Mesoscale Modeling of Heterogeneous Materials Systems: From Solid Oxide Fuel Cells to Bulk Metallic Glasses

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Abstract

Heterogeneous materials systems hold the key to the future development of a broad range of increasingly complex technological applications. For example, multi-phase and/or multi-component materials are at the forefront research on the development of efficient energy devices, and the future generation of structural materials with optimal mechanical properties. In this dissertation, we focus on two materials systems, namely, solid oxide fuel cells (SOFCs) and bulk metallic glasses (BMGs), where we investigate, through theoretical and mesoscale computational models, the role of microstructure on the properties of these heterogeneous systems.

For the solid oxide fuel cell project, a computational framework is developed to investigate the topological evolution of Ni phase in SOFC porous anodes, and the accompanying changes to a wide range of microstructural attributes that affect electrochemical performance. Additionally, with the aid of this framework, we study the reduction-oxidation instability, mechanical deformation and damage accumulation in SOFC anodes. In particular, the SOFC project is focused on the role of anode microstructure, characterized by particle size and ratio, on the microstructural stability and mechanical durability of SOFC anodes.

For the bulk metallic glass project, a mesoscale model is introduced that accounts for the structural heterogeneity of monolithic BMGs and BMG composites, and captures the fundamental aspects of plastic deformation in such systems. We examine the effect of internal structure, characterized by rigid/soft short range order (SRO), on the deformation behavior of monolithic BMGs, while for BMG composites, we study the role of ductile phase microstructure, particle size, morphology and area fraction, on the mechanical properties and overall ductility of these systems.
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This dissertation carries T-3273 in the records of the Department of Mechanical and Aerospace Engineering.
To the olive groves for my sense of rootedness.
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Preface

The research exploration presented here focuses on the development of theoretical and mesoscale computational models for the description and quantification of microstructure evolution in heterogeneous materials systems. This thesis is comprised of two parts: i) The development of mesoscale models for the degradation mechanisms in solid oxide fuel cells (SOFC). More specifically, we study the morphological evolution of Ni phase in porous SOFC anode systems and its impact on several microstructural attributes affecting the electrochemical performance. Furthermore, we develop a microstructure-based continuum model to examine the reduction-oxidation (redox) instability, mechanical deformation, and damage accumulation in porous SOFC anodes. ii) The development of a mesoscale model for the inelastic deformation and shear strain localization ("shear banding") in bulk metallic glasses (BMGs) and composites. For monolithic BMGs, we investigate the role of local structural heterogeneity on the inelastic deformation and shear band propagation in these systems, while for BMG composites, we study the role of ductile phase microstructure, characterized by particle size, morphology and area fraction, on the deformation mechanisms and overall ductility in these systems.

In Chapter 1, we highlight the abiding theme of this thesis, which is the investigation and quantification through theoretical and mesoscale models of the role of materials microstructures on the behavior and properties of these systems, whether these properties are mechanical, chemical, topological, and/or electrochemical in na-
ture. We provide an overview of solid oxide fuel cells, how they operate, basic components, key advantages, and the main degradation mechanisms that hinder their use in commercial applications. For bulk metallic glasses, we introduce the concept of a metallic glass, key properties of these metallic alloys, especially the mechanical ones, and discuss inelastic deformation mechanisms and shear banding in these systems.

“If you would understand anything, observe its beginning and its development”, Aristotle (384 BC - 322 BC) once said, which motivated me to provide brief accounts on the evolution of a relatively new branch of materials science coined “computational materials science”, and the history of SOFCs, glass and BMGs. These accounts were intentionally made brief, the purpose of which is to immerse the reader into years, hundreds and even thousands, of materials science evolution and development.

In Chapter 2, we survey the published literature for the research work relevant to SOFCs and BMGs. We first discuss findings concerning the degradation mechanisms in SOFCs, namely, the coarsening of Ni phase and redox instability in porous SOFC anodes. Next, we survey the literature for various observations regarding the deformation mechanisms in monolithic BMGs and the role of ductile phase on the enhancement in ductility in BMG composites.

In Chapter 3, we present our theoretical and computational models that are informed by the experimental observations discussed in Chapter 2. More specifically, we present a phase field model for the coarsening of Ni phase in porous SOFC anodes. Additionally, we present a continuum model for the mechanical deformation and damage accumulation in SOFC anode microstructures due to Ni phase expansion (“swelling”) that is associated with redox cycles. For the BMG project, we present a mesoscale model that accounts for the structural heterogeneity of monolithic BMGs and BMG composites, and captures the fundamental aspects of plastic deformation in such systems.
In Chapter 4, our research findings concerning the degradation mechanisms in SOFC anode systems are presented. More specifically, we examine the role anode microstructure on Ni phase coarsening and the accompanying changes in several topological features affecting electrochemical performance. Simulation results highlight the importance of initial anode microstructure on the stability of SOFC anodes. Smaller initial Ni particles yield topological features that optimize electrochemical performance provided Ni phase contiguity is maintained. In broader terms, our modeling approach can be used as a design tool to identify optimal combinations of morphological parameters, such as particle size and ratio that yield multifunctional anode microstructures that are more stable against Ni coarsening. As for the redox project, we examine the role microstructure on the development of mechanical stresses and evolution of damage in SOFC porous anodes. The hallmark of our approach is the ability to track the spatial evolution of mechanical damage and its interaction with the local microstructure. Notably, mechanical damage in coarsened anode systems exhibits essentially no dependence on the initial Ni particle size. This is in contrast to the as-synthesized anode systems, which displays a strong Ni particle size dependence, where anodes with smaller Ni phase features are more resistant to mechanical damage due to redox than the ones with larger Ni domains.

In Chapter 5, our results for the inelastic deformation of BMGs are presented. We examine the role structural heterogeneity on shear banding in monolithic BMGs, while for BMG composites, we examine the role of ductile phase, characterized by particle size, morphology and area fraction, on the enhancement in ductility. Our results suggest that in monolithic BMGs, mechanical properties are highly dependent on the connectivity of the rigid short range order (SRO) backbone, where overall ductility can be enhanced by reducing the fraction of elements that exhibit rigid SRO characteristics. As for BMG composites, our results suggest that ductility is a
nonlinear function of the crystalline phase area fraction, and inversely proportional
to the crystal particle size.

In Chapter 6, concluding remarks and future work that is aimed to improve the
models are presented. The appendices contain mathematical derivations that are
pertaining to both projects, SOFCs and BMGs.
List of Journal Articles

The research work presented in this dissertation was carried out between the Spring of 2009 and Summer of 2013 and it yielded the following peer-reviewed journal articles; two of which are to be submitted.


List of Presentations

Conference Presentations


6. A. Zaheri, F. Abdeljawad, and M. Haataja, “Phase-field Simulation Study of Nucleation and Propagation of Shear Bands in Bulk Metallic Glasses with Stress-
Induced Precipitation of Martensitic Nanocrystals”, *TMS Annual Meeting and Exhibition*, (2012) Orlando, FL.


**Invited Talks**


Chapter 1

Introduction

1.1 Computational Materials Science

This thesis focuses on two aspects of physics and engineering science: the theoretical description, at the mesoscopic scale, of the behavior of materials systems in the condensed state, more specifically the solid state, and the development and implementation of numerical algorithms to solve the resulting governing equations, usually in the form of nonlinear partial differential equations. The analysis of materials systems using physical theories, mathematical descriptions and numerical tools form the basis of a relatively young research field that is termed “computational materials science”. A central pillar in the analysis of materials systems is the structure-property paradigm, which provides a direct link between geometric structures and materials properties. The complexity of many materials systems can be rooted to the multiple temporal and spatial length scales that control many physical phenomena and processes in these systems. At the quantum scale, the electronic structure of a materials system yields valuable information on the crystal ground states and type of atomic bonding. At the molecular scale, several properties, such as viscosity and bulk transport can be calculated. When averaging over many degrees of freedom, or
coarse-graining, one arrives at the mesoscopic scale. Models at this scale are typically informed by properties that are at the atomic scale, such as surface energy, grain boundary mobility and diffusion coefficient. Finally, at the macroscopic scale, continuum-based models incorporate parameters such as bulk and shear moduli that are used in elasticity theory.

The field of computational materials science is an indispensable tool in modern research on materials systems [1]. It adds a new dimension to the classical approaches of theory and experiments [3]. The use of computers in scientific research goes back to the invention of the first programmable computer (the Z3 computer) by Konrad Zuse in the 1930s in Germany. The Electronic Numerical Integrator And Computer (ENIAC) was developed at Los Alamos Laboratories in 1946. ENIAC was utilized for hydrodynamics calculations and it weighted 30 tons, refer to Fig 1.1. In 1946, A. Burks, H. Goldstine and J. Von Neumann published a paper stating the principles of building an efficient computer to be used in scientific calculations. These principles were later coined the “von Neumann principles” [1, 4]. Over the next 50 years, advancements in the technology of building computer circuits, introduction of more efficient programming languages, and innovations in computer architecture along with miniaturization of integrated circuits led to increasing the availability of fast computers that can be used to numerically simulate materials systems, and predict their properties and performance.

Many technological applications utilize heterogeneous materials systems that are characterized by features across various length scales, which form during various
formation processes [5]. In these systems, there exists a hierarchy of geometric structures and length scales, where properties depend not only on the geometry at the atomic scale but also at larger spatial scales [2]. The geometric description of materials starts with the atomic spatial configurations and these atomic-scale features are often “enriched” with defects (point, line, and/or planar) and/or inhomogeneities (compositional or structural) at various scales [2,5]. The resulting materials systems with structures that span many length scales are not generally in global thermodynamic equilibrium and the evolution of such features greatly affects the properties of these systems.

Within the context of this thesis, a \textit{microstructural feature} is defined as any compositional and/or structural inhomogeneity, whose length scale is on the order of $\mathcal{O}(nm)$ to $\mathcal{O}(\mu m)$. Distributed phases of different compositions, grains of different crystallographic orientations, particle size and distribution in a multiphase system, internal interfaces, and structural defects are all examples of microstructural features that exist in real materials systems. The main theme of this thesis is the description through theoretical and mesoscale models of the microstructure evolution in materials systems that are subjected to multitude of physical, chemical, and/or mechanical cues. In this work, we focus on two materials systems, namely, solid oxide fuel cells (SOFCs) and bulk metallic glasses (BMGs), where we explore how their respective microstructures greatly affect their properties. For the SOFC project, we explore the role of microstructure on the morphological evolution and mechanical behavior of these systems, while for the BMG project, we study the mechanical properties, ultimate strength and ductility, of monolithic BMGs and BMG composites. We demonstrate that these properties can be optimized by fine-tuning several microstructural features in these systems.
1.2 Solid Oxide Fuel Cells

1.2.1 A Brief History

The historical introduction presented here is based on the comprehensive books by J. Milewski et al. [6] and K. Huang and J. Goodenough [7]. Fuel cells are devices that convert chemical energy from fuels into the much needed electricity through electrochemical reactions. Fuel cells have been known to humanity for around 170 years. In 1839, the Swiss scientist Christian Friedrich Schoenbein discovered the principles of operating fuel cells and demonstrated the possibility of a fuel cell that combines hydrogen and oxygen [8]. The English scientist William Robert Grove, who is regarded by many as the father of the fuel cells, constructed a “voltaic gas battery” that combined hydrogen and oxygen in the presence of platinum [9]. The basic principles connecting electrochemistry with thermodynamics were explained by H. von Helmholtz in 1882. Friedrich Wilhelm Ostwald in 1894 provided the theoretical foundations of how fuel cells can potentially produce electricity with higher efficiency than steam engines [6, 7].

