PHASE-FIELD STUDY OF DIFFUSION CONTROLLED PHENOMENA:
REORIENTATION OF ZIRCONIUM HYDRIDES
AND OXIDATION OF METALS

by
Alireza Toghraee
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Golden, Colorado
Date _________________________

Signed: _______________________
Alireza Toghraee

Signed: _______________________
Dr. Mohsen Asle Zaeem
Thesis Advisor

Golden, Colorado
Date _________________________

Signed: _______________________
Dr. Jason Porter
Professor and Head
Department of Mechanical Engineering
ABSTRACT

Materials under extreme conditions, such as under high temperatures and/or corrosion environments, undergo different microstructural changes that can significantly affect their properties and performance during operations. In this Ph.D. research, by means of computational modeling, we aim to understand the re-orientation mechanisms of zirconium hydrides in nuclear fuel claddings and oxidation induced stresses in steels, which are among two critical problems in materials used in water-cooled nuclear reactors. For this purpose, we developed micro-scale computational frameworks based on the phase-field method.

We investigated the shape evolution and reorientation of zirconium hydrides under applied external loads, resulting in embrittlement of zirconium alloys. Two-seed and multi-seed hydride simulations revealed the significant influence of neighboring hydrides on the required load for reorientation. For the first time, we could explain that hydride reorientation happens more easily when clusters of hydrides are present, due to the strain fields around the hydrides, and the required external load for reorientation is within the elastic limit of the cladding material, similar to reported experiments.

In addition, we studied the interaction between induced stresses and the formation of oxides for both internal and intergranular cases. The evolution of oxide layer occurs to reduce the localized stress concentration, and increasing the temperature may alter the stress levels by changing the contribution of eigen strains on the elastic energy. By considering different diffusivities at the grain boundaries, depending on their structures, the simulations captured intergranular oxidation and oxidation resistance of certain low Σ grain boundaries, as observed in experiments.
# TABLE OF CONTENTS

ABSTRACT ................................................................................................................................... iii

LIST OF FIGURES ....................................................................................................................... vi

LIST OF TABLES ....................................................................................................................... viii

ACKNOWLEDGMENTS ............................................................................................................. ix

CHAPTER 1 INTRODUCTION .....................................................................................................1

  1.1 Embrittlement of Zr Alloys .............................................................................................. 1

  1.2 Oxidation and Oxidation Induced Stresses in Steels......................................................... 6

  1.3 Objectives and Thesis Layout ........................................................................................ 11

CHAPTER 2 EFFECTS OF APPLIED LOAD ON FORMATION AND REORIENTATION
OF ZIRCONIUM HYDRIDES: A MULTIPHASE FIELD MODELING STUDY .......................13

  2.1 Introduction .................................................................................................................... 14

  2.2 Multiphase Field Model and Simulation Details ........................................................... 16

  2.3 Results and Discussion ................................................................................................... 20

  2.4 Conclusion ...................................................................................................................... 29

  2.5 Acknowledgment ........................................................................................................... 30

  2.6 References ...................................................................................................................... 31

CHAPTER 3 OXIDATION INDUCED STRESSES IN HIGH-TEMPERATURE
OXIDATION OF STEEL: A MULTIPHASE FIELD STUDY ............................................34

  3.1 Introduction .................................................................................................................... 35

  3.2 Multi-Phase Field Model................................................................................................. 37
LIST OF FIGURES

Figure 1.1. Hydrogen pick up process in Zr which leads to r embrittlement ......................... 2

Figure 1.2. Orientation of δ hydrides in HCP Zr matrix and their reorientation under loads [12]. ......................................................................................................................... 4

Figure 1.3. (a) Applied stress for hydride reorientation as a function of temperature and hydrogen concentration [12], and (b) Evolution of radial hydride as a function of tensile load [13]. ............................................................................................................... 4

Figure 1.4. (a) Grain boundary diffusion coefficient in [110] tilts boundary in Al [41]. (b) calculated and energies for [110] tilt boundaries in Al [43]. ......................................................... 10

Figure 1.5. (a) Back scattered electron image of the oxide formed in austenitic stainless steel; (b) EBSD map overlaid with grain boundaries. Red lined represent Σ 3 and black lines represent random grain boundaries [48]. (Bottom) The difference of intergranular oxidation between random boundaries (R) and coincidence ones (Σ) of Ni-Fe alloy [40]................................................................. 11

Figure 2.1. Schematic view of δ hydride inside Zr cladding: a) 3D and 2D views before reorientation, b) 3D view after reorientation, and c) a 2D cut of the cladding shell showing the hydrides before (top) and after (bottom) reorientation. .......... 16

Figure 2.2. Single seed of ζ phase hydride transforms to γ then to the stable δ hydride, (a) no applied strain, (b) and (c) applied strain of 0.02 in the radial and circumferential directions, respectively. The x-axis is the [1120] direction and the y-axis is the [0001] direction. Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H. .................................................................................. 22

Figure 2.3. Single seed of already formed δ hydride under an applied radial compressive strain (y direction) of 0.02. Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H................................................................. 24

Figure 2.4. Two-seed simulations: (a) two ζ hydride seeds with the distance of d=21 nm under compressive strain of 0.002 (radial direction), and (b) two δ hydrides under compressive strain of 0.0015 (radial direction) and d/a=0.6. Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H. ....................... 27

Figure 2.5. A cluster of δ hydrides under applied compressive strain of 0.0007. Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H. .... 28
Figure 2.6. The minimum applied strain necessary to cause δ hydride reorientation for different simulation cases compared with that of the experiment [4] ................. 28

Figure 3.1. Oxide layer growth at different temperatures (°C) for a diffusive interface thickness of (a) $\lambda = 40nm$ and (b) $\lambda = 800nm$. Experimental results are obtained from [31]. ................................................................................................. 45

Figure 3.2. Evolution of phase-field (PF) variables during oxidation at temperature of 850 °C. (a) phases (b) concentration of Iron (c) concentration of oxygen .... 47

Figure 3.3. Oxide layer growth and evolution of induced stresses in planar oxidation (T = 850 °C). Domain size is 0.5 mm $\times$ 0.5 mm. Top left snapshot also shows the mechanical boundary conditions. ............................................. 48

Figure 3.4. Oxide layer growth and evolution of induced stresses for the oxidation of a sharp corner (T = 850 °C). Domain size is 0.5 mm $\times$ 0.5 mm ............... 51

Figure 3.5. Variations of stress levels for oxidation at 850 °C and 1180 °C for (a) planar oxidation, and (b) sharp corner oxidation ...................................................... 53

Figure 4.1. Intergranular oxidation and corresponding stress map (von Mises) for the case with random grain boundaries, (a) Mobility map, (b) grains orientation, (c-e) oxide phase evolution, and (f-h) corresponding stress map .................................. 69

Figure 4.2. Intergranular oxidation and corresponding stress map (von Mises) for case with mixture of random grain and $\Sigma 3$ grain boundaries, (a) Mobility map, (b) grains orientation, (c-e) oxide phase evolution, and (f-h) corresponding stress map .................................................................................. 70

Figure 4.3. Stress evolution and critical point for the case with mixed grain boundaries (Figure 4.2), (a) location of critical points: tip of oxide at GB R1 and point P, (b) evolution of stress levels for points marked in (a). Comparing the stress evolution at point P’ with and without plasticity, simulation domain size is 100 x100 μm, (c-e) evolution of oxide, (f) evolution of stress levels for point P’ ................................................................. 73
LIST OF TABLES

Table 2.1. Material properties and model parameters used in simulations for all phases. Elastic constants, Bulk ($B$) to shear modulus ($G$) ratio from DFT and experiment [24-27], Interfacial energies from Thuinet or approximated [28], gradient energy coefficients chosen to give interfacial energies noted, and stress free transformation strains given in [13, 16, 29]. ..................................................... 21

Table 3.1. Material properties and model parameters. Elastic constants are from [20, 46], thermal expansion coefficient is from [47], and $\epsilon_{ij00}$ is calculated based on $\text{PBR} = 1.67$ for FeO and $\omega = 0.11$ [44]. .................................................................................. 42

Table 3.2. Steel composition (wt%) used in the experiment [31]. .................................................... 43

Table 4.1. Materials and model properties. ................................................................................. 66
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CHAPTER 1
INTRODUCTION

Extreme environmental conditions, such as high temperatures, corrosion environments, and large mechanical loads result in material microstructural changes that can significantly affect their properties and performance during operations. Nuclear power plants represent such a harsh environment where materials must tolerate a combination of high temperature, high mechanical loads, corroding fluids and intense radiation fluxes. Among the many materials used in nuclear power plants, some experience the most extreme conditions (stress, corrosion, radiation, etc.), which are the most critical ones in designing different components. Steels are some of those leading materials used in power generation industries, due to retaining a high strength at elevated temperatures. In addition, zirconium (Zr) alloys play a very critical role in nuclear reactors, because they are the primary material for the fuel rod cladding, due to their low neutron absorption cross section. Since these materials play important roles in reliable and safe operation of the power plants [1, 2], understanding their microstructure-controlled material properties and performance at different conditions is of great importance. Among many problems and challenges that these materials experience during their manufacturing and operating conditions, embrittlement of Zr alloys and oxidation of steels are among the most significant ones which require further investigations in order to predict and avoid catastrophic failures.

1.1 Embrittlement of Zr Alloys

Zr alloys are used in the core of all light water reactors (LWR) as the cladding of the fuel rods. This selection is based on their promising properties, such as low neutron absorption cross section, low irradiation void swelling, as well as good strength and corrosion resistance at the
operation temperature [3]. Despite their beneficial material properties, Zr alloys suffer from an important flaw due to their reactivity with Hydrogen (Figure 1.1). Since LWR uses water as the coolant fluid, the outer layer of the Zr alloy cladding reacts with water producing Zr oxide and Hydrogen. The Hydrogen beyond the solubility limit [4] will precipitate in forms of Zr hydrides. The hydrides have less ductility than the Zr matrix, which can lead to degradation of strength of Zr alloys and promotion of cracking, especially if the hydrides orient perpendicular to the loading direction [5-8].

![Image of fuel assembly and rod cross section](image)

Figure 1.1. Hydrogen pick up process in Zr which leads to embrittlement [6].

There are four types of Zr hydrides [9] and the $\delta$ - hydride ($\text{ZrH}_{1.5-x}$), with face-centered cubic (fcc) structure, is the most common one found in the cladding materials. In the absence of a stress field, hydrides generally precipitate as narrow platelets (disks) with their normal along the basal pole of hexagonal close-pack (hcp) Zr matrix (Figure 1.2). However, in the presence of high enough stress field, hydrides tend to precipitate perpendicular to the stress direction[10]. In
order to prevent the hydride to orient perpendicular to hoop stresses in the cladding, the Zr alloys go through various manufacturing processes, such that the Zr basal plane orients close to the circumferential direction of the cladding [11]. However, during the operation, storage and restoring of claddings, the Zr alloys experience cycles of thermal, mechanical and irradiation loads which result in reorientation of the hydrides; hydrides will reorient perpendicular to tensile loads or parallel to compressive loads [9]. Hydride orientation plays an important role in the embrittlement of Zr alloys, especially when they are oriented in the radial direction of the cladding.

The formation and reorientation of hydrides have been the subject of several studies in recent years. Krishna et al. studied the effect of grain boundaries on formation and orientation of the hydrides, and showed that the presence of low Coincidence Site Lattice (CSL) grain boundaries can reduce the probability of hydride precipitations [12]. Relation between thermal cycling, hydrogen content and stress level for reorientation was studied by Chu et al. [13]. By relating formation energy, defect energy and strain misfit energy to temperature and hydrogen composition, they could find a threshold stress for reorientation of hydrides. Using transmission diffraction experiments, Colas et al. [14-16] found the hydride precipitation and dissolution temperatures during their wet to dry storage transmission, and they also suggested a threshold stress for the reorientation of hydrides. Based on their findings, upon applying stresses above 80 MPa, 40% of hydrides reorient such that their habit planes become normal to the load direction (Figure1.3). In addition, it was shown that thermomechanical cycles have significant effect on hydride re-orientation, and by increasing the number of cycles the fraction of re-oriented hydrides also increases [16].
Figure 1.2. Orientation of $\delta$ hydrides in HCP Zr matrix and their reorientation under loads [13].

Figure 1.3. (a) Applied stress for hydride reorientation as a function of temperature and hydrogen concentration [13], and (b) evolution of radial hydride as a function of tensile load [14].
Despite the fact that experimental methods can provide valuable insights on the behavior of materials, they are not time and cost effective. Also, performing experimental measurements at high temperatures and lower length scales are very complex and not always possible. Because of these obstacles, most of the experimental studies on the hydride formation and reorientation in Zr alloys have been done in a postmortem fashion, and not much information exists on the microstructural evolution during these phenomena.

Computational methods have become important tools to study materials, especially at the nano and micro scales. Phase-field modeling (PFM) is one of those tools that has progressed in the last two decades to study microstructure evolution and phase transformations in different material systems [17-19]. Diffusion of mass, which is conserved, is tracked by conserved variables, and evolution of phases is tracked by non-conserved variables. Incorporating and coupling various energy types (chemical, elastic, magnetic, etc.) are done in PFM by linking these energies through the PF variables. This makes the PFM a suitable tool to study diffusion-controlled processes such as formation and evolution of hydrides.

