardness was used to determine hardness of the Fe-Y cores, as well as the Fe billet. An MTS Nanoindenter XP was used to measure the hardness in targeted regions throughout all samples, specifically the internally oxidized circumferences of the Fe-Y cores. Traces were also taken along the edge of the Fe billet and from the edge of the billet to the center to identify changes in the deformation of the Fe. The

indenter used a Berkovich tip and a fixed penetration depth of 2 μ m. 10-15 indents were taken in each region, as depicted by Figure 8.2.



Figure 8.2. Nanoindentation scheme used to analyze ECAP samples.

8.3 Results

8.3.1 Post-ECAP Microstructures

Microstructures taken with backscattered electron microscopy from the unoxidized Fe-Y cores of each ECAP sample (A-G) are shown in Figure 8.3. Light grey phases again correspond to

Fe₁₇Y₂, while the dark grey is α -Fe. Microstructures from the samples that were oxidized prior to ECAP (A-D) can be seen in Figure 8.4. These micrographs show the interface between Fe billet and Fe-Y rod near the top, the internally oxidized zone in the Fe-Y rod in the center, and the unoxidized core of the Fe-Y rod at the bottom. Table 8.2 contains grain size measurements for samples A-D within the oxidized region and in the unoxidized center.



Figure 8.3. Backscattered electron images of the unoxidized Fe-Y centers of ECAP samples A-G. Experimental conditions noted as number of passes (4P/8P), room temperature pressing or 350 °C (RT/Hot), and oxidized or unoxidized (Ox/UnOx)



Figure 8.4. Backscatter SEM images of ECAP samples A-D, showing the Fe billet near the top of each micrograph, the internally oxidized Fe-Y core, and the unoxidized Fe-Y core near the bottom. Number of passes (4P/8P) and pressing temperature (RT/Hot) are noted.

Table 8.2. Grain size measurements for samples A-D in both the oxidized and unoxidized Fe-Y regions with standard deviations

Sample	Region	Grain Size (µm)	
Λ (4 Passag 25 °C)	Oxidized Fe-Y	0.36 ± 0.06	
A (4 Fasses 25 C)	Unoxidized Center Fe-Y	0.42 ± 0.07	
D (8 Degree 25 °C)	Oxidized Fe-Y	0.35 ± 0.07	
B (8 Passes 25 C)	Unoxidized Center Fe-Y	0.36 ± 0.06	
C (4 Passage 250 °C)	Oxidized Fe-Y	0.49 ± 0.06	
C (4 Passes 330 C)	Unoxidized Center Fe-Y	0.75 ± 0.11	
D(8 Passas 350 °C)	Oxidized Fe-Y	0.53 ± 0.24	
D (8 Passes 550 C)	Unoxidized Center Fe-Y	0.81 ± 0.20	

8.3.2 Post-ECAP Annealing

No observable effects of annealing were identified in the unoxidized ECAP samples (E-G). Micrographs of the oxides in ECAP samples A-D, both before and after annealing at 1000 °C, are shown in Figure 8.5.



Figure 8.5. Backscattered electron images of oxides in samples A-D, both before and after an anneal of 1000 °C for 10 hours.

8.3.3 Hardness

Vickers microhardness is plotted for all seven samples post-ECAP and after the 1000 °C annealing treatments in Figure 8.6. This includes indents taken from the Fe-billet, and the Fe-Y core of each sample. A similar plot is shown with the addition of the low temperature anneal in Figure 8.7. Figure 8.8 shows microhardness values taken from pure, undeformed Fe, an undeformed Fe-1.5 wt% Y alloy, and the pure Fe centers of ECAP bars for comparison. Nanohardness indentation results are shown in Figures 8.9 and 8.10. Figure 8.9 compares hardness values of the unoxidized Fe-Y core to that of its oxidized circumference. Figure 8.10 shows the average hardness value for indentations taken along the edge of the Fe billet (red line), and hardness traces as a function of distance away from the edge, towards the center of the sample. Missing values and uneven distribution of indents as a function of distance in Figure 8.10 were likely caused by abortion of the indentation process due to abnormally high drift.