The beginning of the 1900s formed a paradigm shift in the design of fuel cells. Using liquid electrolytes in fuel cells was found to cause performance degradation due to the electrodes absorbing the liquid electrolyte. Therefore, much of the research was geared towards constructing solid electrolytes. However, it was not until 1899 with the discovery of zirconium oxide $\text{ZrO}_2$ by the German scientist Walther Nernst that a solid electrolyte material can be used in fuel cells [7]. Nernst studied solid ionic conductors (high temperature ceramics) for the potential use as filaments in light bulbs. He discovered that stabilized zirconia (zirconium oxide doped with by calcia, yttria, etc.) is an insulator at room temperature and a good conductor of ions at temperatures in the range $600 – 1500^\circ\text{C}$. The first demonstration of a fuel cell with a solid electrolyte (or a solid oxide fuel cell) was in 1937 by the Swiss scientists Emil
Bauer and Hans Preis using zirconia ceramics as the electrolyte [10]. In 1960, NASA used fuel cells to power electrical systems on the Apollo journey to the moon [11]. In 1962, engineers from Westinghouse Electric Corporation developed and tested the first tubular solid oxide fuel cell stack. H. Spacil filed a patent in 1964 that described the use of a composite material containing nickel and zirconia to be used as the anode in solid oxide fuel cells [12]. This composite material remains the standard material of choice for solid oxide fuel cell anodes. The period from the 1970s till now marks an important era in the advancement of materials systems and cell designs of solid oxide fuel cells with the ultimate goal of utilizing these devices in the efficient conversion of chemical energy into electricity.

1.2.2 Principles and Components of a Solid Oxide Fuel Cell

A solid oxide fuel cell (SOFC) is a high temperature energy conversion device that converts the chemical energy of a fuel gas to electricity and heat through electrochemical combination of a gaseous fuel (hydrogen) and an oxidant gas (oxygen from the air). In SOFCs, the conversion to electricity occurs directly without a combustion step thereby avoiding Carnot cycle limitations [11]. An SOFC cell operates as long as gaseous fuel and oxidant gases are continuously supplied. SOFCs are appealing systems in terms of conversion efficiency (chemical to electrical efficiency is 45% to 65% and 85% in a combined heat and power applications) [13], fuel flexibility [14, 15], and low pollutant emissions [11, 16].

There are four basic physical components, which are all in the solid state, to an SOFC cell: an air electrode (cathode), electrolyte, a fuel electrode (anode), and interconnect. The electrolyte is a thin layer that only allows for the continuous transport of oxygen ions from the cathode to anode under a gradient of oxygen chemical potential. The cathode in turn converts oxygen molecules (O$_2$) to oxygen ions (O$_{2-}$) in a process known as oxygen reduction. The anode utilizes (O$_{2-}$) in a fuel oxidation
reaction that generates electrons \((e^-)\), along with \(H_2O\) and/or \(CO_2\) depending on the fuel gas used. In order to attain the desired voltage and power, multiple SOFC cells have to be connected in series and/or parallel with the aid of interconnects. Hydrogen (or hydrocarbon) fuel is supplied to the cell from the anode side and oxygen (from the air) enters the cell through the cathode. On the side of the electrolyte that is in contact with the anode (or fuel electrode), oxygen ions are depleted due to fuel gas oxidation reactions. These reactions lead to releasing of electrons \((e^-)\) and result in gradients in oxygen chemical potential across the solid electrolyte. When an electrical connection is created between the two electrodes, the flow of electrons from the anode to cathode allows for reduction reactions of oxygen at the cathode. Reduction of oxygen at the cathode maintains a continuous supply of oxygen ions \((O^{2-})\) for the electrolyte and preserves electrical charge balance \([7, 11]\). Fig. 1.2 is a schematic illustrating a working principle of an SOFC cell, where hydrogen is used as the fuel gas. In this case, SOFC electrochemical reactions are:

\[
\text{At the anode: } H_2 + O^{2-} \rightarrow H_2O + 2e^-. \quad (1.1a)
\]

\[
\text{At the cathode: } O_2 + 4e^- \rightarrow 2O^{2-}. \quad (1.1b)
\]

In state-of-the-art SOFCs that operate at temperatures in the range 800 - 950°C \([17, 18]\), a thin film of yttria stabilized zirconia (YSZ) is employed as a ceramic membrane that allows for the transport of oxygen ions while blocking the transport of electrons. A porous composite of lanthanum strontium manganate (LSM) and YSZ is typically used for the cathode in order to facilitate the reduction of oxygen molecules to oxide ions and allow gas diffusion to and from the interface with the electrolyte. Porous Ni/YSZ ceramic metal (cermet) composites are usually employed as the anode materials of choice \([19]\). Nickel is both an excellent conduit of electronic charges and a good electro-catalyst for the oxidation of fuels, while YSZ serves as
Figure 1.2: A schematic illustrating the working principle of an SOFC cell. Here, hydrogen is used as the fuel gas.

a conducting network for oxygen ions. Furthermore, the addition of YSZ in SOFC anodes improves thermal expansion compatibility between the composite anode and the electrolyte layer [20, 21]. Figure 1.3 is a representative cross-sectional view of the electrode-electrolyte structure in conventional SOFCs. In general, the electrolyte is a thin membrane that is a few microns in width. For the case of anode-supported SOFCs, the anode is typically a graded microstructure that consists of two layers; the first is a fine layer that is adjacent to the electrolyte, where the fine distribution of Ni and YSZ particles is intended to maximize the electrochemically active regions where the Ni, YSZ and pore space meet, commonly known as three phase boundary (TPB). The second is a coarse anode layer that enables rapid transport of fuel gases into and removal of reactant gases out of the anode, and serves as a structural support for the cell [18, 22].
1.2.3 Key Advantages of Solid Oxide Fuel Cells

SOFCs offer many advantages over conventional power generating systems in terms of high efficiency (fuel input to electricity output) [13], fuel flexibility [14, 15], and low pollutant emissions [11, 16]. A higher electrical efficiency infers reduced emissions per unit electricity produced, if hydrocarbons are used as fuels [18]. This has become a crucial factor in the efforts to minimize greenhouse emissions in future power generation. The solid state nature of all of SOFC’s components, lack of moving parts and low vibration levels make SOFCs a suitable alternative in stationary power generation.

On the other hand, SOFCs, during operation, provide high quality heat byproduct, which effectively activates electrochemical oxidation processes within the cell. Additionally, the co-production of heat and power, where the effective recovery of waste heat along with the production of electricity increases the total energy efficiency of SOFC systems. SOFCs offer the possibility of co-generation, where SOFCs in combination with gas turbine power systems can be combined to fully exploit both
electricity and heat, thereby enhancing the efficiency \cite{7, 18}. Finally, SOFCs do not contain noble metals, thereby lowering their overall cost \cite{11}.

1.2.4 Degradation Mechanisms in Solid Oxide Fuel Cells

To increase SOFC durability and performance characteristics vis-à-vis other energy conversion devices, several degradation mechanisms in these systems need to be resolved. This thesis is primarily focused on the degradation mechanisms in SOFC porous anode microstructures, which are regarded as one of the most essential components in SOFC stacks as it is in these electrodes that electrochemical reactions take place.

Electrochemical performance degradation in SOFC cermet anodes is attributed to several phenomena and processes at the microstructural level, such as poisoning by fuel impurities, coking, thermal and redox cycling \cite{20, 23, 28}, as well as microstructural coarsening processes associated with Ni particles in Ni-based cermet anodes \cite{18, 29, 30}. This thesis is focused on modeling two of the most detrimental mechanisms to the durability and integrity of SOFC anodes, namely Ni phase coarsening and reduction-oxidation (redox) instabilities.

1.2.4.1 Ni Phase Coarsening and Microstructural Changes in SOFC Anodes

The high operating temperatures of SOFCs provoke the anode systems to undergo microstructural changes that ceaselessly decrease their performance. More specifically, active Ni transport mechanisms lead to agglomeration and coarsening of Ni particles resulting in anode morphologies that are continuously evolving during operation. Coarsening, or Ostwald ripening, is a capillary-driven and competitive growth process, which leads to a reduction in the excess free energy associated with interfaces \cite{31, 32}. For a distribution of particles in a matrix of a second phase and in
accordance with the Gibbs-Thomson effect, diffusional flux exists, which leads to the transfer of atoms from smaller to larger particles [32]. Furthermore, coarsening takes place via capillary-driven surface evolution processes. In such cases, spatial variations in the mean interface curvature induce diffusional fluxes, which lead to the transfer of mass from regions of high to low mean curvature [32]. A more in depth review of coarsening processes will be presented in Section 2.1.1.

Indeed, Ni coarsening in SOFC anodes has been the subject of several experimental investigations [23, 33–36]. These studies have revealed that performance degradation can be directly linked to changes in several microstructural features that accompany Ni coarsening processes, such as extent of three phase boundaries (TPBs), where Ni, YSZ and pore meet, total interfacial areas, contiguity of anode phases, and pore space microstructure. In particular, the density of TPB lines, which is often employed as a simple metric to predict electrochemical performance, is found to decrease due to Ni coarsening [35]. Simwonis et al. [33] studied Ni/YSZ composite anodes under operating environments and observed a decrease in the effective anode electronic conductivity due to Ni coarsening. Moreover, Ni phase coarsening is found to affect phase contiguity [37]. The experimental results of Cronin et al. [38] revealed that Ni coarsening affects several microstructural attributes, such as pore percolation, total pore interfacial area, and average pore size.

1.2.4.2 Redox Instability and Evolution of Mechanical Stresses in SOFC Anodes

Reduction-oxidation (redox) instability is chemo-mechanical in nature and is caused by Ni phase instabilities against rapid oxidation [39]. This type of instability was first reported by Cassiday et al. [39, 40], where they measured volume changes in SOFC anodes due to a redox cycle. At SOFC operating temperatures, Ni phase is stable against oxidation when the anode is kept in a reduced state and an uncon-
taminated fuel is utilized. In cases of interruption to the fuel supply, seal leakage, system shutdown or high fuel utilization, re-oxidation of Ni occurs via the reaction \( \text{Ni} + 1/2\text{O}_2 \rightarrow \text{NiO} \) \[^{39, 41}\]. Dimensional changes and bulk expansion associated with redox reactions of Ni are due to the large ratio of NiO to Ni molar volume. This ratio is known as the Pilling-Bedworth ratio and is \( \sim 1.66 \) for Ni \[^{39}\], which implies an effective expansion, or swelling, of the Ni particles given by a volumetric strain \( \sim 0.66 \) for complete oxidation. Dimensional changes that are associated with Ni oxidation are not completely accommodated by the local pore space; therefore, the transformed Ni particles exert local strains on the YSZ skeleton, which in turn lead to mechanical stress evolution and crack formation along the interface with the electrolyte or within the YSZ backbone itself \[^{20, 42, 43}\]. Furthermore, during SOFC utilization, the morphological changes to the Ni network during coarsening were found to yield microstructures that are unable to accommodate the large bulk expansion strains during the re-oxidation of Ni \[^{39, 42}\]. Dimensional changes and internal strains resulting from redox cycles in Ni/YSZ anodes have been examined experimentally over a wide range of operating parameters, such as temperature and humidity level \[^{44}\], sample geometry \[^{42}\], and microstructure and particle size \[^{21, 22}\]. Relaxation mechanisms by irreversible deformation and micro-cracking, which are detrimental to the electrochemical performance and structural integrity of the cell, have also been experimentally observed \[^{43, 45, 46}\].

1.3 Bulk Metallic Glasses

Having provided an overview of relevant SOFC systems, we now turn to bulk metallic glasses. The universally accepted definition of a glass is by what it is not: a well-ordered crystal \[^{47}\]. Glasses differ from conventional crystalline materials by their lack of long range order \[^{48}\]. When a material in the liquid state is cooled below
its melting temperature, \( T_m \), two scenarios can occur: the first is crystallization and the second is undercooling. Crystallization is a first-order phase transition that is characterized by a discontinuity at \( T_m \) of the extensive properties such as volume and enthalpy. In conventional engineering crystalline materials, a repetitive crystal structure can be tessellated to generate a space filling material. The underlying crystal structure is responsible for the electrical, mechanical, thermal and optical properties. Upon crystallization, atoms find a spatial arrangement that optimize their bonding, leading to the nucleation of small crystallites (“embryos”) that grow to form the final materials system \([47]\).

On the other hand, during undercooling, nucleation of the crystalline phase is suppressed and if the cooling rate is sufficiently high, nucleation of crystalline phases can be completely avoided. As the temperature keeps decreasing, the undercooled liquid becomes more viscous and finally falls out of equilibrium into the arrested glassy state. At the microscopic scale, the glassy state is characterized by a lack of long-range atomic order, where the material is in the solid state but has liquid-like atomic arrangements. Changes in the slopes of properties, such as volume and enthalpy occur at the glass transition temperature, \( T_g \).