Considering chemical and elastic energy, Shi et al. developed a non-dimensional PFM for the evolution of $\gamma$-hydrides. Using this model they could study the evolution of hydrides under applied load in single and bicrystal matrix [20, 21], and also under non-uniform load and in the matrix with stationary cracks [22]. Even though they could show that the direction for the growth of hydrides is affected by the applied load and stress distribution, their model did not consider the actual formation energy of hydrides and the interface energies between different hydride phases. Formation and interface energies are key parameters toward a quantitative PFM study. Recently, Bair et al. developed a multiphase field model based on the actual formation and interface energies to study the effect of metastable phases $\zeta, \gamma$ on the formation of the stable $\delta$
hydrides [23]. They showed that metastable phases have an influential role in the shape evolution of hydrides. However, the effect of applied load on the orientation of the $\delta$ hydrides was not considered. A PFM study of $\delta$ hydrides reorientation under applied stress was completed recently in a work by Shin et al. [24]. They could simulate the microstructure evolution of $\delta$ hydrides in the presence of applied external stresses, and show that hydrides rotate and reorient in the presence of an external load. Even though the model was 3D, they reported that a stress level as high as 9 GPa is required to cause the reorientation. This level of stress is two order of magnitude higher than those observed in experiments (Figure 1.3). One of the objectives of this Ph.D. research is to explain why other modeling efforts could not quantitatively determine the required load for reorientation of hydrides.

1.2 Oxidation and Oxidation Induced Stresses in Steels

Due to their unique and exceptional mechanical properties, cost and availability, steels are irreplaceable and demanding materials in all power generation industries, as well as other industries. However, it is well-known that they suffer from corrosion and oxidation. Higher temperatures accelerate the oxidation kinetics in steels. Thus, oxidation resistance and protection in high temperatures becomes more challenging. Diffusional protective coating is one of the famous oxidation protection practices. A diffusion zone is developed in the substrate, which allows a protective scale to form by selective oxidation [25-27]. Even though addition of alloying elements which form protective scales will add levels of oxidation protection, these approaches are not always possible, since they are not financially feasible and detrimental to mechanical properties [28]. Another oxidation protection practice is hot-dip galvanizing, where the pre-heated steel strip is submerged into a Zinc bath. During the preheating stage, the steel is
exposed to oxidation and layers of oxides are formed. Oxidation and formation of oxide scales can also happen during the manufacturing processes, such as hot rolling, as well as during operating conditions [29-31]. Evolution of oxide layers corresponds to inducing stresses [32] due to the volume change of the oxide and the mismatch between metal and oxide lattice. These induced stresses may lead to failures (spalling, bulking, fracture, etc.) that will affect surface quality and the successful formation of protective coatings. Experimental studies have shown that there is reciprocal interaction between oxide growth and generated stresses and parameters, such as temperature and diffusion mechanism, that will affect this relationship [33, 34]. Stress generation under combined effect of oxidation and thermal-mismatch was studied by Tolpygo et al.[35], where they showed very high compressive stress can be generated in protective Al oxide layer. Schutze et al. [36-38] investigated oxide scales mechanical properties and their failure modes due to induced stresses.

Furthermore, oxidation at grain boundaries or intergranular oxidation will also happen, which can be particularly detrimental, since it promotes and enhances intergranular fractures [39-41]. The structure of grain boundaries is a key in the kinetics of many high-temperature processes, since the transport of materials along grain boundary is much faster than throughout the bulk. The intergranular oxidation is generally attributed to this higher diffusion rate of elements at grain boundaries. Studies have shown that the diffusion rates along grain boundaries are at least one order on magnitude higher than the lattice diffusion. However, some grain boundaries can have higher or lower diffusion rates depending on the misorientation angle and coincident site lattice (CSL) number (Σ type) [42-46]. This relation has been depicted in Figure 1.4.a. Also, there is a correlation between diffusion rate and grain boundary energy (Figure 1.4.b). This combination of grain boundary diffusion and energy makes grain boundaries with
higher energy and diffusion rate more susceptible to oxidation, while the grain boundaries with lower energy and diffusivity (Low-$\Sigma$ type) are more resistant to the oxidation [41, 47-49]. Effect of grain boundary structure on the intergranular oxidation has also been subject of experimental studies. Yamaura et al. [41] investigated the oxidation of Ni-Fe based alloys and observed that $\Sigma 3$, $\Sigma 11$ and $\Sigma 19$ grain boundaries have more resistance to oxidation than other $\Sigma$ and random grain boundaries. Studies on the grain boundary oxidation of ferritic and austenitic steels also reported that the oxidation rates on $\Sigma 3$ grain boundaries are lower compared to the random ones [47, 49]. This difference in oxidation resistance of grain boundaries can be utilized to control the oxidation protection and crack resistance of materials. Kim et al. suggested that when the formed oxide scale is protective, decreasing the grain size will accelerate the transport of elements through grain boundaries and helps faster formation of protective layer [49]. On the other hand, oxidation-resistant grain boundaries can improve the resistance of materials to stress corrosion cracking by arresting the crack propagation. This was observed in a work by Gasterman et al. [39], where increasing the fraction of $\Sigma 3$ twin boundaries slowed down the intergranular stress corrosion cracking (SCC) in austenitic Ni-based alloy. Wagenhuber et al. [50] also reported that engineering of grain boundaries can benefit from the resistance of low-$\Sigma$ grain boundaries on oxidation to improve the fatigue life of the Ni-base superalloys. Thus, investigating the evolution of oxides and their interaction with the resulting stresses (both in forms of oxide scales and intergranular oxidation) is of great importance. In addition, being able to understand and predict the oxide growth and the corresponding stresses is essential to better design oxidation and SCC resistant materials.

PFM has also been applied to diffusion-controlled oxidations of metals. Nijdam, et al. [51, 52] developed a coupled thermodynamic-kinetic oxidation model which could compute the
composition profiles of the amount of each developed oxidation phase as a function of oxidation time. Despite the fact that their model could predict the phase and composition evolution, it was not capable of calculating strains and stresses generated during the oxidation and formation of different phases, which have significant effects on the morphology of oxidation microstructures [53]. Coupling the mechanical and diffusion equations has been considered in works of Zhou et al. [54, 55] and Asle Zaeem et al. [56] to study stress–oxidation relation and oxidation induced metal depletion in metals and alloys. However, due to lack of non-conserved variables, application of such model is challenging, if at all possible, for the multiphase cases. High temperature oxidation in Iron-based alloys was investigated in a work by Yang et al. [57]. Their work did not consider effect of geometry and temperature change on the stress generation, and also multiphase oxidation was not considered.

In the area of grain boundary oxidation, Mai et al. [58, 59] applied PFM to simulate the stress corrosion cracking. Their model incorporates both chemical and mechanical energies and captures the oxide film rapture and stress concentration effects on the corrosion kinetics. However, their model considers single crystal domain and no corrosion/oxidation on the grain boundaries were reported in their results. Other researchers also used PFM with mechanical and chemical coupling to simulate oxidation and corrosion [60]. While these models could study the interaction of mechanical loading and electrical fields and on the stress corrosion cracking (SCC), they lacked considering polycrystalline domains. Thus, formation of oxides at grain boundaries could not be simulated. Modeling the intergranular oxidation was done by a work by Jahns et al. [61] using cellular automata. Their model considers the higher diffusivity at grain boundaries and shows oxidation along grain boundaries. Nevertheless, it fails to consider the mechanical contributions in the model; as a result, obtaining a stress map and determining
critical zones for crack nucleation and growth is not possible. One of the objectives of this Ph.D. research is to develop a PFM framework to simulate and predict intergranular oxidation and the critical zones with high stress intensities prone to cracking.

Figure 1.4. (a) Grain boundary diffusion coefficient in [110] tilt boundaries in Al [42]. (b) calculated and energies for [110] tilt boundaries in Al [44].
1.3 Objectives and Thesis Layout

Even though $\delta$ hydrides are the most stable, their evolution and reorientation under applied mechanical loads have not been thoroughly studied yet. One objective of this Ph.D. study is to develop a computational framework based on PFM to study the reorientation of hydrides in Zr alloys and determine the required external loads and mechanics for reorientation of hydrides.

With respect to oxidation in metals, the main shortcomings of previous studies are the lack of proper coupling between oxide formation and induced stresses, and not fully considering the effects of grain boundaries on oxidation kinetics and the resultant stresses. The second main objective of this Ph.D. study is to investigate the microstructure evolutions in oxidation of
metals, considering the mechanical interactions and grain boundary structures. For this purpose, we will develop and implement multiphase field model.

The results of this Ph.D. research are presented in the three peer-reviewed journal papers described in the following chapters. In the first paper, we studied the evolution and reorientation of Zr hydrides under applied mechanical load. Based on experimental observations, our hypothesis is that the hydride configurations affect the stress threshold required to for reorientation of hydrides. The hypothesis is confirmed using the developed PF framework. In the second paper, we studied the interaction between evolution of oxides and the induced stresses. The effects of geometry and higher temperatures are considered, and the PFM results are validated against experimental results. Finally in the third paper, we studied grain boundary effects on oxidation pathways. We showed that our PFM framework is capable of capturing oxidation resistance of low-$\Sigma$ grain boundaries, as observed in experiments.
CHAPTER 2
EFFECTS OF APPLIED LOAD ON FORMATION AND REORIENTATION OF ZIRCONIUM HYDRIDES: A MULTIPHASE FIELD MODELING STUDY

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Alireza Toghraee\textsuperscript{a}, Jacob Bair\textsuperscript{b,c}, and Mohsen Asle Zaeem\textsuperscript{a}\textsuperscript{*}

\textbf{Abstract:} The effects of applied load on the formation and reorientation of $\delta$ hydrides in $\alpha$-zirconium matrix are studied by a multiphase field model. Simulations with only one hydride seed indicate that the hydride reorientation occurs only when a tensile or compressive strain of $\sim0.02$ is applied along $[\overline{1}\overline{1}20]$ (hoop or circumferential direction) or $[0001]$ (radial direction aligned with the basal pole direction), respectively. However, two-seed and multi-seed hydride simulations show the significant influence of neighboring hydrides on the required load for reorientation, reducing it by more than one order of magnitude and making it comparable to the experimental results. Through phase-field simulations, this work suggests that the hydride reorientation happens more easily when clusters of hydrides are present, and the required external load for reorientation is within the elastic limit of the cladding material.

Keywords: Hydrides; Reorientation; Zirconium; Applied strain; Metastable phases; Phase-field model.

\textsuperscript{*} Corresponding author and editor
\textsuperscript{a}: Department of Mechanical Engineering, Colorado School of Mines, 1500 Illinois St., Golden, Colorado, USA
\textsuperscript{b}: Department of Mechanical Engineering, Oklahoma State University, 201 GAB, Stillwater, Oklahoma, USA
\textsuperscript{c}: Pacific Northwest National Laboratory, 906 Battelle Boulevard, Richland, Washington, USA
2.1 Introduction

Zirconium (Zr) nuclear fuel claddings are constantly being water-cooled during operation and in the storage period. Reaction of water and claddings causes oxidation and releases hydrogen (H) atoms, some of which enter the cladding and cause formation of Zr hydrides. During the operation, nuclear fuel claddings are under constant hoop stresses caused by a combination of the pressure created by fission gases within the claddings and the helium fill gases in the cladding tubes. Other stresses occur during the transfer of spent nuclear fuel rods from operation to the storage, where the temperature changes and the internal pressure may cause re-precipitation and reorientation of Zr hydrides. The reorientation of hydrides has a significant effect on the mechanical behavior of the claddings and may cause facture and failure of the claddings, and this has been the subject of various experimental studies [1-5].

Claddings are fabricated to create a texture that promotes mostly circumferential orientations of hydride platelets [6]; however, reorientation of hydrides to radial direction has often caused a brittle fracture through the thickness of the cladding by a process known as Delayed Hydride Cracking (DHC). DHC is known as the most limiting factor to the lifetime of nuclear fuel rod claddings [7, 8]. Previous experimental studies indicate that understanding the effects of external loads on the formation and reorientation of $\delta$ hydrides in cladding materials is important in operating conditions, during transferring of the used fuel rods and also during the long-term storage [8].

The formation and shape evolution of stable $\delta$ hydrides in Zr alloys also depend on the metastable $\zeta$ and $\gamma$ phases [9, 10]. In a previous work, we developed a multiphase field model and studied the effects of metastable $\zeta$ and $\gamma$ phase hydrides in Zr-based nuclear fuel rod claddings without considering the effects of external loadings [11]. Although some phase-field
Simulations have been used previously to study the metastable $\zeta$ and $\gamma$ phases under various applied loads [12-14], there are only few works studied the effects of external loads (strains) on the stable $\delta$ phase [15]. With the exception of our recent work, there is only one phase-field modeling study that included the $\delta$ phase and focused on the effects of interface energies and temperature gradients in which the metastable phases were ignored and considered a direct formation path from $\alpha$-Zr matrix to $\delta$ phase hydrides [16].