Figure 8.6. Microhardness data for ECAP specimens A-E from the pure-Fe billet and the Fe-Y core, both before and after annealing at 1000 °C.


Figure 8.7. Microhardness data for ECAP Specimens A-D from the pure-Fe billet and the Fe-Y core, both before and after 1000 and 250 °C annealing treatments.



Figure 8.8. Microhardness data for pure Fe from the center of the ECAP billets, an undeformed Fe rod, and an undeformed Fe-1.5wt% Y alloy.







Figure 8.10. Nanohardness data showing the average hardness of the edge of the Fe billet, and a trace of hardness from the edge of the billet to the interface between billet and core.

8.3.4 Post-ECAP Oxidation

Samples that were oxidized after ECAP (E-G) can be seen in Figure 8.11, with the front of internal oxidation distinguished. Table 8.3 summarizes measured penetration depth, and shows corresponding data from Chapter 5 for Fe-1.5wt% Y alloys as a comparison.



Figure 8.11. Backscattered images of samples (E-G) shown after undergoing a post-ECAP oxidation treatment at 800 °C for 24 hours in a Fe/Fe_2O_3 Rhines pack. Dotted line shows depth of internal oxidation.

Table 8.3. Penetration depth of post-ECAP oxidation treatment (800 °C, 24 hours, Fe/Fe₂O₃ Rhines pack) and corresponding values for similar alloys.

Sample	X (μm), 24 hours
1.5 wt% Y, Unrolled [91]	80.22 ± 4.42
1.5 wt% Y Rolled [91]	40.97 ± 3.82
E (4 Passes, 25 °C)	72.44 ± 5.20
F (8 Passes 25 °C)	96.90 ±8.95
G (8 Passes 350 °C)	60.10 ± 16.75

8.4 Discussion

8.4.1 Microstructure

Figure 8.3 shows the Fe-Y center of each sample post-ECAP. Similar to past results, the lighter gray phase is $Fe_{17}Y_2$, and the darker gray is α -Fe. Samples A and E, both pressed four times at

room temperature, retain some degree of networked Fe₁₇Y₂, though there are still some disrupted regions when compared to the as-cast microstructure. Increasing the number of passes at room temperature to eight (B and F) breaks up the intermetallic and disperses it evenly throughout the microstructure, similarly to the rolling treatments performed in previous experiments. This also corresponds to a slight reduction in grain size, as indicated in Table 8.2. All ECAP performed at 350 °C, both four and eight passes, achieved this dispersion as well. Increasing amounts of plastic deformation have been shown to break up and isolate Fe₁₇Y₂ previously at room temperature, so this result was expected. While four passes at room temperature did not achieve an even distribution of the phase, elevating temperature should theoretically increase the ease of flow of the Fe in the microstructure, allowing for the dispersion of the hard intermetallic even after four passes. Increasing temperature also caused average grain sizes to increase. While the same amount of strain was applied regardless of temperature, differences in microstructure were expected based on theory presented in Chapter 2. These micrographs show clear evidence that the hard intermetallic phase present at the center of the Fe billet can be refined and dispersed with increasing passes.

Figure 8.3 also contains sparsely distributed, relatively circular, dark regions. These are similar to regions observed in micrographs from previous chapters during oxidation studies. Two reasonable explanations exist for these pore-like regions. First it is possible that some degree of porosity formed during the solidification of the alloy. Another possible explanation is that a minor oxygen impurity during arc melting resulted in the premature oxidation of some of the yttrium powder. Upon polishing samples, it is likely that these larger oxides were pulled out of the microstructure leaving these regions behind. If significant differences in this porosity were

present from sample to sample, this would likely alter the results of ECAP, but there did not appear to be a noticeable change.