### 1.3.1 A Brief History

Almost every civilization known to humanity contributed to the evolution of the glass-making industry. The historical account that is presented in this Section is not inclusive by any means. It is our humble effort to immerse the reader into 4,000 years of glass history.

The place and time of the discovery of glass is uncertain, the earliest known glass objects, in the form of small pieces used for inlay work, date back to the Bronze Age by the middle of the third millennium BC. The glass industry, which was first founded in Mesopotamia, spread quickly to Cyprus, Syria, Egypt and the Aegean,
where glass was used as a semi-precious material \[ 49 \] \[ 50 \]. In fact, it is argued that the military campaigns of *Thutmose III* into the eastern Mediterranean after 1481 BC caused a migration of glass craftsmen and the establishment of glass industry in Egypt. The emergence of new kingdoms in the tenth century BC, such as the Phrygian of Anatolia, the Greeks in the Aegean, the Phoenicians along the eastern Mediterranean and the Assyrians in the Tigris-Euphrates region led to the revival of the glass-making industry \[ 49 \]. The first glassmaking “manual” dates back to 650 BC, where instructions on how to make glass are contained in clay tablets discovered in the library of the Assyrian king *Ashurbanipal* (A·shur·ba·ni·pal) \[ 49 \] \[ 51 \]. It was around this time, where the glass-industry entered Italy and the western Mediterranean. A growth of the use of glass products occurred throughout the Roman world and over the next 1,000 years glass-making industry spread through southern Europe and beyond.

Metallic glasses are the newcomers to the world of glasses. The first successful demonstration of producing a metallic alloy in the glassy state using rapid-solidification was by Klement et al. \[ 52 \] in 1960, where they prepared a glassy \( \text{Au}_{75}\text{Si}_{25} \) (at.%) metallic alloy. In a 1954 study by Buckel and Hilsch \[ 53 \], glassy metallic solids were prepared by condensation of elemental metal vapor onto cold substrates. Upon rapid cooling, metallic alloy melts become increasingly viscous and fail to crystallize, thus forming metallic glasses. We noticed that it is common in the literature to use amorphous or glass interchangeably to describe non-crystalline systems. The term “amorphous” is associated with solids that are made by a variety of techniques, whereas “glasses” are a subset of amorphous systems, where vitrification of liquids is done only through rapid cooling techniques \[ 48 \].

In general, amorphous and glassy metals can be produced with a wide variety of techniques, such as rapid liquid cooling \[ 52 \] \[ 54 \], evaporation \[ 53 \], sputtering \[ 55 \], electrodeposition \[ 56 \], irradiation by heavy ions \[ 57 \] or electrons \[ 58 \], or via mechanical grinding \[ 59 \]. The significance of the work of Kelement et al. \[ 52 \] is that it opened
new avenues for the improvement of cooling techniques that resulted in the generation of metallic glasses with large length scales and thus the formation of bulk metallic glasses (BMGs). It is worth noting here that this thesis is focused on the unique combination of mechanical properties that BMGs exhibit and less attention is paid to the endless number of BMG forming techniques. Therefore, we will skip 60 years of research on metallic glass-forming methods, and end this Section with the quote “There are almost as many criteria for glass formation as there are for the good life” by R. W. Cahn [51].

1.3.2 Key Advantages of BMGs: Mechanical Properties

The rapid cooling of metallic alloy melts yields BMGs in which local arrangements and bonding is similar to the corresponding crystalline counterpart but long range order is absent. This in turns allows BMGs to exhibit a unique combination of properties. At high temperatures, viscous flow allows superplastic forming techniques to be applied to BMGs. At low temperatures, BMGs exhibit a large elastic strain limit $\sim 2\%$ compared with the 0.2% for conventional crystalline materials. BMGs have the best values for the modulus of resilience $U_r = \sigma_y^2/(2E)$, where $\sigma_y$ is the yield strength and $E$ is Young’s modulus [60]. Modulus of resilience defines the ability of a material to absorb energy when it is deformed elastically and then, upon unloading, to have this energy recovered [61]. Due to the tight atomic packing in glasses, BMGs are characterized by their low damping (less absorption and greater release of mechanical energy), where they generally return mechanical energy by rebounding elastically to the initial shape [62]. These excellent elastic properties of BMGs allowed their use in some niche applications, such as sports equipment [63].

BMGs are featureless structures and due to the lack of dislocation-mediated crystallographic slip, they exhibit, along with large elasticity limits, high mechanical strength values that are close to the theoretical limit [48, 64, 67]. Fig 1.4 is a map of
Figure 1.4: A map of tensile strength vs. elastic strain limit for a wide range of materials. Notice that Zr-based BMGs exhibit high tensile strength and elasticity limits. Taken from Ref. [63].

the tensile strength vs. elasticity limit for a variety of engineering materials, where it can be clearly seen that Zr-based BMGs occupy the upper right corner of the map, indicating high strength and elasticity limits, both of which are desirable properties in structural materials. Tensile strengths for Co-, Fe-, Ni- and Zr-based BMGs are \( \sim 5.5, 4, 3, 2 \) GPa, respectively [60].

In general, BMGs are corrosion resistant [48, 63, 68, 69] due to the absence of structural defects, such as grain boundaries, which could act as local active sites [70]. BMG systems have high hardness, which has given them excellent wear resistance [63, 71]. Therefore, BMG coatings are suitable in applications, where materials are required to withstand aggressive environments, such as in coriolis mass flow meter and pressure sensor devices used on drilling pipes [72], and audio recording/playback magnetic heads [73].
1.3.3 Inelastic Deformation and Shear Banding

Despite the excellent combination of mechanical properties that are unique to BMGs, it is simply their low ductility and the lack of global plasticity that hinder their use in commercial applications and limit their widespread use in structural applications. Generally, the lack of ductility in BMGs can be discerned from strain-strain curves of tensile specimens, where limited plasticity occurs beyond the elastic limit. Stress-strain curves of tensile samples of a monolithic Zr$_{59}$Cu$_{20}$Al$_{10}$Ni$_8$Ti$_3$ BMG, which is considered as one of state-of-the-art BMG alloys, are shown in Fig. 1.5(a), where the glassy alloys deform elastically until the peak point, after which the samples fail in a brittle manner. A fracture surface in a tensile specimen that is representative of all BMGs is shown in Fig. 1.5(b), where the surface is relatively smooth and runs along the maximum shear stress plane, which is characteristic of brittle failure.

In crystalline materials, ductility is dictated by slip systems that arise due to symmetrical crystal structures and the relatively low lattice resistance for the motion of dislocations, which are the main carrier of slip. At ambient temperatures,
the plastic behavior and hardening in conventional crystalline systems are highly dependent on many microstructural features, which affect the resistance to dislocation glide, such as Pierels-Nabarro forces, grain size, concentration of impurities and alloying elements, dispersions, and geometric structure of grain boundaries [61]. The aforementioned list of microstructural features controlling plastic deformation and ductility in crystalline systems are absent in BMGs. At ambient temperatures and when loaded beyond the elastic limit, the deformation of BMGs is spatially inhomogeneous, during which thin regions $\sim 10 \text{ nm}$ (three-dimensional regions with large aspect ratios) known as shear bands are formed, where plastic flow is confined to these slipped band regions [71, 77–80]. Figure 1.6 is a SEM micrograph showing shear bands in a BMG sample of Zr$_{57}$Nb$_{5}$Al$_{10}$Cu$_{15.4}$Ni$_{12.6}$ alloy, commonly referred to as Vitreloy 106 [76]. Further localization of plastic strains within shear bands leads to shearing-off failure at planes of maximum shear stress with little macroscopic plasticity [60, 74, 76, 81–83]. In a study by Lund and Schuh [84], they surveyed the reported angles that these catastrophic shear bands make with the loading axis, and revealed slight variations from the maximum shear stress planes.

Many technological applications require the optimization of mechanical properties of materials systems along with ensuring non-catastrophic failure modes in service; a property of which BMGs lack [75]. Therefore, the enhancement of BMG ductility
characteristics has been the subject of extensive research explorations \[65\]. Experimental findings on the mechanical properties of BMGs suggest that the overall ductility of these systems can be improved by either fine-tuning the alloy composition of monolithic BMGs or by introducing ductile particles into the glassy matrix, thus forming a BMG composite. Both routes to enhancing the overall ductility in BMG systems aim at creating microstructures that promote a more homogeneous state of deformation and eliminate the catastrophic failure by single shear band propagation.

In the former case, variations in the critical shear stress were proposed to correlate with the degree of short- (SRO) and medium-range order (MRO) \[86\]. SRO is related to first shell neighbors and the associated solute centered polyhedra that form in monolithic BMGs. The packing of these clusters (polyhedra) through solute-solute bonds yields to MRO. Several studies have shown that deformation in monolithic BMGs changes from homogeneous flow, with improved ductility, to a more localized state as the fraction of atoms exhibiting SRO increases \[87\].

In the latter case, enhanced overall ductility in several BMG systems has been achieved by introducing ductile crystalline dendrites, resulting in BMG composites \[88\]. Figure 1.7 shows an SEM image that is representative of all BMG composite microstructures, where crystalline molybdenum particles were introduced to a

Figure 1.7: SEM image of a BMG composite combining a glassy matrix phase of Zr\textsubscript{57}Nb\textsubscript{5}Al\textsubscript{10}Cu\textsubscript{15.4}Ni\textsubscript{12.6} with a 50% volume fraction of molybdenum (Mo) crystalline particles. The inset image shows the area around a single Mo particle at a higher magnification. Taken from Ref. \[85\].
$\text{Zr}_{57}\text{Nb}_{5}\text{Al}_{10}\text{Cu}_{15.4}\text{Ni}_{12.6}$ glassy alloy. Ductile dendrites can act both as shear band initiation sites and as arrest barriers to shear band extension [89]. When a propagating shear band interacts with a soft crystalline domain, additional applied loads can be accommodated via dislocation-mediated slip in the crystal particle, which in turn leads to arresting, or delaying, the advancement of the shear band in the BMG matrix phase. The mechanical properties of BMG composites can be optimized with respect to ductile phase microstructure, i.e., morphology, particle size, and volume fraction [90].
Chapter 2

Related Work

In this Chapter, we survey the published literature for both experimental observations and theoretical treatments concerning both materials systems that are studied in this thesis, namely, degradation mechanisms in SOFCs and deformation mechanisms of BMGs.

2.1 Degradation Mechanisms in SOFCs

One of the design criteria of SOFCs in stationary power applications calls for a long-life expectancy of more than 40,000 hours [91, 92]. Hence, it is important that SOFC systems are designed and materials are developed, such that long-term stability and durability of phases under high SOFC operating temperatures are ensured. In this section, experimental findings and modeling results pertaining to the microstructural stability and mechanical durability in SOFCs are reviewed. More specifically, we review the role of Ni phase coarsening on the evolution of various attributes that affect the electrochemical performance of SOFCs. Furthermore, we survey the published literature for mechanical durability characteristics of Ni/YSZ porous anodes that are under redox cycles.
2.1.1 Microstructural Evolution of SOFC Anodes

By definition of their role, SOFC anodes should be good electronic conductors and electrocatalytically sufficiently active. Therefore, the anode microstructure must allow for the transport of oxygen ions and fuel gas, where they can react at electrochemically active zones, i.e., three phase boundary (TPB) regions. Furthermore, transport and removal of reaction byproducts in the gaseous state should be facilitated. The use of porous Ni/YSZ composites was first introduced by Spacil [12] in the 1960s. Spacil used the combination of Ni and YSZ for the following reasons: i) Nickel is an excellent conduit of electronic charges and a good electro-catalyst for the oxidation of fuels, ii) at SOFC operating temperatures, YSZ is a good conductor of oxygen ions, iii) the porous nature of the Ni/YSZ composite allows for the effective transport of fuel gas and removal of reactions byproducts in the anode, and iv) the use of porous Ni/YSZ composites mitigates mechanical stresses that arise at the anode-electrolyte interface due to the mismatch in thermal expansion [19].