Significant differences in elastic properties of different hydride phases and their stress-free strains indicate that applied loads will affect the formation and shape evolution of these phases. The metastable phases were shown to affect the formation and shape evolution of $\delta$ hydrides without an applied load [11], therefore it is reasonable to assume that they also can play a role in presence of external loads. In addition, the external loads can also affect the shape and orientation of the $\delta$ hydrides after they are formed, which this usually happens during the storage period and triggers the reorientation of the $\delta$ hydrides. Significant differences in the evolution of different hydride phases under various applied loads could lead to the discovery of preferable pre-stress treatments or improved operating conditions to avoid or mitigate the reorientation of hydrides. In this work, we first study the formation and reorientation of multiphase hydrides (metastable phases to stable $\delta$ phase) under applied load, and then we investigate the reorientation of the already formed stable $\delta$ hydrides under applied load. Furthermore, the effect of configuration and distance of hydrides from each other on the required load for reorientation is investigated.
2.2 Multiphase Field Model and Simulation Details

In the current study, the effect of applied load on evolution and reorientation of Zr-hydrides is investigated. Fig. 1 shows the schematic orientation of hydrides with respect to the Zr cladding. In order to simulate the cross section of a cladding, a two-dimensional (2D) domain is considered where the x-axis is in $[1\bar{1}20]$ direction and y-axis is in $[0001]$ direction (normal to basal plane in HCP Zr). $[0001]$ direction is typically oriented close to the radial direction in a cladding tube thus the y-axis will be noted as the radial direction, and the x-axis will be noted as the hoop or circumferential direction.

![Figure 2.1. Schematic view of δ-hydride inside Zr cladding: a) 3D and 2D views before reorientation, b) 3D view after reorientation, and c) a 2D cut of the cladding shell showing the hydrides before (top) and after (bottom) reorientation.](image)

Following our recent work [11], the multiphase field model uses one conserved phase-field variable to control the hydrogen concentration $C$, and six non-conserved structural field variables $\eta_i$, one for $\alpha$-Zr, one for $\zeta$-Zr$_2$H, one for $\delta$-ZrH$_{1.5+x}$, and three for the three eigenstrain variants of $\gamma$-ZrH. The total free energy of the system is defined as the summation of the chemical free energy and the elastic free energy:
\[ F = F_C + F_{el}, \]  

where \( F_C \) is the total chemical free energy and \( F_{el} \) is the elastic free energy:

\[ F_C = \int_V \left[ f(C, \eta, T) + \sum_{i,j}^n \frac{K_{ij}}{2} \| \nabla \eta_i \| \nabla \eta_j \right] d\tilde{r}, \]  

\[ F_{el} = \int_V f_{el} d\tilde{r} = \frac{1}{2} \int_V \sigma_{ij} \varepsilon_{ij}^{el} d\tilde{r} = \frac{1}{2} \int_V C_{ijkl}^{el} \varepsilon_{ij}^{el} d\tilde{r}, \]  

\[ \varepsilon_{ij}^{el}(\tilde{r}) = \varepsilon_{ij}^{el}(\tilde{r}) - \varepsilon_{ij}^{00}(\tilde{r}) = \varepsilon_{ij}^{el}(\tilde{r}) - \sum_{n=1}^6 \varepsilon_{ij}^{00}(n) \eta_n^2(\tilde{r}) = \frac{1}{2} \left( \frac{\partial u_i(\tilde{r})}{\partial r_j} + \frac{\partial u_j(\tilde{r})}{\partial r_i} \right) - \sum_{n=1}^6 \varepsilon_{ij}^{00}(n) \eta_n^2(\tilde{r}), \]  

\[ C_{ijkl}^{el} = \sum_{n=1}^6 \eta_n C_{ijkl}^m. \]

In the mentioned equations, \( f \) is the chemical free energy density of the bulk, \( K_{ij} \) is related to the interfacial free energy between the matrix and precipitates, \( T \) is the temperature, \( \sigma_{ij} \) is the stress, \( C_{ijkl} \) is the elastic tensor, \( \varepsilon_{ij}^{el} \) is the elastic strain, and \( \varepsilon_{ij}^{00} \) is the stress free transformation strain for each orientation variable. The value of \( n \) varies between 1 and 6 summing the values for all phases (\( \alpha, \zeta, \gamma_1, \gamma_2, \gamma_3, \) and \( \delta \)). The displacements are represented by \( u_i \). \( \zeta \) phase is coherent with the \( \alpha \)-Zr matrix and has the same crystallographic orientation. \( \gamma \) and \( \delta \) phases have a \((111)_{\gamma,\delta} \parallel (0001)_{\alpha}\) plane relationship and a \([1\bar{1}0]_{\gamma,\delta} \parallel [11\bar{2}0]_{\alpha}\) directional relationship with the \( \alpha \)-Zr matrix. These crystallographic relationships lead to stress-free strains with no shear components. The derivation of these strains is given in details in a work by Carpenter for \( \gamma \) and \( \delta \) phases [17], and by Thuinet et al. for the \( \zeta \) phase [13, 18]. The elasticity tensor transitions smoothly between phases using the non-conserved order parameters, by multiplying the elasticity
tensor of each phase by its associated order parameter, as shown in Eq.(5). In this model, all interfaces are controlled through the non-conserved order parameters. Gibbs free energies from Christensen et al. are used [19] to present the formation of different phases.

Lattice mismatch strains caused by hydrogen diffusion through the matrix are not included in this model, which may affect the diffusion in the model but should not considerably affect the elastic responses of each phase. No defect (cracks, etc.) is considered in this work so high stress concentrations are not expected anywhere in the domain of study, therefore ignoring the lattice mismatch strains will not have any noteworthy effect on the results. Other recent two-phase models have also neglected these strains [10, 13] for similar reasons. In larger simulation domains, when diffusion could become a significant limiting factor on hydride growth, or in simulations with stress concentrators such as cracks, the model needs to include the lattice mismatch strains [12].

The maximum hydrogen solubility, used in calculating the chemical bulk free energy of the $\alpha$ phase as described in [11], is described using the equation given by Une et al. in 2009 defining the terminal solid solubility of precipitation of hydrides in wtpm [20]:

$$C_\alpha = 3.27 \times 10^4 \exp \left( \frac{-25,042}{RT} \right). \quad (2.6)$$

The governing equations of the multiphase field model include evolution equations for the non-conserved field variables, Fick’s diffusion equation for the conserved diffusion of hydrogen, and the mechanical equilibrium equation to control the evolution of stresses and strains:

$$\frac{\partial \eta_i}{\partial t} = -L_i \left( \frac{\partial f}{\partial \eta_i} + \frac{\partial f}{\partial \eta_i} - \sum_{i,j}^n K_{ij} \nabla^2 \eta_i \right), \quad (2.7)$$
\[
\frac{\partial C}{\partial t} = M \nabla^2 \left( \frac{\partial f}{\partial C} \right),
\]
(2.8)

\[
\nabla \sigma_0 = 0 = \nabla (C_{ijkl} \varepsilon_{kl}),
\]
(2.9)

where \( L_i \) is the structural relaxation coefficient, and \( M \) is the mobility.

The material properties and model parameters used in this work are given in Table 1, where the other variants of stress-free strain of \( \gamma \) hydride are obtained by rotating the given stress-free strains about the \( z \) axis (the [0001] direction in the \( \alpha \)-Zr matrix). The usual average grain size of cladding is in the micron length scale (e.g., 5 \( \mu \)m [21]), and our domain of study is sub-micron. Also, the manufacturing process of claddings creates a texture that promotes similar orientations for \( \alpha \)-Zr grains which makes the basal pole of HCP crystal aligned with the radial direction. Thus, single crystal simulations should be sufficient to provide necessary knowledge on the process and mechanisms of hydride reorientation in Zr claddings. Constants \( A_\alpha, A_\gamma, A_\delta \), and \( A_\zeta \) which are used to set the curvatures of the parabolic chemical free energy densities and the process used to determine the gradient energy terms and the barrier terms are explained in details in our recent work [11].

The governing equations, Equation (2.7), (2.8) and (2.9), are solved using the weak forms through the finite element implementations in the Multiphysics Object Oriented Simulation Environment (MOOSE) developed by Idaho National Laboratory [22, 23]. Neumann boundary conditions were used for all phase-field variables and Dirichlet boundary conditions were applied on displacement variables to create the desired applied strains. The initial hydrogen concentration in the matrix was set at 0.03 in the multiphase simulations and 0.01 for the case of stable \( \delta \) hydrides accounting for consumption of hydrogen to form \( \delta \) hydrides. The domain of
study is a section of cladding bounded in radial and circumferential direction and along the length of the cladding (Fig. 1). This makes the thickness very large in comparison with other dimensions of the domain, and the strain in the direction normal to the plane can be neglected, thus, plane strain conditions were considered for our 2D simulations. An adaptive mesh algorithm was used to reduce the computational usage, and after a mesh convergence study, the smallest mesh size of 0.1 nm at the interfaces was chosen, and the mesh size elsewhere could increase to a size of 1.6 nm. Small mesh sizes were necessary due to the small interface energies between several of phases. These small interface energies led to small interface widths, which in turn required a very small mesh. The algorithms controlling the mesh adaptivity as well as the adaptive time stepping are described in detail elsewhere [11]. Simulations were run using the actual material properties to obtain quantitative results.

2.3 Results and Discussion

First, we consider the condition that a hydride starts to form and evolve from its metastable phase without and with an applied load. A single seed of metastable $\zeta$ phase was placed in the middle of the 2D domain at the $\{10\bar{1}0\}$ plane; $\{10\bar{1}0\}$ plane is often seen in the cross section of cladding tubes. Random nucleation of the other hydride phases was also considered. Results in Fig. 2a show the evolution of the single $\zeta$ seed into the $\delta$ phase under no applied load. The nucleation for $\gamma$ and $\delta$ hydrides is controlled using the probability of formation of a nucleus by the classical nucleation theory [11]. This sets the center of the nucleus, and in some cases a nucleus can be formed entirely inside the parent phase, or in other cases a nucleus may be formed at the interface between phases. The simulation results in Fig. 2a show that with no applied load no reorientation occurs.
Table 2.1. Material properties and model parameters used in simulations for all phases. Elastic constants, Bulk ($B$) to shear modulus ($G$) ratio from DFT and experiment [24-27], Interfacial energies from Thuinet or approximated [28], gradient energy coefficients chosen to give interfacial energies noted, and stress free transformation strains given in [13, 16, 29].

<table>
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<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
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<td>$\sigma_{a\zeta}$</td>
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<td>$\sigma_{a\gamma}$</td>
<td>0.1 J/m²</td>
<td>$\sigma_{a\delta}$</td>
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<td>13</td>
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<tr>
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<td>$(B/G)_{\zeta}$</td>
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<td>$(B/G)_{\delta}$</td>
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To investigate the effect of compressive loads during formation of hydrides, simulations were run by applying a displacement boundary condition on the top and bottom boundaries (the radial direction in Fig. 1) to cause a desired compressive strain. Fig. 2b shows reorientation of a single seed after an applied compressive strain of 0.02 in the radial direction. While the initial $\zeta$
Hydride transforms to other phases it reorients, and the final stable δ hydride is aligned with the radial direction.

Figure 2.2. Single seed of ζ phase hydride transforms to γ then to the stable δ hydride, (a) no applied strain, (b) and (c) applied strain of 0.02 in the radial and circumferential directions, respectively. The x-axis is the [1120] direction and the y-axis is the [0001] direction. Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H.

Hoop stresses occur naturally in cladding tubes due to the internal pressure caused by fission gases created during operation, and additional stresses occur when the claddings are transferred from operation to the storage. Therefore, to determine the strains necessary to cause
reorientation of a single hydride, simulations were conducted with applied tensile strains in the circumferential direction ([1\![\!\!2\!\!0\!) direction) by applying a displacement boundary condition on the left and right boundaries of the 2D domain to create the desired strain. Simulation results showed that when the hoop strain of 0.02 is applied, as shown in Fig. 2c, the \( \delta \) phase reorients in the radial direction. It should be mentioned that smaller applied strains did not cause reorientation. By comparing the results in Fig. 2b and Fig. 2c, the reorientation process is faster when the compressive radial load is applied causing formation of hydrides parallel to the radial direction, while the tensile hoop strain courses a slower process of reorientation of hydrides in the direction perpendicular to the applied strain.

In the second scenario, we study the case where the \( \delta \) hydride has already been formed in the circumferential direction and no reorientation occurred during formation of hydrides, and then an external load is applied (Fig. 3). This simulates the condition where a cladding is in the storage and the hydrides have already formed in the circumferential direction. A single ellipsoidal seed of \( \delta \) hydride is placed in middle of the domain. The ellipsoid is oriented in the circumferential direction and it has the aspect ratio of 1:5 to represent the shape of an evolved \( \delta \) hydride with no applied load (Fig. 2a). Displacement boundary conditions were applied similar to the previous cases. Results revealed that the strain required for reorienting the \( \delta \) hydride to radial direction is 0.02 for the compressive radial load (Fig. 3) and 0.03 for tensile hoop load (not shown). Fig. 3 also shows the strain maps around the hydride during the reorientation, and we will discuss shortly the importance of the strain field around the hydrides at the initial stage of loading when the hydride is still oriented in the circumferential direction.
In both of the previous scenarios, the strain necessary to cause reorientation of a single seed in simulations is significantly higher than that in experiments. Colas et al. [3, 4] found the threshold tensile stress necessary to cause reorientation of 40% of hydrides in the cladding to be around 85 MPa, or an applied strain of approximately 0.001 is required. One reason for a higher strain necessary for reorientation in our simulations could be due neglecting the effects of three-dimensional stresses in the 2D simulations. Simulations of δ phase evolution by Radhakrishnan et al. [30] showed that a 3D single seed of δ hydride reoriented after an applied strain of 0.01, and in their 2D simulations an applied strain of 0.02 was necessary. However, even a 0.01 strain
is one order of magnitude higher than the experimentally determined strain necessary to cause reorientation of hydrides. Another possible reason, which is the focus of this study, is the configuration of hydrides and how they are formed in the vicinity of each other. Other studies have shown that when the hydrides are formed on top of each other, they increase the total energy of the system comparing to the case when they are formed side to side [31]. Furthermore, as the distance between these hydrides decreases, more increase in the total energy of the system is observed.