The front of internal oxidation around the circumference of the Fe-Y core is easily observed after ECAP in Figure 8.4 with the use of backscattered electron microscopy. The width of the region is also roughly the same in each microstructure, about 150 μ m. Oxides were easily visible at low magnifications. Past results showed that depletion of oxygen at the front of internal oxidation can lead to the nucleation of larger oxide particles over time. This likely occurred during this experiment, as oxidation times were two days longer than any previous experiments that were conducted.

Higher magnification images of the oxides in each sample are shown in Figure 8.5, along with the sample's annealed counterpart. Samples A, B, and C show a network of oxides, following the same distribution of the initial $Fe_{17}Y_2$ intermetallic phase. Sample D contains a much more sparse distribution of oxide. Oxide size is largest in sample A, and slightly smaller in B, C, and D. After annealing, there appeared to be minimal change in the oxide structure in sample A, though in B and C, the signs of the oxide network disappeared, and the microstructure was left with a dispersed oxide phase. Samples B, C, and D did not appear subject to any significant coarsening.

8.4.2 Hardness

Microhardness results suggested significant changes in samples that were not necessarily visible with SEM. Immediately after undergoing ECAP, Figure 8.6 shows clear data that Fe in samples B and F was hardest. These correspond to samples processed at room temperature for eight passes. Increasing pressing temperature to 350 °C or decreasing the number of passes to four

leads to a decrease in hardness. These trends are also observed in Figure 8.7. This agrees with theory as outlined in Chapter 5, more passes during ECAP leads to increased plastic deformation and a corresponding increase in hardness. Increasing pressing temperature allows softening and potential dynamic recrystallization of the Fe phase, decreasing hardness. This agrees with grain size data, indicating increases at higher temperatures. All ECAP samples have hardness values that are higher than pure, undeformed Fe.

Observing the microhardness of the Fe-Y core in Figure 8.8 shows similar trends. Holding temperature constant, an increased number of passes leads to increased hardness. Increasing pressing temperature in this case, leads to a more significant drop in hardness than it did in the Fe billet. Comparison of samples with identical processing parameters (A and E, B and F, C and G) shows that the presence of oxides decreases hardness in all cases. This effect was likely muted in this data, as the microhardness measurements incorporate both oxidized and unoxidized Fe-Y regions.

Annealing at 1000 °C also caused decreases in hardness for all regions of each sample. Along with the decrease there was a general normalization of values, with all samples converging to about 0.65 GPa in the Fe billet and 0.8 GPa in the Fe-Y core. This is expected, as the annealing treatment was likely at a high enough temperature and for a long enough time for microstructural recovery to occur. Past examples of annealed Fe-alloys after ECAP showed limited grain growth, but were often annealed at lower temperatures, indicating the possibility of both decreased dislocation density and increased grain size is possible in this instance. In order to better compare to these results, the low temperature anneal was performed. As shown in Figure 8.7, this anneal resulted in no identifiable changes in hardness, indicating a stable microstructure. Nanohardness data in Figure 8.9 showed that the oxidized Fe-Y in the samples pressed at 25 °C had marginally lower hardness than the unoxidized region. Oxides were not small enough to provide significant hardening, especially when compared to that of the brittle $Fe_{17}Y_2$. When pressing occurred at high temperatures, oxidized regions were measured to be harder. This shows that much of the decrease in hardness after high temperature ECAP that was observed by the microhardness data was mostly occurring within the unoxidized Fe-Y region, as opposed to being an undesired manipulation of oxide rich regions, such as coarsening. This result is corroborated by Figure 8.5, which showed an increased dispersion of oxide phase at higher temperatures, which likely led to strengthening of the material.

The plots in Figure 8.10 show the average nanohardness value of the edge of the Fe billet after ECAP (red line), and points from a trace of nanohardness from the edge to the center of the billet. Values nearly monotonically increase until reaching the interface between billet and Fe-Y center. At this point, immediately adjacent to the oxidized Fe-Y, there is a drop in hardness. These trends are present in all samples, and this likely points to an incompletely equiaxed microstructure post-ECAP.