SOFC anode systems have been fabricated using various techniques [28, 93–96]. A typical starting process includes mixing NiO and YSZ powders, which are then homogenized by crushing, milling and mixing to get the desired particle size [94]. Both tape casting and screen printing are established processes in the electroceramics industry [96], where they require a high temperature sintering step to yield anodes with the desired microstructure [95]. The high operating costs of other alternative techniques, such as atmospheric plasma spray, vacuum plasma spraying, electrochemical vapor deposition and laser reactive deposition have limited their use in the fabrication of SOFC anodes [95].

One of the main degradation mechanisms in SOFC anodes is the microstructural evolution of Ni due to coarsening processes. Coarsening, or Ostwald ripening, is a process by which a materials system reduces its excess free energy that is associated
with interfaces. This process was first observed by Wilhelm Ostwald in 1900 who reported particle-radius dependent solubility in HgO particles \[97, 98\].

Lifshitz and Slyozov \[99\] and Wagner \[100\], independently, developed what is now called the LSW theory of particle coarsening. In their mean-field treatment, they considered spherical second phase particles, with fixed positions, that are embedded in a matrix phase. The concentration surrounding each particle has an equilibrium value that is inversely proportional to the particle radius. Variations in the concentration lead to a flux of atoms from smaller to larger particles. This flux causes the smaller particles to shrink and the larger ones to grow. Within the LSW theory, the morphology of the particle dispersion is treated by examining the time evolution of the particle radius distribution, where it can be shown that this distribution is self similar under scaling using a characteristic particle size, which displays \(\sim t^{1/3}\) scaling.

The effects of the precipitate phase volume fraction on coarsening behavior have been the subject of numerous investigations, where it was shown that the temporal law for diffusion-limited coarsening (i.e., average particle size \(\sim t^{1/3}\)) is valid for all volume fractions, but the proportionality constant, or rate constant, is dependent on the volume fraction of the second phase. The reader is referred to Refs. \[31, 97, 101\textendash}104\] for more on extensions to the classical treatment to account for volume fraction effects.

The role of elastic energy is another factor that arises when considering particle coarsening in two-phase microstructures. Elastic interaction between particles, anisotropy effects, elastic inhomogeneity, state of stress, and the stress-free, or eigen, transformation strain of precipitates can greatly affect equilibrium particle shapes and distributions \[32\]. Under applied loads, precipitates in systems undergoing coarsening can develop into platelet- or rod-like shapes \[105\]. Furthermore, elastic interactions between particles can lead to a stabilizing effect against coarsening, where the interplay between the elastic and interfacial energies affects the coarsening behavior.
The reader is referred to Refs. [105–109] for more on the role of elastic energy on coarsening in two-phase microstructures.

Additionally, coarsening takes place via capillary-induced evolution of morphologies, where the driving force again is the reduction in the excess free energy associated with interfaces. In the case of isotropic interfaces, which do not exhibit any orientational dependence, the evolution of these surfaces leads to a reduction in the total interfacial area [32]. Surface smoothing, thermal grooving in crystalline materials, and fragmentation of morphologies into smaller ones are examples of capillary-driven interface evolution. In general, the theoretical treatment of these evolution processes starts with the diffusional flux that is dependent on the local interface mean curvature. Regions of high mean curvature exhibit larger fluxes than the ones with smaller curvatures. The dominant transport mechanism (i.e., surface and volume diffusion, or vapor transport) dictates the final form of the governing equation, which describes the normal velocity of the interface in terms of the mean curvature or its derivatives. The reader is referred to the pioneering work of Mullins on the kinetic models of surface evolution due to capillary forces [110–113].

In SOFCs, the high operating temperature $\sim 1000^\circ$C [19], which is $\sim 70\%$ and 40\% of the melting temperature of Ni and YSZ, respectively [38, 114], leads to enhanced mass transport kinetics for the Ni atoms. Spatial variations in the local interface mean curvature of the Ni network in combination with enhanced Ni atomic mobility lead to a mass transport and redistribution of the Ni phase, where Ni atoms are transferred from re-
regions of high to low mean curvature. At SOFC operating temperatures, Ni bulk self
diffusion $\sim 10^{-16} \text{m}^2\text{s}^{-1}$ [115], Ni surface self diffusion $D_{Ni} \sim 10^{-11} \text{m}^2\text{s}^{-1}$ [116], and
$Zr^{4+}$ surface diffusion in YSZ is $\sim 10^{-18} \text{m}^2\text{s}^{-1}$ [117] indicating that the coarsen-
ing process is driven by mass transport along Ni surfaces, while the YSZ phase is
stationary, or non-evolving, relative to the Ni coarsening time scales [34, 38]. Addition-
ally, when two solid phases are in contact, a local equilibrium wetting angle is
established as a result of balance of interfacial forces [32]. For the Ni/YSZ system at
SOFC operating temperatures, the wetting angle of Ni droplets on YSZ substrates
was experimentally determined to be no less than $117^\circ$ [118]. This large angle, greater
than $90^\circ$, indicates that Ni particles do not thermodynamically favor wetting YSZ
substrates. Figure 2.1 is a schematic illustrating the equilibrium wetting angle of a
Ni droplet on a static YSZ substrate, where $\alpha > 90^\circ$.

Several experimental investigations have focused on the role of Ni phase coarsening
in Ni/YSZ anodes on the evolution of several microstructural attributes that affect
the electrochemical performance of SOFCs. In an experimental study by Faes et
al. [35], microscopy techniques were utilized to image SOFC anodes that were under
operation for up to 2,000 hours. They measured several microstructural features,
such as average Ni and YSZ particle size, and total length of three phase boundary
(TPB) regions normalized by the system volume, which is typically referred to as TPB
density. Several SOFC stacks were studied and the authors observed $\sim 30\%$ decrease
in the TPB density, and $\sim 30\%$ increase in average Ni particle size. Their observations
are consistent with other experimental studies on the evolution of average size of Ni
particles [29, 119]. The continuous decrease in TPB density leads to a reduction
in the total number of active sites, where electrochemical reactions take place, with
electrons in the Ni phase, oxygen ions from the YSZ phase, and fuel and product
molecules moving into the pores.
A study by Simwonis et al. [33] on SOFC anodes under operation for up to 4,000 hours at 1000°C in turn revealed a shift in the Ni particle size distribution towards larger Ni particles, which was accompanied by \( \sim 33\% \) decrease in the effective electrical conductivity in SOFC anodes. Ni phase contiguity, which is a measure of the percolation degree of Ni networks, was found to decrease in SOFC anodes that are under utilization [37]. In another study, Tanasini et al. [34] examined the evolution of Ni domains and revealed the existence of a threshold volume fraction for the Ni, below which percolation of Ni clusters will be lost due to Ni coarsening. This is an indication that, during SOFC utilization, the initially percolating Ni networks break into small and spatially isolated ones that are unable to contribute to the electric current paths. In a 1996 experimental study, Iwata [120] observed microstructural changes to the pore space in Ni/YSZ anodes. Initially, the pore radius distribution exhibited two peaks; one \( \sim 50\ nm \) and the second \( \sim 2,000\ nm \). After 1015 hours of SOFC utilization, it was found that the peak with the small radius range shifted so far in the direction of the peak with larger radius that they disappeared. Moreover, the pore radius distribution developed a tail in the direction of larger radii, which is an indication that larger pores developed.

In a study published in 2011, Cronin et al. [38] employed impedance spectroscopy and three-dimensional tomography via Focused Ion Beam-Scanning Electron Microscopy to examine SOFC degradation due to Ni phase coarsening. Interfacial areas of the Ni, YSZ and pore space were characterized for SOFC anodes that were annealed for 100 hours at 1,100°C. A \( \sim 25\% \) decrease in the total pore interfacial area was observed, while the average pore space increased in size indicating that pores evolved into more equiaxed domains; a shape that minimizes Ni-pore interfacial areas. Additionally, it was found that these changes were accompanied by a \( \sim 30\% \) decrease in TPB density.
While the aforementioned experimental studies have provided important insights to the evolution of anode microstructures in operating environments, they do not examine the effects of interrelated physical phenomena on coarsening rates. Computational models on the other hand are ideally suited for exploring the various hypothesized mechanisms that control microstructural evolution processes in SOFC anodes. Existing computational studies of Ni coarsening in SOFC anodes include simplified two-dimensional two-particle systems that do not account for the YSZ phase [121] or diffuse-interface models, which do not examine the role of particle size and/or ratio on Ni coarsening nor do they incorporate the polycrystalline nature of Ni and the associated Ni grain boundary energies [122] [124].

In summary, various experimental observations indicate that Ni phase coarsening in SOFC anodes leads to: i) Ceaseless decrease in the total density of TPB regions, which ultimately leads to reduction in the total number of electrochemically active sites. ii) Evolution of the pore space microstructure, where the total pore interfacial area decreases, and the average pore space grows in size. Pore space properties affect the transport of fuel gases and reaction byproducts. iii) Ni phase contiguity and electronic conductivity decrease continuously. When Ni clusters become spatially isolated, they can no longer conduct electrons to the current collector.

2.1.2 Redox Instability and Mechanical Damage in SOFC Anodes

Reduction-oxidation (redox) cycling is a chemo-mechanical instability that occurs in SOFC anodes due to the reduction and oxidation reactions of the Ni phase. At SOFC operating temperatures, Ni phase is stable against oxidation when the anode is kept in a reduced state and an uncontaminated fuel is utilized. In cases of interruption to the fuel supply, seal leakage, system shutdown or high fuel utilization, oxygen will continue to pass through the electrolyte and result in re-oxidation of the Ni via the
reaction $\text{Ni} + \frac{1}{2}\text{O}_2 \rightarrow \text{NiO}$. Redox instability in SOFC anodes was first reported by Cassiday et al. [39, 40], where they measured the volume increase in the anode support due to re-oxidation and cracking of the thin electrolyte. As discussed earlier, dimensional changes and bulk expansion of SOFC anodes that are associated with redox reactions of Ni are due to the large NiO to Ni molar volume ratio.

Figure 2.2 is a schematic that illustrates the microstructural changes that occur during a redox cycle. SOFC anodes are typically prepared by combining NiO and YSZ powders whose particle size distributions are controlled by several mechanical and milling processes. Then, the powders are sintered at high temperatures in order to form a dense microstructure of NiO and YSZ networks as is shown in Fig. 2.2(a), where NiO (green) and YSZ (pink) phases form interconnected networks. The anode is then subjected to reducing environments in order to transform NiO particles to Ni, which yields a porous Ni/YSZ cermet as is shown in Fig. 2.2(b), where the pore phase develops due to the shrinkage that is associated with NiO to Ni transformation. During SOFC utilization, where the anode is kept at a reduced state and Ni phase is stabilized against oxidation, Ni coarsening takes place, where Ni particles along with several microstructural features evolve in order to reduce the total interfacial energy.
Figure 2.3: A cross-sectional view of an SOFC anode after a sintering process at 1400°C. The anode (a) in the pristine state and (b) after passing through four redox cycles, where micro-cracks started to develop in the YSZ ceramic phase. Note that microcracks first develop along YSZ grain boundaries. Taken from Ref. [21].

of the Ni phase. This is illustrated in Fig. 2.2(c), where Ni (grey) particles coalesced and grew into larger ones. Now, if an anode system is subjected to an oxidizing environment, the rapid transformation of Ni into NiO yields large bulk expansion strains, which can not be accommodated by the local porosity due to re-arrangement and coarsening of Ni. This process leads to the development of mechanical stress in the ceramic YSZ phase, which causes damage and micro-cracking when the stresses exceed the strength limit of YSZ. Figure 2.2(d) is a schematic that represents an anode system, where Ni transformed into NiO (green) and resulted in the development of cracks within the YSZ, and along the anode/electrolyte interface.