Our hypothesis is that the configuration of hydrides has a significant influence on the strain field created around hydrides, and this can significantly affect the reorientation process of the neighboring hydrides. However, these effects cannot be seen in single seed simulations. By analyzing the strain map around a hydride, we found that in different stages of hydride formation and growth, tensile strain in the hoop direction and compressive strain in the radial direction exist around the hydride. These strains vary between -0.003 to +0.003 (corresponding to stresses around -400 to +400 MPa) at the distance $a$ from the hydride, where $a$ is the hydride length. In experiments, with only 40% of hydrides reorienting to the radial direction with an applied strain of approximately 0.001, it is entirely possible that some of the hydrides which did not reorient, formed first and created a strain field around them, which in combination with the applied load caused some other hydrides to nucleate and grow in the radial direction. In addition, when two hydrides are formed close enough on top of each other, they will increase the total energy of the system. If we assume that there is an energy threshold at which the reorientation initiates, in the case that the hydrides are formed close to each other, less outside energy, i.e. applied load, would be required to reorient the hydrides. To test this aforementioned hypothesis, several simulations
were completed with seeds placed in various distances \((d)\) from each other to investigate the effect of neighboring hydrides on the required applied strain to cause reorientation.

Simulations were set up with two seeds placed on top of each other in radial direction with a distance \(d\) from each other and under several compressive radial strains. Similar to the one-seed case, two scenarios were considered: transforming from initial \(\zeta\) hydride and evolving from already formed \(\delta\) hydride. Results of both cases (Fig. 4) revealed that when there are two hydrides in the vicinity of each other, the required load (strain) for reorientation will decrease significantly compared to a single isolated hydride. For instance, for the case of already formed \(\delta\) hydrides, the required strain for one single seed of \(\delta\) hydride to reorient is 0.02, but when two \(\delta\) hydrides are placed close to each other \((d/a=0.6)\), the required strain for reorientation drops more than one order of magnitude to 0.0015. To investigate the relation between distance and the required strain, several other simulations were run by varying the distance \(d\) and the applied strain required for reorientation was determined for each case. As expected, the results confirmed that as the distance between hydrides decreases, a lesser amount of applied strain/stress is required to initiate the reorientation. This significant decrease in the required strain for reorientation confirms our hypothesis that the configuration of hydrides has a significant effect on the required load for reorientation, and the strain/stress fields created around the hydrides affect the reorientation. It should be mentioned that for some cases where multiphase transformation was present, the seeds did not reorient even though the strains were at the threshold strain for the given seed distance. In these cases, one of the seeds transformed to \(\gamma\) before the other one transformed to \(\gamma\), absorbing the other seed and leaving just a larger single seed, with no reorient. Nevertheless, the simulations without any phase transformation showed that an applied strain as low as 0.0008 can cause reorientation of formed \(\delta\) hydrides.
Figure 2.4. Two-seed simulations: (a) two \( \zeta \) hydride seeds with the distance of \( d=21 \) nm under compressive strain of 0.002 (radial direction), and (b) two \( \delta \) hydrides under compressive strain of 0.0015 (radial direction) and \( d/a=0.6 \). Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H.

Finally, to represent a case somewhat similar to the real situation, a cluster of hydrides were considered. In this case, five \( \delta \) hydrides were placed inside the Zr matrix and then the required strain to cause the reorientation was determined. Simulations for this case (Fig. 5) showed that a strain as low as 0.0007 can make a cluster of hydrides to reorient. This value of strain is in good agreement with the strain value of 0.001 reported in experiments, which again indicates the importance of the configuration of hydrides and its effect on the required strain/stress for reorientation. These necessary applied strains required for reorientation for different cases are summarized plotted in Fig. 6.
Figure 2.5. A cluster of $\delta$ hydrides under applied compressive strain of 0.0007. Domain size is 75 nm by 75 nm. The colorbar shows the concentration of H.

Figure 2.6. The minimum applied strain necessary to cause $\delta$ hydride reorientation for different simulation cases compared with that of the experiment [4].

Previous 3D simulations of reorientation of a single hydride needed very high stresses, as high as 9 GPa corresponding to ~8% applied strain, to cause reorientation [15], which is at least one order of magnitude higher than experimental values [4]. From the results in Fig. 6, it can be concluded that strain fields from surrounding hydrides can cause the reorientation of hydrides at...
applied stress levels much less than 9 GPa and in the order of ~100 MPa. It should be mentioned that the calculated threshold strains versus distance of seeds could be slightly different in 3D simulations, similar to what was seen in single seed simulations [30]. Also, since the applied stain/stress is well below the elastic limit of the material, we expect that the inclusion of dislocations and plastic strain/stress in the model does not meaningfully alter the conclusions of this study, however, to more accurately determine the applied strain/stress necessary for reorientation, simulations should be done in 3D including dislocations and plastic relaxation.

It is also important to notice the significant differences in the time of formation of $\delta$ phase for different cases. When the tensile hoop strain was applied, the seed transformed to the $\delta$ phase much slower than when the radial compressive strain was applied. The radial compressive strain seems to significantly increase the driving force for $\delta$ hydride nucleation from the $\gamma$ hydride phase. It is possible that there is a threshold tensile hoop stress above which $\delta$ hydrides will no longer be the stable phase and $\gamma$ hydrides will become stable. The $B/G$ values (Table. 1), which is proportional to ductility of the material, indicate that the $\gamma$ hydrides are more ductile than $\delta$ hydrides. Thus, further investigation of the $\gamma$ hydrides stabilization could be important as they are significantly more ductile than $\delta$ hydrides, and also more ductile than the $\alpha$ Zr, as shown by a density functional theory study [25]. This could potentially help resolving the embrittlement of claddings due to formation of hydrides.

### 2.4 Conclusion

The effect of applied load on the formation and reorientation of hydrides in nuclear fuel claddings is studied by phase-field modeling study. Single seed simulations showed that to cause significant reorientation of $\delta$ hydrides, an applied strain with a magnitude of at least 0.02 is
required. On the other hand, simulations of two-seed hydrides stacked closely on top of each other, and separately simulations of a cluster of hydrides, both showed that the stress fields surrounding the hydrides reduces the necessary strain by more than one order of magnitude; in these cases, a strain as low as 0.0008 can cause the reorientation of hydrides, and the same is also reported in the experimental studies. This confirms the hypothesis that the configuration of hydrides has significant effect on the required load for reorientation, and as hydrides are formed closer to each other, much less strain/stress is required for reorientation. Distance between hydrides was shown to be a significant factor in determining the threshold strain necessary for reorientation, and as this distance decreases the required strain decrease accordingly. In addition, when several hydrides are in the proximity of each other, the process of reorientation of several hydrides includes the growth of smaller precipitates on top of one another forming a larger hydride aligned in the radial direction. The coalescence of smaller hydrides forming larger hydrides assists the reorientation process, lowering the required applied load for reorientation.

Simulations also showed that the tensile hoop stresses significantly reduce the driving force for the transformation of $\gamma$ to $\delta$ hydrides. This may indicate that $\gamma$ hydrides can be made stable under some specific applied stress conditions. The possibility of stabilizing the $\gamma$ phase should be studied further both experimentally and computationally to determine if it could reduce the risk of hydride embrittlement in cladding materials since $\gamma$ hydrides are much more ductile than $\delta$ hydrides.

2.5 Acknowledgment

We would like to thank the MOOSE team in Idaho National Laboratory for their support in debugging the code.
2.6 References


CHAPTER 3

OXIDATION INDUCED STRESSES IN HIGH-TEMPERATURE OXIDATION OF STEEL:
A MULTIPHASE FIELD STUDY

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Alireza Toghraee\textsuperscript{a} and Mohsen Asle Zaeem\textsuperscript{*}

Abstract: Oxide growth and the induced stresses in the high-temperature oxidation of steel were studied by a multiphase field model. The model incorporates both chemical and elastic energy to capture the coupled oxide kinetics and generated stresses. Oxidation of a flat surface and a sharp corner are considered at two high temperatures of 850 °C and 1180 °C to investigate the effects of geometry and temperature elevation on the shape evolution of oxides and the induced stresses. Results show that the model is capable of capturing the oxide thickness and its outward growth, comparable to the experiments. In addition, it was shown that there is an interaction between the evolution of oxide and the generated stresses, and the oxide layer evolves to reduce stress concentrations by rounding the sharp corners in the geometry. Increasing the temperature may increase or decrease the stress levels depending on the contribution of eigen strain in the generated elastic strain energy during oxidation.

Keywords: oxidation; steel; phase-field model; oxidation induced stress

\textsuperscript{*} Corresponding author and editor
\textsuperscript{a} Department of Mechanical Engineering, Colorado School of Mines, 1500 Illinois St., Golden, Colorado, USA
3.1 Introduction

Designs of advanced energy systems such as nuclear power plants, combustion boilers, and steam and gas turbines, require materials that reliably work in complex and harsh environments under various mechanical, chemical, and thermal loads and contaminations [1, 2]. Steels are one of the main materials commonly used in these harsh environments due to their unique and exceptional mechanical properties. However, it is well-known that they suffer from oxidation, especially at high temperatures, during manufacturing and operation. Different oxide phases, either protective or non-protective, are formed during the oxidation process [3–9]. The evolution of oxide layers may result in the generation of stresses that can lead to several forms of failure in the oxide scale [10, 11]. This may also affect the successful formation of protective layers as well as the surface structure of the final products. The large volume change due to metal/oxide phase transformation (Pilling–Bedworth ratio) accompanied by different thermal expansion of metal and oxide phases are two of the important sources of stress generation in oxides [12–16]. Many experimental works have investigated oxide scale failures due to induced stresses and tried to determine the stress states and strain regimes that lead to decohesion and failure of the various protective and non-protective oxide layers [17–20]. However, most of the experimental and numerical approaches are based on assuming equilibrium condition and have not considered the interaction between chemical and elastic energies.

Recently, the phase-field method (PFM), due to its ability to combine different physics, has emerged as a powerful computational method to study the interaction between microstructure evolution and the resulting stresses [21–25]. Oxidation of metals under dual oxidant and without elastic effects was studied in by Wen et al. [26]. Nijdam et al. [27,28] developed a coupled thermodynamic-kinetic oxidation model to predict the composition profiles of each developed
oxidation phase. However, their model could not capture the strains and stresses generated during the oxidation. In studies by Krishnamurthy et al., a sharp-interface approach was used to study stress distribution in growing oxide films in very simple geometry of single and polycrystalline oxidation [29,30]. High temperature oxidation behavior and kinetics of steels have been studied by various studies [3,8,9,31–37]. However, investigating the high temperature oxidation of steels using the phase-field method has only been done by a few works in the literature. For example, coupling the mechanical and diffusion equations has been considered in the works of Zhou et al. [38,39] to study the stress—oxidation relation and oxidation induced metal depletion in metals and Fe-Cr alloys. However, due to a lack of non-conserved variables, the application of such a model is challenging, especially for multiphase (metal/oxide/fluid) cases. Yang et al. analyzed high-temperature oxidation of Fe-based alloys using PFM [40]. Even though their results showed good agreement with experimental results, their work did not consider the effect of geometry and temperature change on the stress generation, and their model did not also allow the capture of outward oxidation.

In this paper, a multiphase field model was developed to study the short-time oxidation of steel at high temperatures. Even though three types of iron oxides can be found in the high temperature oxidation of steel, several works have reported than during early stages of oxidation (less than 5 min) only wüstite (FeO) is formed [31,41]. Following the experimental observations by Chen and Yuen [31], where they observed only the formation of the FeO oxide phase in a short time period of the oxidation of steel, our model considered only one phase of oxide, but the model was developed in a way that can be later advanced to study the multiphase oxidation of steels. The model incorporates both chemical and elastic energies and is capable of capturing outward oxide growth, elemental concentration changes as well as the evolution of induced
stresses. Due to the very short duration of the oxidation, creep is not considered in this work. Different temperatures and geometries are considered to investigate the effect of these parameters on the interaction between generated stresses and oxide layer evolution.

### 3.2 Multi-Phase Field Model

A diffusion controlled multiphase field model was developed for the oxidation of metals. To mimic the oxidation process, three non-conserved parameters ($\eta$) are considered to represent three phases of metal (steel), oxide (FeO), and the phase containing oxygen (air). Two conserved parameters ($c$) are also considered to track the concentration (amount of material/vol.) of the oxygen and iron as the elements contributing in the oxidation to form the FeO phase. Including the fluid phase will allow us to capture the outward oxidation, which is the dominant case in the formation of FeO [11, 31].