8.4.3 Oxidized Microstructures and Kinetics

Oxidized microstructures showed clear evidence of *in situ* oxidation, with EDS confirming the presence of oxygen only in Y-rich regions of the microstructure. Penetration depths listed in Table 8.3 provide a general basis for comparison to past experiments. Values should theoretically be closer to those from the rolled 1.5wt% Y alloy studied in Chapter 5, listed in Table 5.2. Fast path diffusion along oxide/matrix interfaces was previously connected to accelerated kinetics, and it was shown that disrupting the network of oxidizable intermetallic

reduced oxidation rates, effectively cutting off high-diffusivity pathways. After four passes, with the Fe₁₇Y₂ slightly disrupted, oxidation depths begin to skew closer to that of the rolled 1.5wt% Y alloy. Sample F oxidized approximately notably faster than sample E, and slightly faster than undeformed Fe-1.5wt% Y samples, despite an even less well-connected intermetallic structure. It is likely that the increased number of passes during ECAP increased the dislocation density throughout the microstructure, providing an enhanced opportunity for fast-path diffusion of oxygen, and therefore increasing oxidation rate. The penetration depth was closest to the undeformed 1.5 wt% Y alloy in sample G, which underwent eight passes at 350 °C. In this instance, the elevated temperature during ECAP did not promote the same high dislocation density, so the fast path diffusion could not occur substantially along either the oxide/matrix interfaces or along dislocations.

Oxides were visible even at relatively low magnifications throughout the microstructure. It was anticipated that they would be similarly sized as those formed in other Rhines pack oxidation experiments, about 20-80 nm in diameter, but were orders of magnitude large. [75] It is possible that smaller oxides are also present in the microstructure, but they were not readily resolved. Deformation of the microstructure during ECAP may have allowed for small amounts of local Y diffusion, and a resulting oxide coarsening, or it is possible that Fe oxides may have formed near the Fe surface during ECAP, which are now more readily visible. Further analysis is necessary to verify oxide composition.

8.5 Conclusions

• Connected networks of unoxidized $Fe_{17}Y_2$ intermetallic are readily disrupted and dispersed evenly throughout the microstructure during ECAP. While increasing the number of passes to gain an even dispersion is necessary when processing occurs at room temperature, elevated temperatures allow easier flow of the Fe matrix and a more rapid Fe dispersion.

- Obtaining an even dispersion of oxides around the perimeter of the Fe-Y alloy cores was more difficult, and best-accomplished when processing occurred at both increased temperature and with more passes. Oxide size remained relatively constant. Annealing produced small degrees of coarsening. Micro and nanohardness results confirmed microstructural observations throughout.
- Oxidation penetration depths were inconsistent with past work on microstructural effects on *in situ* oxidation kinetics. After ECAP at room temperature, the deformation accelerated internal oxidation kinetics despite the break up and dispersion of Y-rich phases. This was likely explained by the introduction of dislocations during severe plastic deformation allowing for fast-path oxygen diffusion. After pressing at high temperatures, oxidation rates better-matched predictions, theoretically because of a reduction in dislocation density due to dynamic recrystallization.

Chapter 9

Conclusions and Future Work

9.1 Hypothesis

The following hypotheses were examined:

1) Deviations from traditional Wagner oxidation kinetics during in situ oxidation of binary, twophase, Fe-Y alloys are due to the distribution and connectivity of the intermetallic phase. The shape, size, and distribution of formed oxides determines the extent of enhanced solid state diffusion.

- In situ internal oxidation was promoted in binary two-phase Fe-Y alloys with Y content between 1.5 and 15 wt% using Fe/Fe₂O₃ Rhines packs and dilute gas atmospheres. Accelerated oxidation kinetics were observed as expected, though a single parabolic rate constant could not define the total duration of the experiment. Over time oxidation slowed, though microstructural evidence was not immediately observed to corroborate this observation.
- Rolling Fe-Y alloys to evenly disperse and isolate regions of intermetallic Fe₁₇Y₂ decreased oxidation rates as potential fast diffusion paths along oxide/matrix interfaces were isolated from one another. This required slower solid state diffusion through the Fe matrix to occur and acted as a rate limiting step. Monotonic decreases in oxidation rate with increasing solute content were

attributed to possible depletion of oxygen over time as the volume fraction of oxidizable phase increased, potentially exacerbated by the atypical Rhines pack methodology that was used. This confirmed the hypothesis that microstructural distribution of the oxidizable phase is critical to determining oxidation rate during *in situ* oxidation. Further work remained necessary to fully explain changes in oxidation rate with changes in a sample's bulk solute content and examine potential mass transfer effects between the oxidizing medium and the sample.