Irreversible mechanical damage in the YSZ phase can occur if only a fraction of the Ni phase in the anode is oxidized or even during the first redox cycle. Sarantaridis et al. [45] examined the role of oxidation procedure on mechanical damage modes. It was observed that in free-standing anodes that were oxidized in air, mechanical damage and cracking occurred after oxidation of approximately 50% of the Ni, while for anodes that were oxidized electrochemically, cracking caused failure after only ca. 5% of the Ni was oxidized, mainly due to the non-uniform nature of oxidation in the anode. In a study by Laurencin et al. [43], Ni/YSZ anodes under direct oxidation in air developed cracks under a conversion degree of Ni into NiO ranging between
58 and 71%. Fouquet et al. [21] examined the role of initial sintering temperature on the redox behavior. It was found that during anode preparation, sintering at high temperatures (1400°C) yields microstructures that are more prone to mechanical damage and cracking in the YSZ phase. They also observed the development of intergranular microcracks along YSZ grain-boundaries, which is a sign of brittle damage. Figure 2.3(a) presents a cross-sectional view of an anode microstructure in the initial as-sintered state, while Fig. 2.3(b) represents an anode that passed through four redox cycles, where intergranular cracks along YSZ grain-boundaries can been seen.

In a 2010 study, Jeangros et al. [125] have performed in situ experiments and atomistic calculations to examine the detailed atomistic redox mechanisms in SOFC anodes and investigate the nature of Ni/YSZ and NiO/YSZ interfaces. During the reduction cycle, they observed the formation of epitaxial Ni layer on YSZ, in agreement with previous experimental observations of Dickey et al. [126]. On the other hand, during the oxidation cycle, the outward diffusion of Ni ions along microstructural defects leads to a NiO layer that is polycrystalline in nature. This suggests that the newly formed NiO/YSZ interfaces are not fully coherent, or epitaxial, with pores forming along internal interfaces. Importantly, this partial loss of coherency would facilitate the relaxation of expansion strains parallel to NiO/YSZ interfaces, while the expansion strains perpendicular to such interfaces would impart stresses within the YSZ regions.

Finally, existing theoretical and computational treatments of redox cycling, and the accompanying mechanical deformation and damage are based on simplified geometries and statistical failure models [43, 45, 127]. Some of the geometries, which do not resemble real three-dimensional SOFC anodes, that are used in these models include two-dimensional layers of Ni and YSZ, or a spherical Ni particle embedded in a YSZ matrix. Other continuum models for the redox instability assume homogenized
properties for the anode, and strain localization is only captured at anode/electrolyte interfaces [128, 129].

2.1.3 Thermal vs. Electrochemical Effects

The aforementioned degradation mechanisms in SOFCs are mainly due to the high operating temperature of these cells. In this thesis, our modeling efforts focusing at Ni phase coarsening and its impact on features affecting the performance, assume that coarsening dynamics and mass transport processes are solely driven by the high operating temperature, which is \( \sim 70\% \) of the melting temperature of Ni. Electrochemical reactions will have a direct impact on several kinetic parameters that affect Ni coarsening. For example, Ni mobility is dependent on the temperature and water content that are associated with these reactions. Furthermore, additional heating effects exist due to the localized nature of these reactions, which are typically confined to regions at and in the vicinity of TPB.

For the redox analysis, we focus on the mechanistic aspect of the redox behavior since this instability leads to the evolution of mechanical stresses and accumulation of damage in the YSZ skeleton. The kinetics of Ni to NiO transformation are dependent on the electrochemistry, and can influence overall redox rates and development of stresses. Motivated by several experimental studies that focus on examining the redox instability of SOFC anodes under reducing and oxidizing environments in the absence of electrochemical effects, i.e., SOFCs are typically placed in high temperature ovens over a period of time then removed and exposed to air in order to examine re-oxidation of Ni, our continuum redox model is formulated to only account for the mechanical behavior due to redox cycles.
2.2 Mechanical Deformation of BMG Systems

At temperatures far below the glass temperature, $T_g$, monolithic BMGs exhibit high strength and large elasticity limits. On the other hand, the deformation of BMGs is highly inhomogeneous, spatially and temporally, due to localized regions of intense shear strain, or shear bands. Several research efforts have focused on developing mechanistic models to describe the heterogeneity of BMG deformation [130–134]. The shear transformation zone (STZ) model proposed by Argon [131] provides a useful mechanistic picture of deformation in BMGs. Within this formalism, an STZ element is a small cluster of randomly close-packed atoms that undergo a spontaneous atomic rearrangement to accommodate an increment of strain under an applied shear stress. Figure 2.4 is a schematic that represents an STZ element, where a local atomic rearrangement takes place under applied shear stress. Local shear transformation occurs when atoms within an STZ element move relative to each other in a certain favorable direction, or undergo a slip event. The motion of STZs causes a local distortion in the surrounding atoms, which in turn triggers the formation of an avalanche of neighboring STZs and the eventual formation of a shear band [65, 135].

Experimental findings on the mechanical behavior of BMGs suggest that the problem of catastrophic failure by shear band propagation can be mitigated by tailoring microstructural features, albeit at different length scales, to promote more homogeneous plastic deformation. In this Section, we survey the literature for the deformation mechanisms in BMGs and the two major avenues to enhance the overall ductility in these systems, namely, tailoring the composition of monolithic BMGs, or the formation of BMG composites, where soft crystalline particles are embedded in the glassy matrix.
2.2.1 Inelastic Deformation and Shear Banding in Monolithic BMGs

Monolithic bulk metallic glasses (BMGs) appear macroscopically homogeneous, yet contain structural and chemical heterogeneities at the atomic scale \[60, 86, 136-138\]. Plastic flow in such featureless structures typically becomes highly localized in shear bands and catastrophic failure subsequently occurs by shear softening on one band \[79, 139\].

One avenue to improve the ductility of BMGs is by fine-tuning the alloy composition of monolithic BMGs. Variations in the critical shear stress are attributed to a unique structure that is correlated with inhomogeneities at the atomic scale \[139, 140\]. These inhomogeneities are dictated by the degree of short- and medium-range order (SRO and MRO, respectively) \[86, 138\], where the SRO is associated with solute-centered polyhedra with varying atomic coordination numbers (CN) and resistance to undergo a shear transformation event, or “slip”. These polyhedra subsequently pack together, giving rise to MRO, which is the next level structural organization and can have a spatial length scale of \(\sim 1 - 2 \, \text{nm}\) \[137, 141\]. It is worth noting that this length scale is of the same order as an STZ, which is the fundamental unit of plas-
ticity in BMGs [65]. Sheng et al. [142] studied the nature of local nearest-neighbor coordination, atomic environment, and the resulting various types of coordination polyhedra in model BMG systems. Cluster packing of these solute-centered polyhedra, albeit having different topology and CN, can yield networks that are connected via solute-solute bonds. Therefore, the concentration of solute atoms greatly affects the structure of SRO and MRO in BMGs.

Several experimental studies on monolithic BMGs revealed that slight variations in the composition of the solute atoms yield large differences in the mechanical behavior [138, 143–145]. For example, Zhang et al. [143] studied the composition-dependent internal SRO structures that influence shear localization behavior of Zr-Cu-Al BMGs. They showed that CN=12 full icosahedra, referred to in their work as “rigid SRO”, have high symmetry, denser packing and higher energy barrier to slip events, while low symmetry polyhedra with unfavorable CN, referred to in their work as “fertile SRO”, are the most favorable sites for mediating shear transformation events. Therefore, the route to improve plasticity is to reduce the resistance to flow initiation by introducing more flow regions and numerous slip events globally, so as to sustain more distributed plastic strain before catastrophic failure. They demonstrated this by examining the behavior of two Zr-Cu-Al monolithic BMGs, namely, Z1: Zr_{45}Cu_{45}Al_{10} and Z2: Zr_{64}Ni_{26}Al_{10}. As is evidenced in the stress-strain curves shown in Fig. 2.5, the Z2 BMG can be
deformed plastically to strains much larger than the Z1 one. The authors observed that the difference in the mechanical behavior is driven by the structural motifs that are present in these systems. It was found that for the Z1 (less ductile) BMG 74% of the atoms are involved in full icosahedra (rigid SRO), while for the Z2 system, only 46% of the atoms are involved in rigid SRO packing polyhedra. They also observed similar trends in other BMG alloys, such as Hf-Ni-Al systems.

Importantly, atomistic simulations of monolithic BMGs provide tantalizing clues to the importance of SRO and the resulting structural motifs on the mechanical properties of these systems [87, 146–149]. Studies revealed that monolithic BMGs derive their exceptional strength from a percolating backbone of SRO. In general, metallic glasses with a large degree of rigid SRO exhibit higher strength and a stronger propensity towards localized deformation [146]. An atomistic simulation study on model BMGs by Shi and Falk [87] has shown that deformation changes from homogeneous flow, with improved ductility, to a more localized state as the fraction of atoms exhibiting rigid SRO increases. A BMG alloy that initiates shear transformations sites that are homogeneously distributed throughout the system is capable of accommodating more applied strain than a BMG system, where only one shear band is operational that localizes the deformation and fail in a brittle manner. Based on the aforementioned studies, alloy composition can be fine-tuned to yield an optimal combination of structural motifs (rigid and fertile SRO) that are homogeneously distributed, such that the desired strength and ductility characteristics of BMGs can be attained.

2.2.2 Enhancement in Ductility in BMG Composites

The second route to enhancing the ductility of BMGs is achieved by introducing ductile crystalline particles (dendrites) with size scales $\sim 0.5 – 10 \mu m$, resulting in the formation of BMG composites [75, 88, 90, 150–152]. BMG composites can be formed via
many techniques, such as phase separation into two or more amorphous phases with distinct mechanical and chemical properties [153], processing ingots by semi-solidly treating the alloy between solidus and liquidus lines in order to control volume fraction and fine-tune the morphology of the precipitated crystalline phase [75, 90], or by physically dispersing crystalline particles with desired volume fraction and shapes into the molten matrix alloy and quench to produce a BMG composite [85]. The overall ductility of BMG composites depends on several factors, such as the volume fraction and morphology of the reinforcing phase, and its mechanical properties (Young’s $E$ and shear $\mu$ moduli) relative to the glassy matrix phase. In an experimental study by Hofmann et al. [151], it was revealed that BMG composites with enhanced ductility can be produced if the shear modulus of the reinforcing crystalline phase is lower than the one for the glassy matrix phase. Their conclusion was motivated by the linear-elastic crack deflection mechanics solution by He and Hutchinson [154] that considers the conditions under which a crack that impinges on a bi-material interface penetrates or deflects away from the interface. They defined Dundurs’ parameter $\alpha = (\mu_{\text{dendrite}} - \mu_{\text{glass}})/(\mu_{\text{dendrite}} + \mu_{\text{glass}})$, where crack penetration occurs if $\alpha < 0$ and deflection if $\alpha > 0$. Therefore, “soft” crystalline domains are needed to ensure that shear bands are attracted towards them, where they can be arrested via dislocation-mediated plasticity within these crystalline inclusions.

Soft ductile dendrites can act both as shear band initiation sites and as arrest barriers to shear band extension [75, 90]. Shear band branching due to the ductile phase leads to a more uniform distribution of plastic strain; therefore, the mechanical properties of BMG composites can be optimized with respect to the volume fraction and morphology of the ductile phase [90]. For example, it was shown in a study by Hays et al. [152] that the ultimate strain $\gamma_{\text{tot}}$ in a BMG composite $\sim w_{\text{SB}}/\lambda$, where $w_{\text{SB}}$ and $\lambda$ denote shear band thickness and spacing, respectively, while $\lambda$ was found to correlate with the dendrite morphology, more specifically dendritic arm spacing.
These observations thus suggest that overall ductility can be improved by decreasing shear band spacing by appropriately tailoring the microstructure of the reinforcing crystalline phase. In addition to the dendrite arm spacing, the topology and the percolating nature of the ductile phase greatly affect shear band propagation, arresting, and/or deflection in these systems. In a study on the role of crystalline second phase reinforcements on the mechanical properties of glassy La-Al-Cu-Ni alloys by Lee et al. [90], it was revealed that the ductility and plastic strain increase drastically in a non-linear fashion as the volume fraction of the reinforcing phase increases and approaches the percolation threshold.