The total free energy of the system, $F$, is considered to consist of chemical and elastic free energies:

$$F = F_{ch} + F_{el}$$

where $F_{ch}$ is the total chemical free energy, and $F_{el}$ is the elastic free energy as follows:

$$F_{ch} = \int_V \left[ f(c, n, \eta) + \sum_{i}^{n} \frac{K_i}{2} \left| \nabla \eta_i \right|^2 + \sum_{i}^{n} \frac{\beta_i}{2} \left| \nabla c_i \right|^2 \right] d\bar{r}$$

(3.2)

$$F_{el} = \int_V f_{el} d\bar{r} = \frac{1}{2} \int_V \sum_{ijkl} C_{ijkl} e_{ij} e_{kl} d\bar{r}$$

(3.3)

where $f$ is the chemical free energy density of the bulk; $K_i$ and $\beta_i$ are the gradient coefficients contributing to the interface properties between the different phases; $n$ is the number of reacting
elements, which was two in our case for iron (Fe) and oxygen (O); and \( p \) is the number of
phases which was three for the metal (m), oxide (ox), and the fluid phase (air). We refer to these
phases and elements by their mentioned abbreviated forms, O, Fe, m, ox, and air. Following the
approach used in the literature [42], \( f \) has the following form:

\[
f = \sum_{i}^{p} h(\eta_i) F_i + g(\eta) + \Lambda \left( \sum_{i}^{p} h(\eta_i) - 1 \right)^2
\]  

(3.4)

\[
g(\eta) = \sum_{i,j} W_{ij} h(\eta) \eta_i^2 \eta_j^2
\]  

(3.5)

\[
\bar{F}_i = \Delta \tilde{G}_i \left( A_i (\hat{c}_O - c_O) + B_i (\hat{c}_{Fe} - c_{Fe})^2 - 1 \right)
\]  

(3.6)

where \( h \) is an interpolation function that smoothly changes between 0 and 1 as \( \eta \) changes from
0 to 1. The term \( g \) represents the interface barrier, which along with the gradient coefficients
control the interface properties. The last term in Equation (4) acts as a penalty term to enforce
that the summation of non-conserved parameters is unity. The concentration dependent part of
the free energy for each phase is represented by \( F \), which is assumed to be a quadratic function
of concentrations. \( \hat{c}_O, \hat{c}_{Fe} \) are concentration values chosen to be close to the equilibrium values,
so the energy will be minimum close to those concentrations, and for numerical purposes, they
have been scaled so that they range between 0 and 1. The concentrations of oxygen and iron in
the oxide are \( c_O = c_{Fe} = 0.5 \), and the concentration of iron in the metal phase is \( c_{Fe} = 0.85 \).
Parameters \( A \) and \( B \) are used to create common tangent lines with tangent points close to
equilibrium concentrations. \( \Delta \tilde{G} \) is the difference of Gibbs energy of formation at the desired
temperature and room temperature: \( \Delta \tilde{G} = G(298) - G(T) \). Temperature dependent relations to
calculate $\Delta G$ are given in Equation (7), and parameters $\bar{A}$ through $\bar{G}$ can be found in the National Institute of Standards and Technology (NIST) database [43].

\[
G^* = H^* - TS^* \\
H^* = \bar{A}t + \bar{B}t^2 / 2 + \bar{C}t^3 / 3 + \bar{D}t^4 / 4 - \bar{E} / t + \bar{F} \\
S^* = \bar{A}ln(t) + \bar{B}t + \bar{C}t^2 / 2 + \bar{D}t^3 / 3 - \bar{E} / (2t^2) + \bar{G} \\
t = T[K] / 1000
\]  

(3.7)

In the elastic free energy contribution, Equation (3), $C_{ijkl}$ is the elasticity tensor; $\varepsilon_{ij}^{el}$ is the elastic strain; and $\bar{r}$ represents the spatial coordinate. The total elasticity tensor or $C_{ijkl}^{tot}$ is defined by the smooth interpolation between the elasticity tensors of each phase as below:

\[
C_{ijkl}^{tot} = \sum_q h(\eta_q) C_{ijkl}^q
\]  

(3.8)

The elastic strain itself is defined by

\[
\varepsilon_{ij}^{el}(\bar{r}) = \varepsilon_{ij}^{tot}(\bar{r}) - \varepsilon_{ij}^*(\bar{r}) = \varepsilon_{ij}^{tot}(\bar{r}) - (\varepsilon_{ij}^{00} + \alpha \Delta T) \eta_p^2(\bar{r})
\]  

(3.9)

where $\varepsilon_{ij}^*$ denotes the eigen strain, which contains the contribution of both phase transformation and thermal expansion. $\varepsilon_{ij}^{00}$ is the stress-free phase transformation strain, which is applied in the direction of the oxidation front and is calculated based on the Pilling–Bedworth Ratio (PBR). Since the transverse component of phase transformation strains are much smaller in comparison with the thermal expansion strains, they have been neglected in the transverse direction. $PBR$ is defined by the ratio between the “volume of the oxide produced” to the “volume of the metal consumed”. The relation between stress-free transformation strain and $PBR$ is given by the following equation [16,44]:

39
\[ \varepsilon_{ij}^{00} = \omega (PBR^{ij3} - 1) \]  

(3.10)

where \( \omega \) is a correction factor \([16,44]\) and \( \alpha \) is the thermal expansion coefficient. Considering small displacements, Equation (9) can be rewritten as

\[ \varepsilon_{ij}^{el}(\vec{r}) = \varepsilon_{ij}^{tot}(\vec{r}) - (\varepsilon_{ij}^{00} + \alpha \Delta T) \eta_{ij}^2(\vec{r}) = \frac{1}{2} \left( \frac{\partial u_i(\vec{r})}{\partial r_j} + \frac{\partial u_j(\vec{r})}{\partial r_i} \right) - (\varepsilon_{ij}^{00} + \alpha \Delta T) \eta_{ij}^2(\vec{r}) \]  

(3.11)

where \( u(\vec{r}) \) represents the displacements at each spatial coordinate. To be able to validate and compare the PFM results with the experimental data, the isothermal condition was assumed and oxidation temperatures similar to experiments in [31] were chosen.

The governing equations of the PFM consist of three sets of coupled partial differential equations (PDEs) for the evolution of the non-conserved field variables \( \eta \) (Allen–Cahn equation), conserved variables for tracking concentrations \( c \) (Cahn-Hilliard equation), and the mechanical equilibrium equation to control the evolution of stresses and strains as summarized below:

\[ \frac{\partial \eta_i}{\partial t} = -L_i \left( \frac{\partial f}{\partial \eta_i} + \frac{\partial f_{el}}{\partial \eta_i} - \sum_k K_{ik} \nabla^2 \eta_i \right) \]  

(3.12)

\[ \frac{\partial c_k}{\partial t} = \nabla \overline{M}_k \nabla \left( \frac{\partial f}{\partial c_k} - \sum_k \beta_{kk} \nabla^2 c_k \right) \]  

(3.13)

\[ \nabla \sigma_{ij} = 0 = \nabla (C_{ijkl} \varepsilon_{kl}^{el}) \]  

(3.14)

where \( L_i \) is the structural relaxation coefficient and \( \overline{M}_k \) is the mobility. Mobility is proportional to diffusion coefficients through \( \overline{M}_k = \frac{D_k}{(d^2 F / d c_k^2)} \), which requires fifth order differentiation. To
consider the changes in the mobility in each phase, the mobility is interpolated between phases according to the following relation

$$\bar{M}_k = \sum_{i}^{p} M^i_k \eta_i$$

(3.15)

where $M^i_k$ is the mobility of element $k$ (O, Fe) in phase $i$ (m, ox, air). Since the concentrations are scaled, the exact value of the diffusion coefficients cannot be used. However, the ratio between $M^i_k$ is determined based on the ratio of diffusion coefficients. Since the diffusion coefficients change with temperature [45] the values for $M^i_k$ are modified proportionally. In this way, as $M^i_k$ changes based on phase and temperature, $\bar{M}_k$ is also capable of capturing the changes based on phase and temperature. To make sure that the main factor in the evolution of the oxide is the diffusion of elements (diffusion-controlled reaction), relaxation parameters $L_i$ were selected to be at least one order of magnitude larger than the slowest mobility $M^i_k$ in each phase.

Interface properties such as interface thickness $\lambda$ and interface energy $\sigma$ are determined through model parameters $K_i, \beta_i$ and $W_0$. Analytical relations to calculate the interface properties based on the model parameters are not always available, and numerical approaches should be used to match the simulated interface energy to its actual value. The reported energy for the FeO/air interface is $\sigma_{\text{ox/air}} = 3J/m^2$ [20]. However, to the best of our knowledge, no value for the metal/FeO interface has previously been reported. Thus, the same interface energy as in FeO/air was used here. Following the approach by Bair et al. [42] to determine the interface properties, initial tuning of the model parameters resulted in an interface thickness of $\lambda = 40nm$ and interface energy of $\sigma \approx 3.3J/m^2$. However, as it will be explained in the next section, higher
values of $\lambda$ and $\sigma$ were used for two-dimensional (2D) simulations. The material properties and model parameters used for simulations are shown in Table 1.

### Table 3.1. Material properties and model parameters. Elastic constants are from [20, 46], thermal expansion coefficient is from [47], and $\epsilon_{ij}^0$ is calculated based on PBR = 1.67 for FeO and $\omega = 0.11$ [44].

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}^{m}$</td>
<td>275 GPa</td>
<td>$C_{11}^{ox}$</td>
<td>217 GPa</td>
<td>$K_{ij}$</td>
<td>0.3</td>
</tr>
<tr>
<td>$C_{12}^{m}$</td>
<td>118 GPa</td>
<td>$C_{12}^{ox}$</td>
<td>121 GPa</td>
<td>$\beta_{ij}$</td>
<td>0.3</td>
</tr>
<tr>
<td>$C_{44}^{m}$</td>
<td>78 GPa</td>
<td>$C_{44}^{ox}$</td>
<td>46 GPa</td>
<td>$\Lambda$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>$\epsilon_{ij}^{00}$</td>
<td>0.02</td>
<td>$\alpha$</td>
<td>$1.65 \times 10^{-5}$ [1/K]</td>
<td>$W_{ij}$</td>
<td>$-0.11$</td>
</tr>
<tr>
<td>$A_m = B_m$</td>
<td>3</td>
<td>$A_{ox} = B_{ox}$</td>
<td>3</td>
<td>$A_{air} = B_{air}$</td>
<td>2</td>
</tr>
<tr>
<td>$\tilde{c}_O$</td>
<td>0.001</td>
<td>$\tilde{c}_{ox}$</td>
<td>0.5</td>
<td>$\tilde{c}_{air}$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\tilde{c}_{Fe}^{m}$</td>
<td>0.8</td>
<td>$\tilde{c}_{Fe}^{ox}$</td>
<td>0.5</td>
<td>$\tilde{c}_{Fe}^{air}$</td>
<td>0.002</td>
</tr>
<tr>
<td>$M_{O}^{air}$</td>
<td>10</td>
<td>$M_{O}^{m}$</td>
<td>100</td>
<td>$M_{O}^{ox}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$M_{Fe}^{air}$</td>
<td>0.001</td>
<td>$M_{Fe}^{m}$</td>
<td>0.3</td>
<td>$M_{Fe}^{ox}$</td>
<td>100</td>
</tr>
<tr>
<td>$L_{air}$</td>
<td>20</td>
<td>$L_{m}$</td>
<td>20</td>
<td>$L_{ox}$</td>
<td>20</td>
</tr>
</tbody>
</table>

### 3.3 Simulation Results and Discussions

To benchmark the model against experiments, we used the data that reported oxide scale growth versus time of oxidation by Chen and Yuen [31]. The reported oxide phase that formed in short-time oxidation is FeO with a rock slat crystal structure that formed on the surface of the steel substrate. Steel will undergo phase transformation from Body-Centered Cubic (BCC) to Face-Centered Cubic (FCC) above 900 °C. However, since the experiments were done at steady-state temperatures below 900 °C, there was no phase transformation during the oxidation, hence no phase transformation in the oxide was considered in the simulations. It should be noted that oxidation temperature and phase change affect the elastic constants, thermal expansion, and
mobilities (diffusion). These effects are considered by changing the material properties and model parameters accordingly. The composition of the studied steel is given in Table 2. It is worth emphasizing that even though other elements are present, only the diffusion of the iron and oxygen were tracked in the simulations since other elements did not form oxides (or other phases) in the short-time oxidation experiment [31].

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>P</th>
<th>S</th>
<th>Cr</th>
<th>Ni</th>
<th>Cu</th>
<th>Al</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05</td>
<td>0.21</td>
<td>0.01</td>
<td>0.01</td>
<td>0.014</td>
<td>0.014</td>
<td>0.009</td>
<td>0.012</td>
<td>0.042</td>
<td>0.0032</td>
</tr>
</tbody>
</table>

Table 2. Steel composition (wt%) used in the experiment [31].

We first completed one-dimensional (1D) simulations using an interface energy of \( \sigma = 3.3 J/m^2 \). A narrow layer of oxide with a thickness of \( 2 \mu m \) was initially placed in the middle of a \( 500 \mu m \) long simulation domain, where metal and air phases were placed on the left and right side of this initial oxide, respectively, and the growth of the oxide layer at each time \( t \) was calculated by the difference between the instantaneous and initial thicknesses of the oxide layer. Zero displacements \( u \) and zero flux for phase-field (PF) variables \( \eta \) and \( c \) were assumed as boundary conditions. Since in reality the concentration of oxygen in air is much less than in the solid phases (metal and oxide), a much larger volume of air is required to provide the amount of oxygen for the formation of oxide. However, simulating such a large volume of air would be computationally very expensive and is not feasible. In addition, assuming a larger volume of air will serve no purpose to predict the stress distribution, which was the main objective of this study. As a result, to address this problem, a high concentration of \( c_o(t=0)=0.3 \) was considered as the initial condition of oxygen in the air phase. The coupled
governing Equations (12)–(14) were solved in a finite element scheme using the Multiphysics Object Oriented Simulation Environment (MOOSE) framework. Adaptive meshing was utilized to create a finer mesh where it was required and to guarantee that there were at least four or five elements through the diffusive interface of PFM; also, adaptive time stepping was used to ensure convergence.