2) Manipulation of oxidizing atmospheres and gas flow rates can be utilized to control oxidation behavior. In the presence of accelerated solid state diffusion, gas phase mass transfer can emerge as the rate controlling factor for in situ oxidation.

- Thermogravimetric analysis was able to provide further insight into questions raised during Rhines pack experiments, while eliminating concerns about mass transfer through the pack. Kinetics were again not well described by a single parabolic rate constant, and typically featured a sharp decline after about 1.5 hours of oxidation. Effects of increasing Y-content were relatively clear, resulting in decreased oxidation rates. The effects of partial pressure and flow rate of the oxidant gas were less clear. In order to more easily observe trends within the data set, canonical correlation analysis was used to generate plots of correlation between all input and output variables and reduce dimensionality.
- Flow rate was found to have little effect on observed kinetics, indicating that gas phase mass transfer processes were not rate controlling. This ran counter to the proposed hypothesis. It remained possible that mass transfer processes played a

role in the Rhines pack experiments due to the atypical experimental set up, but thermogravimetric analysis experiments removed this variable as it related to *in situ* oxidation of multiphase alloys. This was corroborated by the absence of linear oxidation kinetics.

While gas phase mass transfer did not play a role in oxidation behavior, deviations from parabolic behavior were still left unexplained. Correlation analysis highlighted the relationship that increasing oxide sizes resulted in decreasing rate constants as a function of time, potentially explaining the observed behavior. In order to theoretically verify this relationship, a value for the effective diffusivity of oxygen along matrix/oxide interfaces was derived as a function of oxide diameter. By integrating traditional parabolic oxidation equations with this effective diffusivity term inserted, and oxide diameter defined as a function of penetration depth, predicted penetration depths were derived for all experimentally oxidized samples. This process was repeated multiple times incorporating varied relationships between penetration depth and oxide size. These different models improved upon traditional Wagner theory, both by increasing the theoretical expected penetration depth of oxidation closer to the experimental value and by altering the shape of oxidation curves to better match the observed decreases in rate constants over time. This chapter of research further strengthened the confirmation of the initial hypothesis that pre- and postoxidation microstructures have a large degree of influence on *in situ* oxidation kinetics.

3) Severe plastic deformation, applied through ECAP, can be used to refine and homogenize the microstructures of oxidized Fe-Y alloys, producing a material with both better mechanical performance and thermal stability than that of pure Fe.

- ECAP results varied depending on the number of passes a sample was subjected to and pressing temperature. Increasingly even dispersions of Fe₁₇Y₂ intermetallic were achieved as temperature increased, leading to easier flow of the Fe matrix. Increasing passes also introduced additional plastic deformation, aiding this dispersion. Oxides formed throughout the perimeter of Y-rich regions were more difficult to distribute evenly. In this case, both increased temperature and more passes were necessary.
- While there was no apparent refinement of oxide phase, coarsening was also not readily promoted during the processing. Observed oxidation behavior was inconsistent with past work on *in situ* oxidation kinetics. Following ECAP at room temperature, accelerated internal oxidation kinetics were observed, despite the dispersion of Y-rich networks. This was attributed to the introduction of dislocations during severe plastic deformation creating an alternate route for fast-path oxygen diffusion. Pressing at high temperatures resulted in oxidation rates that matched predictions and past experiments, as recrystallization eliminated many dislocations for fast path diffusion.