Atomistic studies on BMG composites reveal that plastic deformation initiates in the soft crystalline phase and further deformation localizes within these inclusions, mainly due to dislocation-mediated plasticity in the ductile phase [155, 157]. At the mesoscale, computational studies focus primarily on monolithic BMGs, which do not capture the structural heterogeneity of glass and the accompanying spatial variations in the critical shear stress for local “slip” events [158]. Furthermore, these models do not account for BMG composites and the resulting interaction between shear bands and the soft crystalline phase [159, 160].

In summary, experimental observations reveal that both routes to improving the overall ductility of BMGs are associated with tailoring microstructural features, albeit at different length scales. For monolithic BMGs, mechanical properties can be optimized by fine-tuning the glassy alloy composition, which in turn affects the fraction and spatial distribution of the rigid/soft SRO, where strength is derived from a backbone of rigid SRO, while ductility is associated with soft SRO regions. For BMG composites, enhancement in overall ductility is achieved by introducing soft crystalline dendrites that can act as both shear band initiation sites and arrest barriers to the catastrophic propagation of these bands. Mechanical properties of these composites are controlled by the volume fraction and morphology of the ductile phase.
Chapter 3

Theoretical Models for
Microstructure Evolution

Technological advances in several industries are highly dependent on the ability to fine-tune materials microstructures, through several thermo-mechanical processes, to yield a desired combination of properties. In response to multitude of physical, chemical and/or mechanical cues, materials microstructures evolve in order to reduce their total free energy, which in general has many components, such as bulk chemical, interfacial, elastic, magnetic, etc. Inherent to microstructural evolution phenomena are the geometrical complexity of internal interfaces, which can also evolve, defect structure, multi-physics processes, and disparity in the scales (length and time) controlling these processes. Therefore, computational approaches are considered the method of choice when studying the spatio-temporal evolution of materials microstructures.

Generally, the kinetics of microstructure formation can be modeled by deriving the governing equations for the bulk domains in addition to boundary conditions applied at the internal interfaces. For example, let us consider the solidification of a pure material. The governing equations describe the diffusion of heat in both the solid and liquid phases, whereas at the solid-liquid interface, two boundary conditions
are applied. The first is the advancement of the solid-liquid front that is dictated by the flux of heat from one side of the interface to the other. Also, the temperature at the interface is adjusted by Gibbs-Thomson condition. The governing equations describing the evolution in the bulk phases along with the boundary conditions at the propagating solid-liquid front constitute the so-called sharp interface model, or Stefan problem [161].

The numerical implementation of sharp-interface models is an extremely difficult task, mainly due to the complex topological transformations that occur, such as pinching-off and merging of domains. Furthermore, solving these models requires the explicit tracking and spatial resolution of propagating fronts, which become impractical in three-dimensions [5]. Several numerical methods have been applied to sharp-interface models with propagating fronts, such as level set [162] and front tracking methods [163].

In the level set method, the propagating front, or interface, is embedded as the zero level set of a higher dimensional surface, where no explicit tracking of interfaces is performed. Once the surface is built, the problem of tracking a moving front is traded for moving, expanding, and/or distorting the surface, whose equation of motion resembles a Hamilton-Jacobi equation. To determine where a front is, we cut a slice of surface at the zero level set using a virtual “saw” [164].

In front-tracking methods, propagating fronts are spatially resolved using a computational grid. Boundary motion is implemented by applying the normal velocity at interface grid points and recipes have to be supplied for detecting topological changes [165, 166]. Some of the major drawbacks of front-tracking methods include their computational complexity, the need to restructure the interface grid dynamically as the calculations proceed, and complexity in three dimensions, especially when treating the interaction of a front with another front.
An alternative method to solving problems involving propagating fronts is the use of diffuse-interface, or phase field, models. Within this numerical approach, an order parameter is introduced that takes on a constant value within the bulk phases and varies smoothly across interfaces. The evolution of the order parameter is governed by continuum equations whose form depends on whether the order parameter is conserved or non-conserved. In this thesis, we adopt the phase field approach to solve problems involving propagating fronts.

3.1 The Phase Field Method

The phase field, or diffuse-interface, method is a relatively new approach to solving moving boundary problems. Within this numerical method, a diffuse-interface description, which was developed by van der Waals [167], and Cahn and Hilliard [168], is used for sharp interfaces. The starting point in the phase field framework is the introduction of phase fields (PFs), or order parameters (OPs), that describe the bulk phases. PFs vary smoothly and continuously from one phase into the other across the interface. These types of PFs are introduced to avoid explicit tracking of interfaces. From the condensed matter physics point of view, PFs can represent volume fraction of phases, the degree of order (crystallinity) or disorder (liquid) in a phase, or composition fields for a phase separation process [161]. By construction, PFs represent interfaces as diffuse regions, which yield tractable numerical models that can be used to examine the evolution of complex microstructures. The temporal evolution of PFs is governed by two well-celebrated continuum equations, namely, the Cahn-Hilliard nonlinear diffusive equation and the Allen-Cahn (time-dependent Ginzburg-Landau) equation. The phase field method has been used to model a wide variety of physical phenomena, such as solid-state phase transformation, coarsening, solidification and dendritic growth, crack propagation, dislocation dynamics, electromigration, multi-
phase fluid flow. The reader is referred to Refs. [161, 169–178] and references therein contained for more on phase field models for the phenomena mentioned above. Additionally, the phase field method found its way into other applications, such as image processing [179], planet formation [180], and tumor growth [181].

With the aid of a PF, $\phi$, which defines the state of the system, an additive decomposition of the total energy density, $f_{tot}$, is utilized, where bulk and interfacial terms constitute the main contributions to $f_{tot}$. Then, the total energy functional, $F_{tot}$, of an evolving system is constructed as

$$F_{tot} = \int_{\Omega} d\mathbf{r} f_{tot} = \int_{\Omega} d\mathbf{r} [f(\phi) + g(|\nabla \phi|)].$$

(3.1)

The first term, which is the bulk energy term, on the right hand side of Eq. (3.1) is the Landau polynomial expansion in terms of the PF $\phi$, where the global minima represent the thermodynamic equilibrium phases. Typically, $f(\phi)$ is written as

$$f(\phi) = \alpha_0(T) + \sum_{n=1}^{M_\alpha} \frac{\alpha_n(T)}{n} \phi^n,$$

(3.2)

where $T$ is the temperature and $M_\alpha$ represents the number of terms in the expansion. The coefficients $\{\alpha_n(T), n = 0, ..., M_\alpha\}$ are in principle temperature dependent that can be directly linked to material and thermodynamic properties. In a phase transformation event, two or more phases co-exist and the PF takes on a constant value within each phase and varies smoothly across the interface between the co-existing phases. The constant value of the PF within the bulk phases represents one of the global minima of $f(\phi)$ and the number of terms in the expansion in Eq. (3.2) along with the choice of including/excluding odd or even terms depend on the nature of the phase transformation that we seek to model.

The second term, $g(|\nabla \phi|)$, on the right hand side of Eq. (3.1) represents an energy term associated with the existence of interfaces. A phase transformation often results
in co-existing phases that are separated by interfaces. As previously mentioned, the PF takes on a constant value in each phase and varies smoothly across an interface. Therefore, it is natural to use the mathematical operator $|\nabla \phi|$ to capture spatial variations in the PF $\phi$ across the interface. Within the bulk phase, $|\nabla \phi|^2 = 0$, and across the interface, where $\phi$ varies smoothly, $|\nabla \phi|^2 \neq 0$. Representative curves of the PF $\phi$ and the operator $|\nabla \phi|^2$ in a material with two co-existing phases (A and B) separated by an interface are shown in Fig. 3.1. Generally speaking, $g$ can be written as an expansion in terms of $|\nabla \phi|$ as follows [182]

$$g(|\nabla \phi|) = \kappa_{ij} \frac{\partial \phi}{\partial x_i} \frac{\partial \phi}{\partial x_j} + \Gamma_{ijkl} \frac{\partial^2 \phi}{\partial x_i \partial x_j} \frac{\partial^2 \phi}{\partial x_k \partial x_l} + HOT, \quad (3.3)$$

where $\kappa_{ij}$ and $\Gamma_{ijkl}$ are second and fourth order tensors, respectively. In their treatment of isotropic systems with nonuniform composition, Cahn and Hilliard [168]
arrived at similar results. Assuming a conserved OP, such as concentration \( c \) that is well-behaved, where the total energy density \( f \) is a continuous function of \( c \) and its spatial gradients, they expanded the total energy density in a Taylor series about the free energy of a solution with uniform composition \( f_0 = f(c, 0, 0, \ldots) \) as

\[
f(c, \nabla c, \nabla^2 c, \ldots) = f_0 + \sum_i L_i \frac{\partial c}{\partial x_i} + \sum_{ij} E_{ij} \frac{\partial^2 c}{\partial x_i \partial x_j} + \frac{1}{2} \sum_{ij} G_{ij} \frac{\partial c}{\partial x_i} \frac{\partial c}{\partial x_j} + \ldots, \tag{3.4}
\]

where

\[
L_i = \left[ \frac{\partial f}{\partial (\partial c/\partial x_i)} \right]_0,
E_{ij} = \left[ \frac{\partial f}{\partial (\partial^2 c/\partial x_i \partial x_j)} \right]_0, \tag{3.5}
G_{ij} = \left[ \frac{\partial^2 f}{(\partial c/\partial x_i) (\partial c/\partial x_j)} \right]_0.
\]

Here, \( L_i \) is a vector, and \( E_{ij} \) and \( G_{ij} \) are second order tensors that reflect crystal symmetry. The subscript 0 indicates a homogeneous system with uniform concentration, where all spatial gradients are zero. The total free energy density is invariant under various symmetry operations. Therefore, under reflection symmetry, where \( x_i \rightarrow -x_i \), \( L_i = 0 \). For cubic crystals or isotropic systems, which are the only ones we consider in this thesis, rotational symmetry, where \( x_i \rightarrow x_j \), implies

\[
E_{ij} = E* = \left[ \frac{\partial f}{\partial \nabla^2 c} \right]_0 \text{ for } i = j \text{ and zero otherwise.}
\]

\[
G_{ij} = G* = \left[ \frac{\partial^2 f}{(\partial |\nabla c|)^2} \right]_0 \text{ for } i = j \text{ and zero otherwise.} \tag{3.6}
\]

Using the divergence theorem, Cahn and Hilliard \[168\] broke the \( \nabla^2 c \) term into a \( |\nabla c|^2 \) and a flux term through the system’s boundary, which can be chosen such that it vanishes. With the assumption that the energy is influenced by the concentration
in a small neighborhood, the total energy density reduces to

\[
    f(c, \nabla c, \nabla^2 c, ...) = f(c, 0, 0, ...) + \kappa |\nabla c|^2. \tag{3.7}
\]

The higher order terms in the expansion in Eq. (3.3) are one possible way to account for anisotropy in the interfacial energy. In the work presented in this thesis, isotropic systems are assumed, where reflection and rotational symmetries are invoked, and only the first term in the expansion is included and is written as follows

\[
    g(|\nabla \phi|) = \kappa |\nabla \phi|^2, \tag{3.8}
\]

where \( \kappa \) is a coefficient of the gradient energy term and phenomenological parameter that penalizes the formation of interfaces.

The next step in the phase field framework is the description of the dynamics of evolution of the PF. The general form of the governing equation describing the temporal evolution of the OP is written as follows

\[
    \frac{\partial \phi}{\partial t} = -M (-\nabla^2) \chi \frac{\delta F_{\text{tot}}}{\delta \phi}, \tag{3.9}
\]

where \( M \) is a kinetic coefficient and assumed constant in the above equation. \( \frac{\delta F_{\text{tot}}}{\delta \phi} \) represents the “chemical potential” of the phase field \( \phi \), which drives the dynamics of the system. According to the classification of Hohenberg and Halperin [183], \( \chi = 0 \) defines the so-called “Model A” or the Allen-Cahn (time-dependent Ginzburg-Landau) equation for a non-conserved OP (magnetization in an Ising model), whereas \( \chi = 1 \) yields “Model B” or the Cahn-Hilliard equation for a conserved OP (concentration of species). It is worth noting that other classes of dynamical equations exist in the literature. One of interest, which is used in this thesis work, is “Model C” dynamics, which combines both “Model A” and “Model B” equations. In other words, “Model
C contains both conserved (total mass of a phase) and non-conserved (number of grains of a phase having different crystallographic orientations) PFs. Furthermore, noise terms can be added to the right hand side of Eq. (3.9), making it a stochastic equation, which accounts for thermal fluctuations in the system.