1D simulations were performed at various temperatures ranging from 850 °C to 1180 °C to be able to compare the results with the experimental data [31]. As illustrated in Figure 1a, the predicted oxide growth by the PF model was in good agreement with experimental data for temperatures of 850 °C and 1000 °C, where a nonlinear (parabolic like) growth rate can be observed. To emphasize the need for the inclusion of elasticity in predicting the oxide growth, for the cases of 850 °C, we plotted the results both with and without considering elasticity, and the results clearly indicate that elastic strain energy needs to be considered. When the elastic strain energy is not considered, the effects of transformation strain and the expansion due to the formation of oxide will be neglected. This makes the formation of the oxide phase easier, hence an overestimation of oxide thickness was observed. The PFM simulations for higher temperatures also predicted a nonlinear growth, but the experiments showed a quasilinear trend. This can be due to the fact that the considered model for the concentration dependent energy, \( F(c) \), has a quadratic form. Thus, as the oxygen and Fe are consumed, the driving force for diffusion of the species, which is proportional to \( \frac{\partial f}{\partial c} \times \frac{\partial F}{\partial c} \), decreases linearly and therefore a nonlinear (inverse quadratic like) evolution of oxide is observed. Nonetheless, the PFM simulations predicted the final thickness of the oxide layer with a \(-2.3\%\) error for \( T = 1100 \) °C.
and −3.9% error for $T = 1180$ °C when compared to the experiments at the same time of oxidation.

Figure 3.1. Oxide layer growth at different temperatures (°C) for a diffusive interface thickness of (a) $\lambda = 40\,\text{nm}$ and (b) $\lambda = 800\,\text{nm}$. Experimental results are obtained from [31].

The interface energy of $\sigma \approx 3.3\,J/m^2$ corresponds to a very narrow interface thickness of about 40 nm, which requires a very fine mesh. Although this might not affect 1D simulations, it will make 2D simulations computationally very expensive, especially when the domain size is in the order of millimeters. Since mechanical equilibrium equations are not time dependent, only the thickness of the oxide layer will affect the generated stress. Thus, before running 2D simulations, we ran additional 1D simulations to see if we could increase the diffusive interface thickness without affecting the growth rate and thickness of the oxide layer. We increased the diffusive interface thickness from 40 nm to 800 nm (corresponding to $\sigma \approx 27\,J/m^2$), and without the loss of generality, parameters $L_i$ and $M'_i$, which act as time constants, were scaled down to keep the oxide growth rate and the thickness of the oxide layer at each time, similar to the case with the actual interface energy. This scaling was done while the ratio between mobilities $M'_i$,
which are related to diffusion coefficients, were preserved. Results of the oxide growth rate for this case are depicted in Figure 1b. As can be seen, the patterns were very similar to the cases in Figure 1a, especially for lower temperatures. For higher temperatures, the prediction of PFM simulation for the final oxide layer thickness only had a −3.5% error for oxidation at $T = 1100 \, ^\circ C$ and +2.1% error for $T = 1180 \, ^\circ C$. This similarity between the oxide growth rates and the oxide thicknesses for thin and thick diffusive interfaces allowed us to use a thicker diffusive interface for the prediction of oxide induced stresses in 2D simulations.

Figure 2 shows the evolution of metal, oxide, air phases, and the corresponding concentrations with respect to their initial condition at the isothermal oxidation temperature of $850 \, ^\circ C$. It is evident that the outward oxidation is dominant. Following the concentration evolution of Fe (Figure 2b), the concentration at metal/oxide interface dropped from $c_{Fe} = 0.85$ at $t = 0 \, s$ to the $c_{Fe} = 0.75$ at $t = 60 \, s$, accounting for the migration of Fe atoms from the metal phase to oxide phase. Likewise, for the evolution of oxygen concentration, Figure 2c shows the reduction from $c_{O} = 0.3$ to $c_{O} = 0.19$ at the oxide/air interface due to the consumption of oxygen to form the oxide. This is one of the advantages of this model since the duration of oxidation can be controlled by adjusting the difference between the initial oxidant concentration and its equilibrium value.

Even though 1D simulations can be used to study simple oxide growth, they are not sufficient for determining stresses, especially for different geometries. Simulations beyond 1D are required to account for thermal strains caused by mismatched thermal expansion coefficients of metal and oxide, stress-free transformation strains as well as mechanical constraints depending on geometries and boundary conditions. Since in our case the oxidation time was very
short and creep did not happen, elastic 2D models can be used to study the oxide evolution and the induced stresses. Thus, to study the stresses generated by the oxidation, 2D simulations were performed. The effect of geometry was studied by considering oxidation in flat (planar) and corner-shape geometries. In addition, to investigate the effect of temperature, two extreme oxidation cases at 850 °C and 1180 °C were considered. Plane strain condition is imposed assuming the dimension in the z direction is much larger than the x- and y-directions. For the planar oxidation case, a narrow strip in the middle of a steel plate is considered with the x-direction representing the oxidation direction. No-flux boundary condition for PF variables were assumed and the mechanical boundary conditions are shown in Figure 3. It should be noted that due to the symmetry in the y-direction, only the top half was simulated to save the computational costs. Figure 3 summarizes the results for oxidation at 850 °C.

Figure 3.2. Evolution of phase-field (PF) variables during oxidation at temperature of 850 °C. (a) phases (b) concentration of Iron (c) concentration of oxygen.
Figure 3.3. Oxide layer growth and evolution of induced stresses in planar oxidation (T = 850 °C). Domain size is 0.5 mm × 0.5 mm. Top left snapshot also shows the mechanical boundary conditions.
As the oxide layer forms, it tends to expand due to the stress-free phase transformation and thermal strains, but the interaction with the metal phase prevents this expansion to be free of stress. In the case of planar oxidation, the expansion of oxide in the y-direction is constrained by the metal. Thus, the oxide goes under compression and the metal goes under tension. The compressive stress in the y-direction, $\sigma_{yy}$, in the oxide phase, is the maximum at the bottom of the domain in Figure 3, which is the furthest away from the upper free edge and where the expansion in y-direction is prevented the most. This stress gradually decreases toward the upper free edge. On the other hand, since the stress generated in the metal is induced by oxide expansion, the maximum tensile stress in the y-direction in the metal increases toward the top edge. In the x-direction, since the oxide can expand freely, there generated stress, $\sigma_{xx}$, is negligible (less than 10 MPa) in the oxide phase.

At the metal/oxide interface near the upper free edge in Figure 3, the expansion of oxide in the y-direction on one side and the prevention of movement in the x-direction by metal on the other side create a local counterclockwise bending of the metal/oxide interface. This causes the metal phase to experience a highly localized compressive stress in the x-direction. The trend of stress evolution shows that as the oxide layer evolves, the force it applies on the metal phase increases, hence the generated stresses increase. Looking at the stress maps in Figure 3, these incremental increases in stresses were more noticeable. According to the stress maps, two critical regions could be detected. The first is the metal/oxide interface at the top edge, which shows the maximum equivalent (von Mises) ($\sigma_{eq}$) and the maximum shear stress ($\sigma_{xy}$). Additionally, maximum compressive ($\sigma_{xx}$) and tensile ($\sigma_{yy}$) normal stresses were observable at this region. In addition, the other criterion that makes this region critical is the transition between compression
and tension in the normal stresses. Since the strength is usually lower at the interface of two phases, this region is susceptible to failure and delamination/separation of oxide from the metal substrate may occur. The other critical region that is at risk of failure is at the bottom edge of the oxide phase, which experiences the maximum compressive normal stress $\sigma_{yy}$ as well as high levels of von Mises stress. Since this compressive stress acts on a plane parallel to the oxide/metal interface and perpendicular to the oxide growth direction, any small surface irregularities can initiate spalling and buckling of the oxide scale [19].

To investigate the effect of geometry on the oxide growth and generated stress, oxidation at a sharp corner of a steel plate was considered. In this case, the oxide front is in both the x- and y-directions, and the z direction represents the long dimension along the edge of the steel plate. The results for this case are illustrated in Figure 4. In terms of stress state, the oxide and metal phase undergo compression and tension, respectively, which is similar to the planar case. However, as the oxide layer grows and becomes thicker, the stress levels decrease, which is different from the observed pattern in the planar case where the stress levels increase as the oxide grows. The reason for such behavior can be explained by the shape of oxide growth. Stress distribution at the initial stage of oxidation revealed high levels of stress at the metal/oxide interface right at the sharp corner, where expansion of the oxide in both the x- and y-directions, accompanied by the sharp corner geometry, led to stress intensity at this region. As oxidation continues, instead of keeping those sharp corners, the oxide evolves to round the sharp corners at both metal/oxide and oxide/air interfaces, which reduce the stress concentrations at those areas. This smoothing and rounding of the corners have also been observed in the oxidation of Si [48].
Figure 3.4. Oxide layer growth and evolution of induced stresses for the oxidation of a sharp corner (T = 850 °C). Domain size is 0.5 mm × 0.5 mm.
In Figure 4, in terms of critical areas, the inner corner of the metal/oxide interface is one of the zones where the highest level of equivalent (von Mises), shear and normal stresses occurred in both the oxide and metal phase. This high level of stress with a sharp transition between compression and tension from one side to the other side of the interface makes this region prone to failure and makes it possible to separate the oxide from the base metal. A high level of compressive stress along the oxide layer and far from the corner was observed, which increased the chance of buckling, similar to the case of planar oxidation. It should be noted that in all of these cases, the highest level of stress was observed in the oxide layer, which did not show plastic behavior. Stress levels in the metal phase were also less than 1 GPa in this short-time oxidation, which was below the yield strength of several steels [49].

The effect of increasing the oxidation temperature on oxide growth and the induced stresses was considered by repeating the simulation for 1180 °C. It is expected that increasing the temperature increases the oxidation kinetics, thus thicker oxide layers form. The results showed that elevating the temperature did not change the pattern of stress distribution and stress states, and the maximum and minimum stresses occurred at the same regions as in the lower oxidation temperature of 850 °C. The trend of increasing or decreasing of stress versus time also remained unchanged for both planar and sharp corner oxidation. However, the stress values varied as the temperature increased. For the purpose of comparison, variations of the extremum values of stresses are presented in Figure 5, for both planar and sharp corner oxidation.
Increasing the temperature resulted in increasing the stress levels in both the metal and oxide in the case of planar oxidation, while stress levels were decreased in the oxidation of a sharp corner. Increasing the temperature has effects on both elastic constants $C_{ijkl}$ and thermal expansion strains. This increase in oxidation temperature from 850 °C to 1180 °C resulted in about a 30% reduction of the elastic constants. For the planar oxidation, the oxide could move freely in the x-direction, but it was constrained in the y-direction due to its interface with the base metal. Additionally, for planar oxidation in the y-direction, the main dominant component of the eigen strain was thermal expansion. Comparing the eigen strains of oxide in the y-direction ($\epsilon_{22}^{*}$) for planar oxidation showed a significance increase of 54% from 0.013 to 0.02 when the temperature increased from 850 °C to 1180 °C. Thus, the increase in eigen strain in the y-direction was more dominant than the decreases in elastic constants, which led to elevated stress levels. On the other hand, in the case of oxidation of a sharp corner, there were two oxidation fronts in both the x- and y-directions. Furthermore, the contribution of phase
transformation strain (0.02) was added to the same thermal expansion strain in the case of planar oxidation, resulting in a change of eigen strain from 0.033 to 0.04 when the temperature increased from 850 °C to 1180 °C. This resulted in only a 21% increase in the eigen strain and makes the reduction in elastic constants more dominant, hence reducing the stress levels.

3.4 Conclusions

Stress evolution during the short-time oxidation of low alloy steels at high temperatures was studied utilizing a phase-field model. The phase-field model was capable of capturing the outward growth of the oxide layer (FeO) on the steel substrate in contact with air as well as variations in iron and oxygen concentrations during oxidation. By incorporating elastic strain energy in the model and coupling mechanical equilibrium equations to the phase-field equations, the evolution of stresses during the oxidation was investigated. The effect of geometry on the interaction between oxide evolution and induced stresses was studied by considering oxidation on a flat substrate (planar oxidation) and a sharp corner. Results revealed that in the case of planar oxidation, the growth of oxide increased the stress level in both the oxide and base metal. However, stress intensities in the sharp corners may change the shape of oxide evolution, and the oxide layer evolves so that it rounds the sharp corners in order to reduce the stress levels.

In addition, the effect of temperature elevation was investigated by considering two extreme temperatures of 850 °C and 1180 °C. Results showed that increasing the temperature changes the stress levels by altering the elastic constants and eigen strains, and depending on which one is dominant, the stress level may increase (planar oxidation) or decrease (sharp corner oxidation). Using the stress distribution map, critical zones that are prone to different modes of failure such as delamination and buckling can also be detected. The developed multiphase field
model has the flexibility to be extended for the study of multiphase oxidation. Additionally, plasticity (especially for long-time oxidation) and crack propagation equations [50] can be incorporated to develop a more comprehensive model to study oxidation induced cracks and deformations.