9.2 Future Work

Future steps can be taken to improve and build open the presented theory. Notably the relationship between oxide growth and penetration depth was not precisely determined. The X^3

and $X^{1/2}$ fits were both reasonable, but not ideal, and the $X^{1/2}$ and linear fits match best with previously proposed theory. The model was relatively sensitive to what trend was selected, so better identifying the exact relationship would improve estimated penetration depths. One method to improve this is to incorporate FIB milling to gain a better understanding of how oxides growth in 3-dimensions as opposed to the presently examined 2-dimensional SEM that was performed. It is likely that this would improve the measured values of oxide diameter. Along with this measuring oxides at more penetration depths in each sample would help to better identify the relationship between depth and oxide size. This would likely necessitate further STEM in the majority of samples to gain more precise measurements of oxide size at the surface of the samples and also in the 10^{-20} atm samples where no evidence of increasing oxide size was observed.

While gas phase mass transfer was not found to be relevant to samples oxidized with thermogravimetric analysis, transfer of oxidant through the Rhines pack remains in question. This can be analyzed by repeating some of the Rhines pack experiments in an evacuated quartz tube, as is traditionally done and observing differences between the kinetics. As these effects continue to be quantified alloys of increasing complexity could be oxidized as other alloying elements traditionally found in ODS alloys such as Ti or Mo could be added to solidified alloys.

Analysis of ECAP samples is also incomplete. TEM would help to reveal more information on the dislocation structure of samples both before and after annealing. STEM-HAADF could also be utilized to observe any distribution of yttrium oxide that was not resolved with SEM. Electron backscatter diffraction should also be used to observe how the crystallographic texture of the Fe-Y microstructure was manipulated by the plastic deformation. These characterization techniques would lend further confirmation to conclusions established in Chapter 8 based on SEM and hardness data. More trials oxidizing samples post ECAP should also be performed. This, paired with the aforementioned TEM/EBSD could reveal further conclusions about microstructural effects of oxidation kinetics, particularly the influence of high dislocation densities. Long-term experiments could include performing ECAP on 3wt%Y Fe-Y alloys to observe how a greater volume fraction of the intermetallic phase deforms.



Appendix A: Parabolic Thermogravimetric Analysis Data

Figure A.1. Weight gain per unit area $Fe_{17}Y_2$ squared as a function of time for 1.5 wt% Y alloys oxidized at all oxygen partial pressures and flow rates.



Figure A.2. Weight gain per unit area $Fe_{17}Y_2$ squared as a function of time for 3 wt% Y alloys oxidized at all oxygen partial pressures and flow rates.



Figure A.3. Weight gain per unit area $Fe_{17}Y_2$ squared as a function of time for 15 wt% Y alloys oxidized at all oxygen partial pressures and flow rates.

Appendix B: SEM Imaging of Oxides



Figure B.1. Backscattered SEM images of a 1.5 wt% Y alloy oxidized at 10^{-25} atm P_{O2} under both low and high flow conditions. Micrographs were taken at the sample surface (left), one-half the penetration depth (center), and at the oxidation front (right).



Figure B.2. Backscattered SEM images of a 1.5 wt% Y alloy oxidized at 5 x 10^{-23} atm P₀₂ under both low and high flow conditions. Micrographs were taken at the sample surface (left), one-half the penetration depth (center), and at the oxidation front (right) in the high flow condition, and all three low flow images show the entire depth of penetration.



Figure B.3. Backscattered SEM images of a 3 wt% Y alloy oxidized at 10^{-25} atm P_{O2} under both low and high flow conditions. Images are also representative of a 6 wt% Y microstructure. Micrographs were taken at the sample surface (left), one-half the penetration depth (center), and at the oxidation front (right).



Figure B.4. Backscattered SEM images of a 3 wt% Y alloy oxidized at 5 x 10^{-23} atm P₀₂ under both low and high flow conditions. Images are also representative of a 6 wt% Y microstructure. Micrographs were taken at the sample surface (left), one-half the penetration depth (center), and at the oxidation front (right).