3.1.1 Examples

In this Section, we present two examples, where the phase field method has been successfully applied, namely, phase separation via spinodal decomposition and grain growth in metals.

3.1.1.1 Spinodal Decomposition

Spinodal decomposition is an unmixing process in which an alloy with bulk composition in the central region of the phase diagram undergoes exsolution. For a given binary solution of A and B atoms, if A-atoms are equally content to be in contact with A or B atoms, then there is no enthalpy of mixing. However, if A atoms have a preference for A, and/or B have a preference for B, then a homogeneous solution is energetically disadvantageous. Systems of two constituent atoms become homogeneous above the critical temperature since thermal agitation overcomes the enthalpic attraction of A-A and/or B-B bonds. At temperatures below the critical one, the free energy of the system can be minimized when the homogeneous solution separates into two phases having compositions corresponding to a state with no gradients in the chemical potential.

The treatment in this Section is based on Cahn [184], Fan [185], Provatas and Elder [161] and Porter and Easterling [186]. For the sake of simplicity, let us start with a binary solution of A and B atoms. We assume that A and B have the same crystal structure in their pure states and can be mixed in any proportions to make a solution with the same crystal structure. Let $x_A$ and $x_B$ denote the mole fractions of
A and B, respectively. Before mixing A and B, the free energy of the system $G_1$ is

$$G_1 = x_A G_A + x_B G_B,$$  \hspace{1cm} (3.10)

where $G_A$ and $G_B$ are the molar free energies of pure A and B. Now, assuming a regular solution model, the free energy after mixing A and B is written as

$$G_2 = G_1 + \Delta G_{mix},$$  \hspace{1cm} (3.11)

where $\Delta G_{mix}$ is the free energy change due to mixing and is comprised of enthalpic and entropic terms as follows

$$\Delta G_{mix} = k_B T \left( x_A \ln x_A + x_B \ln x_B \right) + 2k_B T c x_A x_B,$$  \hspace{1cm} (3.12)

where $k_B$ is Boltzmann constant and $T$ is the temperature. In the enthalpic term, $2k_B T c \propto (\epsilon_{AB} - 1/2(\epsilon_{AA} + \epsilon_{BB}))$. $\epsilon_{AB}, \epsilon_{AA}$ and $\epsilon_{BB}$ represent the energy of A-B, A-A and B-B bonds, respectively. As the bounds of the mole fraction (0 and 1) are approached, $\Delta G_{min} \to \infty$, due to the existence of the natural logarithm in Eq. (3.12).

By performing a simple change of variables, where we let $x_A = (1 - c)/2$ and $x_B = (1 + c)/2$, we have

$$\Delta G_{mix}(c, T) = k_B T \left( \frac{1 + c}{2} \ln \frac{1 + c}{2} + rac{1 - c}{2} \ln \frac{1 - c}{2} \right) + \frac{k_B T c}{2} (1 - c^2).$$  \hspace{1cm} (3.13)

Expanding the natural logarithms to the third order and dropping the constants that are independent of $c$ yield

$$\Delta G_{mix}(c, T) = -\alpha_2 \frac{c^2}{2} + \alpha_4 \frac{c^4}{4},$$  \hspace{1cm} (3.14)
Figure 3.2: (a) A representative surface plot of the free energy of mixing $\Delta G_{\text{mix}}$, Eq. (3.14), as a function of the phase field $c$ and temperature $T$. Note that at high temperatures (above $T_c$), one global minimum exists, whereas at low temperatures (below $T_c$), the energy landscape develops two minima corresponding to the equilibrium phases. (b) The phase diagram for the binary solution.

where $\alpha_2 = k_B(T_c - T)$ and $\alpha_4 = 4k_B T/3$. It is worth noting that the resulting polynomial in Eq. (3.14) is an even expansion of the Landau polynomial given in Eq. (3.2). Figure 3.2(a) is a representative surface of $\Delta G_{\text{mix}}$ as a function of the phase field $c$ and temperature $T$. At high temperatures, the energy has one global minimum, whereas at low temperatures (below $T_c$), the energy landscape develops two minima corresponding to the equilibrium values for $c$; one for the A-rich phase and the second is for the B-rich phase. Figure 3.2(b) is a schematic of the phase diagram of such an immiscible binary system.

The homogeneous binary solution can be made unstable with respect to the mixture of A and B via a thermal treatment schedule (cooling or heating). Small fluctuations lead to instability where the two separating phases (A-rich and B-rich phases) co-exist. To account for the excess free energy associated with interfaces that separate the two co-existing phases, a gradient energy term is added to Eq. (3.14) and
the total free energy is written as

\[ F = \int_\Omega d\mathbf{r} \left[ -\alpha_2 \frac{c^2}{2} + \alpha_4 \frac{c^4}{4} + \frac{\kappa^2}{2} |\nabla c|^2 \right], \tag{3.15} \]

where \( \Omega \) is the total volume of the system. As for the dynamics of evolution of the phase field \( c \), we first obtain the diffusional flux in terms of the chemical potential \( \mu \) for the OP \( c \) as follows

\[ \mathbf{j} = -M \nabla \mu = -M \nabla \frac{\delta F}{\delta c}, \tag{3.16} \]

where \( M \) is the atomic mobility (assumed isotropic) and \( \delta \) denotes the variational operator. Next, following the continuity equation we have

\[ \frac{\partial c(\mathbf{r}, t)}{\partial t} = -\nabla \cdot \mathbf{j} = \nabla \cdot \left[ M \nabla \frac{\delta F}{\delta c} \right], \tag{3.17} \]

which is the classic Model B (Cahn-Hilliard) governing equation for a conserved PF. With the aid of variational derivatives, Eq. (3.17) reduces to

\[ \frac{\partial c(\mathbf{r}, t)}{\partial t} = \nabla \cdot \left[ M \nabla \left( -\alpha_2 c + \alpha_4 c^3 - \kappa^2 \nabla^2 c \right) \right]. \tag{3.18} \]

The dynamical equation for \( c \) can be made non-dimensional by using \( \tilde{t} = t/\tau \) and \( \tilde{\mathbf{r}} = \mathbf{r}/d \), where \( \tau \) and \( d \) are the characteristic time and length scales, respectively. For simplicity, we let \( M = M^* \), where \( M^* \) is a constant. Also, we let \( d = \kappa/\sqrt{\alpha_2} \) and \( \tau = \kappa^2/(M^*\alpha_2^2) \). After dropping the tildes for notational convenience, the resulting non-dimensional governing equation becomes

\[ \frac{\partial c(\mathbf{r}, t)}{\partial t} = \nabla^2 \left[ -c + (\alpha_4/\alpha_2)c^3 - \nabla^2 c \right]. \tag{3.19} \]
Figure 3.3: The equilibrium profile for the phase field \( c \) obtained by solving Eq. (3.20). Notice that the interface width is proportional to \( \kappa \).

The use of Eqs. (3.18) and (3.19) to study spinodal decomposition in binary systems has been the subject of extensive research efforts, see for example [168, 184, 187, 188]. In Eq. (3.18), the coefficient of the \( c \) term determines the quench temperature (cooling) and the resulting equilibrium state of the system. At temperature above \( T_c \) \((-\alpha_2 > 0)\), there exists only one global minima, which corresponds to a homogeneous mixture (a uniform \( c \) field). Below \( T_c \) \((-\alpha_2 < 0)\), two phases co-exist that correspond to A-rich and B-rich phases.

Without loss of generality, we can obtain the equilibrium profile in one dimension by solving Eq. (3.18) assuming \( \alpha_2 = \alpha_4 = 1.0 \) with the boundary conditions of \( c \rightarrow \pm 1 \) as \( x \rightarrow \pm \infty \). Under equilibrium, there are no spatial variations in the chemical potential, such that

\[
\mu = \frac{\delta \mathcal{F}}{\delta c} = -c + c^3 - \kappa^2 \nabla^2 c = b_0 = 0,
\]

(3.20)
Figure 3.4: Contours illustrating the temporal evolution of compositional domains during spinodal decomposition in an immiscible binary system of A and B atoms at (a) \( t = 40 \), (b) \( t = 600 \), and (c) \( t = 4000 \). Black (green) domains represent the B-rich (\( c = +1 \)) and A-rich (\( c = -1 \)) phases, respectively.

where the last equality is applied since \( c \to \pm 1 \) as \( x \to \pm \infty \). Eq. (3.20) is a nonlinear differential equation for \( c \), whose exact solution, which is derived in Section A.1.1, is

\[
c(x) = \tanh \left( \frac{x}{\sqrt{2} \kappa} \right).
\]  

The equilibrium profile for the PF \( c \) is shown in Fig. 3.3 where the width of the interface separating the co-existing phases scales linearly with \( \kappa \).

Next, we simulate spinodal decomposition and subsequent coarsening dynamics by numerically solving Eq. (3.19) with \( \alpha_2 = \alpha_4 = 1 \) and an initial uniform mixture of A and B with a ratio of 1:1. Contours of the resulting microstructure are shown in panels (a)-(c) of Fig. 3.4 that correspond to time \( t = 40, 600 \) and 4000, respectively. It can be clearly seen that the A-rich (green) and B-rich (black) phases separate at early time. The gradient energy term in Eq. (3.18) drives the system towards minimizing the total interfacial energy of the system by simply reducing the total interfaces that separate the black and green domains. Therefore, the co-existing phases evolve and their average characteristic length scale grows over time, as is evident by comparing panels (a) and (c) of Fig. 3.4 leading to a reduction in the total interfacial energy.
Figure 3.5: (a) The two-point correlation function $g_2(r, t)$ at different times through the spinodal decomposition and subsequent coarsening processes. Notice the shift in the location of the first minimum of $g_2(r, t)$ as coarsening proceeds. The location of the first minimum is taken as a measure of characteristic domain size. (b) The re-scaled $g_2(r, t)$ based on the characteristic domain size, $R(t)$, at each time step. All curves collapse into one indicating that the re-scaled $g_2(r, t)$ is independent of time.

A convenient measure that is used to track the temporal evolution of the average domain (phase) size, $R(t)$, is the two-point correlation function $g_2(r, t)$. First, let a phase $i$ occupies a volume $\Omega_i$ of the total volume of the system $\Omega$, such that $\Omega_i \subset \Omega \in \mathbb{R}^3$. The phase indicator function for phase $i$ is constructed as follows \[189\]

$$
\Gamma_i(r) = \begin{cases} 
1, & \text{if } r \in \Omega_i, \\
0, & \text{otherwise.}
\end{cases}
$$

In terms of the phase indicator function, the two-point correlation function is defined as $g_2(r, t) = \langle \Gamma_i(r, t) \Gamma_i(r + \Delta r, t) \rangle$ \[189\]. A characteristic length can be extracted from $g_2(r, t)$ in several ways. For example, the location of the first minimum in $g_2(r, t)$ can be used as a measure of the characteristic domain size of the phase under interest. Let us examine the temporal evolution of the average size, $R(t)$, of the B-rich domain, where $\Gamma_B(r) = +1$ within this phase and zero elsewhere. Figure 3.5(a) is a plot of $g_2(r, t)$ for the binary system undergoing spinodal decomposition and
subsequent coarsening. There exists a shift in the first minimum of $g_2(r,t)$ indicating that B-rich domains are growing in size as time proceeds. The curves of $g_2(r,t)$ can be re-scaled using the characteristic domain size $R(t)$ and the results are shown in Fig. 3.5(b), where all curves collapse into one indicating that systems undergoing spinodal decomposition are self similar, i.e., re-scaled $g_2(r,t)$ curves are independent of time. Other measures have been used to extract scaling laws in systems undergoing spinodal decomposition and the reader is referred to Refs. [168, 184, 187, 188] for more on this topic.