3.5 Acknowledgments

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3.6 References


CHAPTER 4
INTERGRANULAR OXIDATION OF METALS AND INDUCED STRESSES:
A MULTI-PHASE FILED STUDY

Prepared for Submission
Alireza Toghaee and Mohsen Asle Zaeem*

Abstract: A multi-phase field model is developed to study intergranular oxidation in metals and alloys. The model incorporates chemical and elasto-plastic mechanical energy to capture the kinetics of oxides coupled with the induced stresses. Since grain boundaries act as fast transporting channels with a diffusion rate one order of magnitude higher than inside the grain, the model is designed such it is capable of assigning different and higher mobilities to different gain boundaries. The model is applied to a polycrystalline with different combination of random and $\Sigma 3$ grain boundary types to simulate cases similar to those observed in experiments. Results show that the model is capable of capturing oxidation along grain boundaries as well as the generated stresses. In addition, $\Sigma 3$ grain boundaries showed more oxidation resistance as observed in experiments. Stresses induced by the intergranular oxidation and the critical zones with high stress intensities prone to cracking are identified.

Keywords: Intergranular oxidation; grain boundary; phase-field model; oxidation induced stress

* Corresponding author and editor
a: Department of Mechanical Engineering, Colorado School of Mines, 1500 Illinois St., Golden, Colorado, USA
4.1 Introduction

Thermal power plants are the first source of energy generation worldwide, and it is estimated that they maintain this position in future decades [1]. Improving the efficiency, while reducing the emission and environmental effects, requires increase in the operation temperature of these power plants. This high temperature accompanied by various mechanical, chemical and radiation loads, as well as contaminations lead to harsh environments and makes the design of materials operating in these conditions very challenging [2-4]. Metallic materials, especially steels, are considered as one the best candidates for use in different parts of thermal power plants, owing to their exceptional mechanical properties. However, it is well known that most metals and alloys suffer from corrosion and oxidation, and they can be oxidized during service. Besides different phases of oxides in different metals, the oxidation pathway and oxidation kinetics are influenced by the grain boundaries, and intergranular oxidation is often observed that can be particularly detrimental to structural reliability, because it usually enhances intergranular fracture [5-7]. As a result, understanding the oxidation behavior at grain boundaries is of great importance in order to improve intergranular oxidation resistance.

The distribution and structure of grain boundaries play an important role in the kinetics of many high-temperature phenomena, since the transport of materials along interfaces is often much faster than throughout the bulk (i.e., inside the grains). The intergranular oxidation is attributed to the higher diffusion rate of elements at grain boundaries. Study of diffusion rate of elements at grain boundaries and investigation of the effect of misorientation and coincident site lattice (CSL) on the diffusion rate has been the subject of several researches [8-12]. These studies reported that the diffusion rates along grain boundaries are at least one order of
magnitude higher than the lattice diffusion. However, some grain boundaries can have higher or lower diffusion rates, depending on the misorientation angle and the CSL number (Σ type).

Several researchers have studied the effect of grain boundary structure and characteristics on the intergranular oxidation [5, 13-17]. Yamaura et al. [5] investigated the oxidation of Ni-Fe based alloys and observed that Σ3, Σ11 and Σ19 grain boundaries have more resistance to oxidation than other Σ and random grain boundaries. In other works [15, 16], the effect of grain boundary characteristics on oxidation of ferritic and austenitic steels was studied, where it was also reported a lower oxidation rate on Σ3 grain boundaries comparing to random ones. Wagenhuber et al. [17] utilized the resistance of low-Σ grain boundaries to prevent inter-crystalline oxidation attack and improve the fatigue response of Ni-base superalloys.

Even though there are analytical approaches available to study oxidation processes, complexities like grain boundaries cannot be adequately taken into account. Experimental approaches also have limitations in harsh environments and nano/micro scales. Thus, it becomes necessary to develop and utilize computational tools to have better insight and understanding of grain boundary oxidation. Among the computational methodologies, Phase-Field Method (PFM) has emerged as a powerful computational tool to study the evolution of microstructures incorporating different physics [18-22]. However, there are a few works studying the oxidation and especially the oxidation along grain boundaries using computational approaches. In addition, most of the PFM studies have their focus either on the electrochemical aspect of the corrosion, or on the cracking induced by corrosion. For example, Mai et al. [23, 24] and Lin et al. [25] applied PFM to simulate stress corrosion cracking. The model captures oxide film rupture and stress concentration effects on the corrosion kinetics. However, their model considers a single crystal domain and no corrosion/oxidation on the grain boundaries were reported in their results.
Intergranular oxidation was simulated by Jahns et al. [26], and their model considered a higher diffusivity at grain boundaries and showed oxidation along grain boundaries. Nevertheless, this model fails to consider the mechanical contributions in the model, as a result, obtaining a stress map and determining critical zones for crack nucleation and growth is not possible using this model.

In this paper, a multiphase field model is developed to study the intergranular oxidation in metals. The model adopts our recent multi-phase field framework for multiphase phenomena, [19] and considers three phases of metal/alloy, oxide and the oxidant fluid. Additional non-conserved PF parameters are introduced to represent different grain orientations in the metal. In addition, the mobility questions are modified in a way that not only can they take higher values along the grain boundaries, simulating higher diffusion rate, but also they can be engineered such that certain grain boundaries have higher mobility with respect to other grain boundaries. Intergranular oxidations for different grain boundary structures, as well as the corresponding generated stresses, are studied.

4.2 Elasto-plastic multi-phase field model

A multiphase field model is developed for oxidation in polycrystalline metals. To simulate the oxidation process, non-conserved parameters ($\eta$) are considered to represent phases of metal (steel) and their grains’ orientations, oxide and oxidant fluid (air). Two conserved parameters ($c$) are also considered to track the concentration of the oxygen and iron as the elements contributing in the oxidation.

The total free energy, $F$, is considered to consist of chemical and mechanical free energies:
\[ F = F_{ch} + F_{mech}, \] 

where \( F_{ch} \) is the total chemical free energy, and \( F_{mech} \) is the mechanical energy as follows:

\[
F_{ch} = \int_V \left[ f(c_n, \eta_p) + \sum_{i,j}^p K_{ij} \frac{1}{2} \left| \nabla \eta_i \right| \left| \nabla \eta_j \right| + \sum_i^p \frac{\beta_i}{2} \left| \nabla c_i \right|^2 \right] d\vec{r},
\]  

\[
F_{mech} = \int_V \left[ f_{el} d\vec{r} = \frac{1}{2} \int V \varepsilon_{el}^{tot} \varepsilon_{el}^{tot} d\vec{r}. \right.
\]  

Here, \( f \) is the chemical free energy density of the bulk, \( K \) and \( \beta \) are gradient coefficients contributing to the interface properties between different phases. \( n \) is number of reacting elements which is 2 in our case for iron (Fe) and oxygen (O), and \( p \) is the number of non-conserved parameters which is six accounting for the four Metal grains’ orientation (m), Oxide (ox) and the fluid phase (air). We refer to these phases and elements by their mentioned abbreviated forms, O, Fe, m, ox, and air. Following our approach used in [19], \( f \) has the following form:

\[
f = \sum_i^p h(\eta_i) \bar{F}_i + g(\eta_i) + \Lambda \left[ \sum_i^p h(\eta_i) \right]^{-1},
\]

\[
g(\eta_i) = \sum_{i,j} W_{ij} h(\eta_i) \eta_i^2 \eta_j^2,
\]

\[
\bar{F}_i = \Delta G_i \left( A (\hat{c}_O - c_O)^2 + B (\hat{c}_{Fe} - c_{Fe})^2 - 1 \right),
\]

where \( h \) is an interpolation function that smoothly changes between 0 and 1. \( g \) is called the interface barrier or penalty term which along with the gradient coefficients determine the
properties of interfaces. The concentration dependent part of the free energy for each phase is represented by \( F \), which is assumed to have a quadratic form. \( \hat{c}_O, \hat{c}_{Fe} \) are concentration values are chosen to be close to the equilibrium values so the energy will be minimum close to those concentrations, and for numerical purposes they have been scaled such that they range between 0 and 1. The concentrations of oxygen and iron in the oxide are \( c_O = c_{Fe} = 0.5 \), and iron in the metal phase is \( c_{Fe} = 0.85 \). Parameters \( A \) and \( B \) are used to create common tangents lines with tangent points close to equilibrium concentrations. \( \Delta \tilde{G} \) is the difference of Gibbs energy of formation at the desired temperature and room temperature: \( \Delta \tilde{G} = G(298) - G(T) \) and its detailed description can be found in [19].

In the elastic free energy contribution, Eq.(4.3), \( C_{ijkl} \) is the elasticity tensor, \( \varepsilon_{ij}^{\text{el}} \) is the elastic strain, and \( \vec{r} \) represents the spatial coordinate. The total elasticity tensor or \( C_{ijkl}^{\text{tot}} \) is defined by smooth interpolation between elasticity tensors of each phase as below:

\[
C_{ijkl}^{\text{tot}} = \sum_{q} h(\eta_q) C_{ijkl}^q.
\] (4.7)

The elastic strain itself is defined by

\[
\varepsilon_{ij}^{\text{el}}(\vec{r}) = \varepsilon_{ij}^{\text{tot}}(\vec{r}) - \varepsilon_{ij}^{00}(\vec{r}) - \alpha(\vec{r}) \Delta T - \varepsilon_{ij}^{p} = \varepsilon_{ij}^{\text{tot}}(\vec{r}) - (\varepsilon_{ij}^{00} + \alpha \Delta T) \eta_p^2(\vec{r}),
\] (4.8)

where \( \varepsilon_{ij}^{00} \) is the stress-free transformation strain which is applied in the direction of oxide front and is calculated based on Pilling-Bedworth Ratio (PBR) [19, 27, 28]. \( \alpha \) is the thermal expansion coefficient and \( \varepsilon_{ij}^{p} \) is the plastic strain. Considering small displacements, Eq. (11) can be rewritten as
\[
\varepsilon_{ij}^\theta(\vec{r}) = \varepsilon_{ij}^{\text{net}}(\vec{r}) - (\varepsilon_{ij}^{\theta} + \alpha \Delta T) \eta^2_{ij}(\vec{r}) - \varepsilon_{ij}^{\theta}, \quad (4.9)
\]

where \( \varepsilon(\vec{r}) \) represents the displacements at each spatial coordinate.

The governing equations of the PFM consist of three sets of partial differential equations (PDEs) for evolution of the non-conserved field variables \( \eta \) (Allen-Cahn equation), conserved variables for tracking concentrations \( c \) (Cahn-Hilliard equation), and the mechanical equilibrium equation to control the evolution of stresses and strains as summarized below.

\[
\frac{\partial \eta_i}{\partial t} = -L_{ij} \left( \frac{\partial f}{\partial \eta_i} + \frac{\partial f_d}{\partial \eta_i} + \sum_{i,j} K_{ij} \nabla^2 \eta_i \right), \quad (4.10)
\]

\[
\frac{\partial c_k}{\partial t} = \nabla \bar{M}_k \nabla \left( \frac{\partial f}{\partial c_k} - \sum_{k} \beta_k \nabla^2 c_k \right), \quad (4.11)
\]

\[
\nabla \sigma_{ij} = 0, \quad (4.12)
\]

where \( L_{ij} \) is the structural relaxation coefficient, and \( \bar{M}_k \) is the mobility. Mobility is proportional to diffusion coefficients which themselves are related to the material, temperature and the grain boundary conditions. It has been observed that oxidation happens faster in grain boundaries since elements have higher diffusion rates along the grain boundaries than inside the grains [15, 16]. To account for different mobilites inside each phase and also along the grain boundaries, the mobility of the form below is considered:

\[
\bar{M}_k = \sum_{i,j} \frac{M^i_k h(\eta_i) h(\eta_j)}{h(\eta_i) h(\eta_j)} + 1, \quad (4.13)
\]
In equation (13), the mobility of element $k$ (O, Fe) in phase $i$ (metal, oxide, air) and the term $\mu_{ij}$ will control the higher diffusion rates along the grain boundaries. $\mu_{ij}$ acts as a multiplier that determines how much the diffusion rate, and consequently mobility, is higher along grain boundaries. Even though there are relations between grain boundary $\Sigma$ types and the increase in the diffusion rate, there is no specific relation between the diffusion rate and the grain boundaries misorientation angle. Thus, the values for $\mu_{ij}$ should be assigned manually for each misorientation angle. It should be noted that $\mu_{ij}$ will have zero values for the interfaces rather than metal grain boundaries and the mobility will be reduced to $M_k^{ij} h(\eta_i)$ for the rest of the domain. Interface properties, interface thickness $\lambda$ and interface energy $\sigma$ are determined through model parameters $K_{ij}, \beta_i$, and $W_{ij}$. More details on the approach to determine these values can be found on [19, 29]. The material properties and model parameters used for simulations are shown in Table 1.