Figure B.5. Backscattered SEM images of a 15 wt% Y alloy oxidized at 10^{-25} atm P_{O2} under both low and high flow conditions. Images are also representative of a 12 wt% Y microstructure. Micrographs were taken at the sample surface (left), one-half the penetration depth (center), and at the oxidation front (right).



Figure B.6. Backscattered SEM images of a 15 wt% Y alloy oxidized at 5 x 10^{-23} atm P_{O2} under both low and high flow conditions. Images are also representative of a 12 wt% Y microstructure. Micrographs were taken at the sample surface (left), one-half the penetration depth (center), and at the oxidation front (right).

Appendix C: Integration of the Parabolic Rate Equation Assuming Linear Oxide Growth

In order to simplify integration of Equation 7.14, all variables containing oxide size (*d*) and penetration depth (*X*) terms needed to be isolated, and constants were introduced to further reduce equations. The equation for effective diffusivity was first altered by defining oxide size as a function of penetration depth, according to Equation C.1. Constants (C_1 and C_2) were also introduced (Equations C.2 and C.3).

$$d = mX + b \tag{Eq. C.1}$$

$$C_1 = D_0 - f_{0X} D_0 \tag{Eq. C.2}$$

$$C_2 = f_{OX} D_O(3996)$$
 (Eq. C.3)

$$D_{eff} = C_1 + C_2 \frac{mX+b+1}{(mX+b)^2}$$
 (Eq. C.4)

These equations could then be substituted into the parabolic rate equation and integration could proceed. This is outlined in Equations C.5 - C.7.

$$\frac{dX}{dt} = \frac{\frac{k_O}{D_O}}{x} \left[C_1 + C_2 \frac{mX + b + 1}{(mX + b)^2} \right]$$
(Eq. C.5)

$$\int_{0}^{X_{0}} \frac{XdX}{\left[C_{1}+C_{2}\frac{mX+b+1}{(mX+b)^{2}}\right]} = \int_{0}^{t_{0}} \frac{k_{0}}{D_{0}} dt$$
(Eq. C.6)

$$\int_{0}^{X_{0}} \frac{(mX+b)^{2}XdX}{C_{1}(mX+b)^{2}+C_{2}(mX+b+1)} = \frac{k_{0}}{D_{0}}t_{0}$$
(Eq. C.7)

From the point shown in Equation C.7, substitution of variables was used to further simplify the integration. It was also assumed that C_1 was orders of magnitude less than C_2 and could therefore be ignored. These steps are shown in Equations C.8 and C.9.

$$mx + b = z$$

$$mdx = dz$$

$$x = \frac{z - b}{m}$$
(Eq. C.8)

$$\frac{1}{m^2} \int_0^{Z_0} \frac{(z-b)(z)^2 dz}{C_2 z + C_2} = \frac{z[-3b(z-2)+2z^2-3z+6]-6(b+1)LN(z+1)}{m^2 6C_2}$$
(Eq. C.9)

The final result was solved for each oxidized sample's given conditions, and yielded a value of total time elapsed to reach a given value of penetration depth. Plotted curves of these effective penetration depth values as a function of time are contained in Chapter 7, Figure 7.4.

<u>Appendix D: Integration of the Parabolic Rate Equation Assuming n^{1/2} Oxide</u> <u>Growth</u>

The integration in Appendix C was carried out assuming oxide growth was a function of penetration depth to the power 0.5, according to Equation D.1. Oxides were assumed to initially nucleate at a diameter of 10 nm.

$$d = ZX^{\frac{1}{2}} + 10$$
 (Eq. D.1)

This was equation was then substituted into the equation for effective diffusivity and simplified to Equation D.2. This could then be plugged in to Equation 7.14 and reduced so that the integration could be performed, again with C_1 assumed negligible. The final result is shown in Equation D.6.

$$D_{eff} = C_1 + C_2 \frac{ZX^{\frac{1}{2}} + 11}{(ZX^{\frac{1}{2}} + 10)^2}$$
 (Eq. D.2)

$$\frac{dX}{dt} = \frac{\frac{k_O}{D_O}}{X} \left[C_1 + C_2 \frac{ZX^{\frac{1}{2}} + 11}{(ZX^{\frac{1}{2}} + 10)^2} \right]$$
(Eq. D.3)

$$\int_{0}^{X_{0}} \frac{XdX}{\left[\frac{1}{C_{1} + C_{2} \frac{ZX^{\frac{1}{2}} + 11}{(ZX^{\frac{1}{2}} + 10)^{2}} \right]}} = \int_{0}^{t_{0}} \frac{k_{0}}{D_{0}} dt$$
(Eq. D.4)

$$\int_{0}^{X_{0}} \frac{\left(ZX^{\frac{1}{2}}+10\right)^{2} ZdX}{C_{2}(ZX^{\frac{1}{2}}+11)} = \frac{k_{0}}{D_{0}} t_{0}$$
(Eq. D.5)

$$\int_{0}^{X_{0}} \frac{\left(ZX^{\frac{1}{2}}+10\right)^{2} X dX}{c_{2}\left(ZX^{\frac{1}{2}}+11\right)} = \frac{\frac{2}{5}Z^{5/2}X + \frac{2Z^{\frac{3}{2}}}{3X} + \frac{9Z^{2}}{2} - \frac{2662LN(X\sqrt{Z}+11)}{X^{4}} + \frac{242\sqrt{Z}}{X^{3}} + \frac{11Z}{X^{2}}}{C_{2}}$$
(Eq. D.6)

Appendix E: Integration of the Parabolic Rate Equation Assuming Cubic Oxide Growth

The integration in Appendix C was carried out assuming oxide growth was a function of penetration depth cubed, according to Equation E.1. Oxides were assumed to initially nucleate at a diameter of 10 nm.

$$d = ZX^3 + 10 \tag{Eq. E.1}$$

This was equation was then substituted into the equation for effective diffusivity and simplified to Equation E.2. This could then be plugged in to Equation 7.14 and reduced so that the integration could be performed, again with C_1 assumed negligible. The final result is shown in Equation E.6.

$$D_{eff} = C_1 + C_2 \frac{ZX^3 + 11}{(ZX^3 + 10)^2}$$
 (Eq. E.2)

$$\frac{dX}{dt} = \frac{\frac{k_O}{D_O}}{x} \left[C_1 + C_2 \frac{ZX^3 + 11}{(ZX^3 + 10)^2} \right]$$
(Eq. E.3)

$$\int_{0}^{X_{0}} \frac{XdX}{\left[C_{1}+C_{2}\frac{ZX^{3}+11}{(ZX^{3}+10)^{2}}\right]} = \int_{0}^{t_{0}} \frac{k_{0}}{D_{0}} dt$$
(Eq. E.4)

$$\int_{0}^{X_{0}} \frac{(ZX^{3}+10)^{2} ZdX}{C_{2}(ZX^{3}+11)} = \frac{k_{0}}{D_{0}} t_{0}$$
(Eq. E.5)

$$\int_{0}^{X_{0}} \frac{(ZX^{3}+10)^{2} X dX}{C_{2}(ZX^{3}+11)} = \frac{1}{330C_{2}Z^{\frac{2}{3}}} \left[66Z^{\frac{5}{3}}X^{5} + 1485Z^{\frac{2}{3}}X^{2} + 5\left(11^{\frac{2}{3}}\right)LN\left(11^{\frac{1}{3}}Z^{\frac{2}{3}}X^{2} - 11^{\frac{2}{3}}Z^{\frac{1}{3}}X + 11\right) - 10\left(11^{\frac{2}{3}}\right)LN\left(11^{\frac{2}{3}}Z^{\frac{1}{3}}X + 11\right) + 10\left(11^{\frac{2}{3}}\right)\sqrt{3}\tan^{-1}\left(\frac{2(11^{\frac{2}{3}}(Z^{\frac{1}{3}})X - 11}{11\sqrt{3}}\right) \right]$$
(Eq. E.6)

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