Table 4.1. Materials and model properties.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{11}^m$</td>
<td>275 GPa</td>
<td>$C_{11}^{ox}$</td>
<td>217 GPa</td>
<td>$K_{ij}$</td>
<td>0.3</td>
</tr>
<tr>
<td>$C_{12}^m$</td>
<td>118 GPa</td>
<td>$C_{12}^{ox}$</td>
<td>121 GPa</td>
<td>$\beta_i$</td>
<td>0.3</td>
</tr>
<tr>
<td>$C_{44}^m$</td>
<td>78 GPa</td>
<td>$C_{44}^{ox}$</td>
<td>46 GPa</td>
<td>$\lambda$</td>
<td>$1 \times 10^6$</td>
</tr>
<tr>
<td>$\varepsilon_{ij}^{(0)}$</td>
<td>0.02</td>
<td>$\alpha$</td>
<td>$1.65 \times 10^{-5}$ [1/K]</td>
<td>$W_{ij}$</td>
<td>$-0.11$</td>
</tr>
<tr>
<td>$A_m = B_m$</td>
<td>3</td>
<td>$A_{ox} = B_{ox}$</td>
<td>3</td>
<td>$A_{air} = B_{air}$</td>
<td>2</td>
</tr>
<tr>
<td>$\hat{C}_O^m$</td>
<td>0.001</td>
<td>$\hat{C}_O^{ox}$</td>
<td>0.5</td>
<td>$\hat{C}_O^{air}$</td>
<td>0.15</td>
</tr>
<tr>
<td>$\hat{C}_{Fe}^m$</td>
<td>0.8</td>
<td>$\hat{C}_{Fe}^{ox}$</td>
<td>0.5</td>
<td>$\hat{C}_{Fe}^{air}$</td>
<td>0.002</td>
</tr>
<tr>
<td>$M_{O}^{air}$</td>
<td>10</td>
<td>$M_{O}^m$</td>
<td>100</td>
<td>$M_{O}^{ox}$</td>
<td>0.1</td>
</tr>
<tr>
<td>$M_{Fe}^{air}$</td>
<td>0.001</td>
<td>$M_{Fe}^m$</td>
<td>0.3</td>
<td>$M_{Fe}^{ox}$</td>
<td>100</td>
</tr>
<tr>
<td>$L_{air}$</td>
<td>20</td>
<td>$L_{m}$</td>
<td>20</td>
<td>$L_{ox}$</td>
<td>20</td>
</tr>
</tbody>
</table>
4.3 Simulation Results and Discussions

A 250 x 100 \( \mu m \) domain is considered, where a narrow layer of initial oxide with a thickness of 5 \( \mu m \) is placed next to a 65 \( \mu m \) thick metal layer; the air phase is placed on the right side of this initial oxide layer. Zero displacements (\( u \)) and zero flux for PFM variables (\( \eta \) and \( c \)) are assumed as boundary conditions. An artificially high concentration of oxygen \( c_o(t=0)=0.3 \) was considered as the initial condition in the air phase to provide the oxygen required for oxidation. It should be noted that the concentration of oxygen in air is much less comparing to the oxide phase. Thus, this high concentration is necessary, otherwise, a large volume of air phase is required to provide the sufficient oxygen for oxidation. The governing equations (10-12) are solved using the Multiphysics Object Oriented Simulation Environment (MOOSE) framework. Adaptive meshing adaptive and time stepping are used for lower computational cost and improved convergence rate.

As it has been observed in experiments, grain boundaries with lower \( \Sigma \) type (\( \Sigma \) 3) have higher resistance to oxidation with respect to random grain boundaries. One of the parameters explaining this higher resistance is the lower diffusion rate of \( \Sigma \) 3 grain boundaries compared to the random ones. To study different grain boundary structures and their effect on the oxidation, we assume that our grain boundaries are mixture of random grain boundaries and \( \Sigma \) 3 ones. \( \Sigma \) 3 grain boundaries are chosen since they are the most observed Low \( \Sigma \) grain boundary types in experiments [15, 16]. Thus to create these grain boundary combinations, three non-conserved parameters are considered to represent three grain orientations in the metal phase. It is assumed that \( \langle 100 \rangle, \langle 010 \rangle \) and \( \langle 001 \rangle \) of the cubic structure is aligned with the X, Y and Z direction of the simulation domain. To create random grain boundaries the grains types 1, 2 and 3 are rotated about \( \langle 001 \rangle \) with -15, 0 and 45 degrees, respectively. For the case with a mixture of random and
\( \Sigma 3 \) grain boundaries, grain type 1 is rotated 116 degrees to create a 71 degree of misorientation, as seen in \( \Sigma 3 \), between grain types 1 and 3 [8]. Diffusion rates at grain boundaries are one order of magnitude higher than the bulk (inside grains) and low \( \Sigma \) grain boundaries have much lower diffusivity than random ones [8, 11, 16]. As a result, for numerical purposes, we assume that mobility at random grain boundaries is 10 times higher than the bulk and in Low \( \Sigma \) grain boundaries (\( \Sigma 3 \)) is 2 times higher than the bulk. Thus the values of \( \mu_{ij} = \mu_r = 9 \) and \( \mu_{ij} = \mu_s = 1 \) are considered for random and \( \Sigma 3 \) grain boundaries respectively.

In the first scenario, a polycrystalline metal phase with all random gain boundaries is considered. This represents the case were there is no texture in the metal phase and no grain boundary engineering has been performed. Figure 4.1 illustrates the intergranular oxidation and the corresponding stress map for this case. As it can be seen, the oxidation progresses quickly along the random grain boundaries (dark red lines marked with R in the mobility map, top left, show random grain boundaries). The grain boundaries in contact with the oxide scale start to oxidize and they penetrate more inside the metal grain as the time evolves. It should be noted that even though there are other random grain boundaries inside the metal, those in contact with the oxide scale are expected to oxidize much faster. The reason is that as oxygen diffuses from air into the oxide scale and inside the metal, those grain boundaries in contact with metal/oxide interface have more access to the diffused oxygen. In the last time steps, a very weak formation of oxide along the grain boundary R5 is observed. This can be due to the diffusion of the dissolved oxygen inside the metal phase to that grain boundary. Regardless, that weak oxide is along one of the random grain boundaries and \( \Sigma 3 \) grain boundaries are not oxidized.
Next, a polycrystalline with a mixture of random and $\Sigma 3$ grain boundaries on the surface is considered. This case replicates a textured metal phase where more $\Sigma 3$ grain boundary types are present. Result of this case has been depicted in the Figure 4.2. As expected, the oxidation on the random grain boundaries is faster than the $\Sigma 3$ ones which shows more oxidation resistance of $\Sigma 3$ grain boundaries compared to the random ones. Similar to previous case, a low-level of
oxidation at internal grain boundaries (R4) is observed, which is again at random grain boundaries with higher diffusivity.

Figure 4.2. Intergranular oxidation and corresponding stress map (von Mises) for case with mixture of random grain and $\Sigma 3$ grain boundaries, (a) Mobility map, (b) grains orientation, (c-e) oxide phase evolution, and (f-h) corresponding stress map.

The stress maps show that as the oxide layer evolves, it tends to expand; since its movement is restrained by the metal, it goes under compression and applies tension (in Y direction) to the adjacent metal. The oxide phase, both in the oxide layer and inside grain
boundaries, experiences stress levels as high as 1.5 GPa. Since those stresses are in a compressive state, they will not initiate cracking; however, any disturbance in the geometry or stress normal to the oxide layer will expose the oxide layer to buckling or spalling. Neglecting the high stresses due to boundary effect (top and bottom of the domain), two critical point can be detected in the metal phase. The first one is at vicinity of the tip of the penetrated oxide inside the grain boundary. As intergranular oxides form and penetrate, they put the metal in front of them in compression in the X direction and in tension in the Y direction. These high tensile stresses, along with stress intensities due to the sharp shape of the oxide tips, makes these point a candidate for crack initiation and stress corrosion cracking. The other zone, which experiences high level of stress, is the point at the middle of the metal and close to the oxide layer as marked with P. This is because as oxide layer gets thicker, it applies more tension at the middle of the metal. The evolution of stress levels for an oxide tip and a point (P) inside a grain are illustrated in Figure 4.3.a. Looking at the stress evolution of these points, two trends can be observed. The stress at the oxide tip increases and it is concaved upward. This is due to the fact that both oxide layer growth and oxide penetration in grain boundaries contribute to the tensile stress at the oxide tip. In other words, the oxide layer growth applies tension and the penetration of oxide intensifies that tension, thus, the curve is concaved upward. On the other hand, the stress at point P increases with being concaved downward. This can be explained by the contradicting stress effects that oxide layer and penetrated oxide have on point P. The evolution of oxide layer applies the same tensile stress. However, as the oxides penetrate along the grain boundaries at top and bottom of the point P, they apply pressure on that in the Y direction. This will oppose the tensile effect and thus the stress evolution curve is concaved downward.
Applying tensile load to the metal phase by the oxide layer is based on the assumption that the oxide keeps its integrity and does not undergo any failure. To check this assumption, simulations were carried out with plasticity added to the oxide layer. The plasticity model considered is an elastic-perfectly plastic model, with yield strength of \( Y_s \), which represents the brittle behavior of the oxides. In order to consider a more general case, the yield strength on the oxide was lowered from 1200 MPa to as low as 400 MPa and the stress levels at the mid-point in metal close to oxide (point \( P' \)) were measured. Results of these simulations (Figure 4.3.b) also show the competing mechanism between oxide layer and grain boundary oxides. In the beginning, the oxide has not penetrated and the effect of oxide layer is dominant. Thus, stress increases as oxide layer evolves. When the oxide penetrates inside the metal it applies pressure and opposes the tensile load; as a result, there is a drop in stress level. As the oxide layer becomes thicker, its effect becomes dominant, hence, the stress level increases again. However, it should be noted that when the yield strength is 400 MPa, simulating the case that oxide layer is weak and undergoes failure, the impact of oxide layer growth is reduced noticeably and the stress level remains almost constant. This suggests that when the oxide coating is weak with respect to the substrate metal, the stress levels inside metal are mainly under the influence of the intergranular oxide penetration.
Figure 4.3. Stress evolution and critical point for the case with mixed grain boundaries (Figure 4.2), (a) location of critical points: tip of oxide at GB R1 and point P, (b) evolution of stress levels for points marked in (a). Comparing the stress evolution at point P’ with and without plasticity, simulation domain size is 100 x100 μm, (c-e) evolution of oxide, (f) evolution of stress levels for point P’.

4.4 Conclusion

Intergranular oxidation and the generated stress inside both oxide and a polycrystalline metal phase were studied using a multiphase-field model. The developed model was able to capture both external and intergranular oxidations. In addition, by introducing variable mobility along grain boundaries, the model was capable of considering different diffusivities in grain
boundaries, depending on their structure. Simulation results showed that this model can capture the different oxidation behavior of grain boundaries and showed that low-\(\Sigma\) grain boundaries (\(\Sigma 3\)) have more oxidation resistance compared to random ones, as observed in experiments.

By incorporating elastic strain energy in the model, the evolution of stresses during the oxidation was also investigated. Results revealed that the critical zones with high stress levels are on the tip of the penetrated oxide along grain boundaries and in the middle of the metal phase near to the oxide. Observing the trend of stress level evolutions showed there is a competing mechanism between the applied stress by oxide scale and the penetrated oxide. Depending on the positions, these mechanisms can intensify their effect (oxide tip), or oppose each other’s effect (mid-point in the metal). Furthermore, the simulation results suggested that when the oxide layer is weak, the generated stress inside the metal is more under the influence of the penetrated oxide. The developed multiphase field model has can be extended to incorporate crack propagation physics for a better study of oxidation induced cracks or stress corrosion cracking.

4.5 Acknowledgments

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4.6 References


5.1 Importance of Hydride Configurations on Their Reorientation

Comparison of the required load for reorientation of single seed, two-seed and multi-seed hydrides revealed that when there are more than one hydride present, strains as low as 0.001 are required for reorientation, which is close to values observed in experiments. However, in the single seed case, much higher strain (at least one order of magnitude higher) is required to initiate the reorientation. This shows the significance of the configuration between hydrides and confirms the hypothesis that the configuration of hydrides has significant effect on the required load for reorientation. As hydrides are formed closer to each other, they create a strain field around themselves, and therefore much less external strain/stress is required for reorientation of hydrides. In addition, when several hydrides are in the proximity of each other, the coalescence of smaller hydrides forming larger hydrides assists the reorientation process, lowering the required applied load for reorientation.

5.2 Effects of Mechanical Energy and Grain Boundary Structure on Intergranular Oxidation and Generated Stresses

Results from oxidation simulations showed that incorporating strain energy in the phase-field models is necessary to capture the interaction between induced stresses and the oxide growth. Specifically, in the more complex geometries, stress intensities can alter the shape of oxide evolution in order to reduce the stress levels. Additionally, considering the grain boundary structures and their effect on the diffusivity of elements is essential for simulating the
intergranular oxidation. The trend of stress evolutions showed a competing mechanism between the applied stress by oxide scale and the penetrated oxide. Depending on the positions, these mechanisms can intensify or oppose each other’s effect. Results indicated that generated stress inside metal is more under the influence of the penetrated oxide when the oxide layer is weak.

5.3 Future Work

Even though the results from two dimensional elastic simulations in estimating the required load for reorientation are in a very good agreement with experimental studies, three dimensional simulations should be considered for more accurate results and better incorporation of interface energies. Hydride simulations also indicate that there is a possibility that $\gamma$ hydrides can be made stable under some specific applied stress conditions. Thus, stabilizing the $\gamma$ phase should be studied further since $\gamma$ hydrides are much more ductile than $\delta$ hydrides and can reduce the risk of embrittlement.

The developed phase-field framework for oxidation already incorporates the mechanical energy, and it has a good potential to be merged with phase-field crack models. This way, the interaction between cracks and stress intensities on the diffusion of elements and evolution of microstructures can be studied. Reciprocally, the effect of the formation and evolution of microstructures on the stress distribution and crack nucleation and propagation should be further explored.

In addition, the effects of voids, vacancies and/or radiation damage can be considered by incorporating appropriate phase-field variables and modifying the total free energy functional. In this way, the influence of defects on diffusion rates, mobility coefficients and other material properties can be tailored by defining the model parameters as functions of phase-field variables.
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APPENDIX A
PERMISSION FOR REUSE OF PUBLISHED MATERIALS

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