3.1.1.2 Grain Growth in Metals

In general, the curvature of a materials interface introduces a thermodynamic driving force that leads to the transport of mass in order to minimize the excess free energy associated with interfaces [32]. Grain growth in metals is such an example of this type of boundary motion. Annealing at elevated temperatures causes the average grain size of a polycrystalline material to increase, where large grains grow at the expense of smaller ones. The thermodynamic driving force for grain growth is the reduction in the total interfacial energy and this kinetic growth process, which occurs in metals at temperatures above $\sim 0.5T_m$, where $T_m$ is the melting temperature, is accompanied by a decrease in the total number of grains and an increase in the average grain size. The mean interface curvature is defined as the local rate of interface area change with a local addition of volume [32]. For a pure material, if the addition of a small volume $\Delta V$ makes the interface develop a localized “bulge”, where $\Delta A$ is the change in the total interfacial area, then the mean curvature $\kappa$ is given by

$$\kappa = \frac{\Delta A}{\Delta V}. \quad (3.23)$$
Therefore, the work to create the bulge is \( \gamma \Delta A = \gamma \kappa \Delta V \), where \( \gamma \) is the interface energy. If this work is equated to the work done by the system \( P \Delta V \), then the pressure \( P \) acting on a grain with a curved interface is given by

\[
P = \gamma \kappa. \tag{3.24}
\]

For a given grain, the pressure due to its curved interface acts normal to it and is directed towards its concave side. Due to the higher pressure on the concave side of the boundaries, atoms in the shrinking grain detach from the lattice on the high pressure side of the boundary and attach themselves on the lattice of the growing grain [186]. The increase in the free energy (\( \Delta G \)) due to the pressure that is caused by a curved boundary is given by the Gibbs-Thomson effect as [186]

\[
\Delta G = \frac{2\gamma V_m}{r}, \tag{3.25}
\]

where \( V_m \) is the molar volume. Furthermore, the boundary velocity \( v \) varies linearly with the pressure caused by the curved interface according to [32, 186]

\[
v = M_B P = M_B \gamma \kappa, \tag{3.26}
\]

where \( M_B \) is the boundary mobility. Eq. (3.26) constitutes the sharp interface law for grain growth, where boundary velocity scales linearly with both interface energy and curvature. For grain growth in two-dimensional systems, von Neumann [190] and later Mullens [110] showed, in what is known as the von Neumann-Mullins relation, that the rate of change of a grain area \( A \) is purely topological and depends on the number of grain sides \( n \), such that grains with \( n > 6 \) grow and those with \( n < 6 \) shrink, while \( n = 6 \) leads to non-evolving grains. The result by von Neumann and Mullins was extended to three-dimensional and higher order systems by MacPherson
and Srolovitz [191], where it was shown that the rate of change of the volume of a grain depends on the size of the grain and not just its shape. Grain growth in pure materials has been the subject of numerous scholarly articles and the reader is referred to [32, 110, 186, 190–194] for more on this topic.

In this Section, we will demonstrate that a phase field framework with “model A” dynamics reduces to the sharp interface model describing grain growth, i.e., Eq. (3.26). The diffuse interface framework is matched to the sharp interface model through an asymptotic analysis that is carried out by performing inner and outer expansions on the fields that describe the dynamics of the system. The outer expansion describes the fields far away from the interface and the inner one describes the fields in the close proximity of the interface. Asymptotic matching refers to the matching of the inner and outer expansions, leading to a smooth global solution. The field of interest in our problem is the non-conserved PF $\psi$ and the asymptotic analysis performed here is similar in spirit to the one by Yeon et al. [195], and Deng [196]. The reader is advised to approach the following analysis with caution due to the endless number of terms containing the expansion parameter. The starting point of the analysis is the introduction of the total energy of the system, which includes bulk and interfacial terms as

$$
\mathcal{F} = \int_\Omega d\mathbf{r} \left[ Bg(\psi) + \frac{w^2}{2} |\nabla \psi|^2 \right] = \int_\Omega d\mathbf{r} \left[ B \left( \psi^2 - 1 \right)^2 + \frac{w^2}{2} |\nabla \psi|^2 \right], \quad (3.27)
$$

where $g(\psi)$ is assumed to have the minima $\psi = +1$ within the grain and -1 elsewhere. $B$ is an energy barrier and $w^2/2$ is the coefficient of the gradient energy term and it controls the grain boundary energy. The temporal evolution is described by the Allen-Cahn (Model A) dynamics as

$$
\frac{\partial \psi}{\partial t} = -L \mu = -L \frac{\delta \mathcal{F}}{\delta \psi} = -L \left[ B \frac{\partial g}{\partial \psi} - w^2 \nabla^2 \psi \right]. \quad (3.28)
$$
The equation can be made non-dimensional by introducing \( \tilde{x} = x/d \) and \( \tilde{t} = t/\tau \), where \( d \) and \( \tau \) are the characteristic length and time scales, respectively. We also use a reference energy density \( \gamma/d \), where \( \gamma \) is the interfacial (grain boundary) energy. We define the expansion parameter \( \epsilon = w^2/(d\gamma) \), \( \tilde{B} = w^2 A/\gamma^2 \), and \( f(\psi) = \partial g/\partial \psi = 4(\psi^3 - \psi) \). The governing equation [Eq. (3.28)] then becomes

\[
\lambda\epsilon^2 \frac{\partial \psi}{\partial \tilde{t}} = \epsilon^2 \tilde{\nabla}^2 \psi - \tilde{B} f(\psi),
\]

(3.29)

where \( \lambda = d^2/(\tau w^2 L) \). For expansion in the inner and outer regions, \( \psi \) and the chemical potential \( \mu = \delta F/\delta \psi \) are expanded in powers of \( \epsilon \) and the asymptotic analysis is performed by solving the field equations order by order in terms of \( \epsilon \). In the outer region, we have

\[
\psi = \psi_0 + \epsilon \psi_1 + \epsilon^2 \psi_2 + \ldots,
\]

\[
\mu = \mu_0 + \epsilon \mu_1 + \epsilon^2 \mu_2 + \ldots
\]

(3.30)

By plugging Eq. (3.30) into Eq. (3.29) and realizing that

\[
\lambda\epsilon^2 \frac{\partial \psi}{\partial \tilde{t}} = \lambda\epsilon^2 \frac{\partial \psi_0}{\partial \tilde{t}} + \lambda\epsilon^3 \frac{\partial \psi_1}{\partial \tilde{t}} + \lambda\epsilon^4 \frac{\partial \psi_2}{\partial \tilde{t}} + \ldots,
\]

\[
\epsilon^2 \tilde{\nabla}^2 \psi = \epsilon^2 \tilde{\nabla}^2 \psi_0 + \epsilon^3 \tilde{\nabla}^2 \psi_1 + \epsilon^4 \tilde{\nabla}^2 \psi_2 + \ldots,
\]

(3.31)

\[
-\tilde{B} f(\psi) = -4\tilde{B} \left[ (\psi_0 + \epsilon \psi_1 + \epsilon^2 \psi_2 + \ldots)^3 - (\psi_0 + \epsilon \psi_1 + \epsilon^2 \psi_2 + \ldots) \right],
\]

where the expression for \( \tilde{B} f(\psi) \) is expanded and simplified to yield

\[
-\tilde{B} f(\psi) = -4\tilde{B} \left[ (\psi_0^3 - \psi_0) + \epsilon \psi_1 (3\psi_0^2 - 1) + \epsilon^2 \left( \psi_2 (3\psi_0^2 - 1) + 3\psi_0 \psi_1^2 \right) + \ldots \right]
\]

\[
= -4\tilde{B} \left[ \frac{1}{4} f(\psi_0) + \frac{1}{4} \epsilon \psi_1 \frac{\partial f}{\partial \psi_0} + \epsilon^2 \left( \frac{1}{4} \psi_2 \frac{\partial f}{\partial \psi_0} + \frac{1}{2} \psi_1^2 \frac{\partial^2 f}{\partial \psi_0^2} \right) + \ldots \right].
\]

(3.32)
Next, we substitute Eqs. (3.31) and (3.32) into Eq. (3.29) and collect terms only to $\epsilon^2$. After a few algebraic manipulations, we have

$$\lambda \epsilon^2 \frac{\partial \psi_0}{\partial t} = -\tilde{B} f(\psi_0) - \tilde{B} \epsilon \psi_1 \frac{\partial f}{\partial \psi_0} - \epsilon^2 \tilde{B} \left( \psi_2 \frac{\partial f}{\partial \psi_0} + \frac{1}{2} \psi_1^2 \frac{\partial^2 f}{\partial \psi_0^2} - \frac{1}{\tilde{B}} \tilde{\nabla}^2 \psi_0 \right) + \ldots \quad (3.33)$$

We now compare terms on the left and right hand sides of Eq. (3.33) order by order in terms of $\epsilon$, which yield the following equations

$$\mathcal{O}(1) : \quad \tilde{B} f(\psi_0) = 0, \quad (3.34a)$$

$$\mathcal{O}(\epsilon) : \quad \tilde{B} \psi_1 \frac{\partial f}{\partial \psi_0} = 0, \quad (3.34b)$$

$$\mathcal{O}(\epsilon^2) : \quad \lambda \frac{\partial \psi_0}{\partial t} = -\tilde{B} \left( \psi_2 \frac{\partial f}{\partial \psi_0} + \frac{1}{2} \psi_1^2 \frac{\partial^2 f}{\partial \psi_0^2} - \frac{1}{\tilde{B}} \tilde{\nabla}^2 \psi_0 \right). \quad (3.34c)$$

Eq. (3.34a) gives the solution $\psi_0 = \pm 1$, whereas Eq. (3.34b) yields the solution $\psi_1 = 0$ and Eq. (3.34c) yields $\psi_2 = 0$. So, for the outer expansion, we have

$$\psi_0 = \pm 1, \quad (3.35a)$$

$$\psi_1 = 0, \quad (3.35b)$$

$$\psi_2 = 0. \quad (3.35c)$$

Now, in the inner region, we transform to a local system of (orthogonal) curvilinear coordinates co-moving with the interface, with one coordinate axis, named $r$, parallel to $\nabla \psi$, where the interface is located at $r = 0$, while the second will be conveniently expressed by the arc length $s$ along the interface. We also introduce the stretched coordinate $z = r/\epsilon$. With the new curvilinear coordinate, the gradient and Laplacian
operators, and the time derivative close to the interface are given by

\[
\nabla^2 = \frac{1}{d^2} \tilde{\nabla}^2 = \frac{1}{\epsilon^2} \frac{\partial^2}{\partial z^2} + \frac{\kappa}{\epsilon} \frac{\partial}{\partial z} + \frac{\partial^2}{\partial s^2},
\]

\[
\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial t} + \frac{\partial r}{\partial t} \frac{\partial}{\partial r} = \frac{\partial}{\partial t} + \nu \frac{\partial}{\partial r},
\]

\[
\frac{\partial}{\partial t} \rightarrow \frac{\partial}{\partial t} + \tau v \frac{\partial}{\partial z}.
\]

(3.36)

We substitute the operators in Eq. (3.36) along with the expression for \(\psi\) in Eq. (3.30) into the non-dimensional governing equation [Eq. (3.29)] and collect terms only to the second order in \(\epsilon\). After a few algebraic manipulations, we have

\[
\epsilon \left[ \lambda \tau v \frac{\partial \psi_0}{\partial z} \right] + \epsilon^2 \left[ \lambda \tau v \frac{\partial \psi_1}{\partial z} \right] + \ldots = \left[ d^2 \frac{\partial^2 \psi_0}{\partial z^2} - \tilde{B} f(\psi_0) \right] + \epsilon \left[ d^2 \frac{\partial^2 \psi_1}{\partial z^2} + \kappa d^2 \frac{\partial \psi_0}{\partial z} - \tilde{B} \psi_1 \frac{\partial f}{\partial \psi_0} \right] + \epsilon^2 \left[ d^2 \frac{\partial^2 \psi_2}{\partial z^2} + \kappa d^2 \frac{\partial \psi_1}{\partial z} + d^2 \frac{\partial^2 \psi_0}{\partial s^2} - \tilde{B} \psi_2 \frac{\partial f}{\partial \psi_0} - \frac{1}{2} \tilde{B} \psi_1^2 \frac{\partial^2 f}{\partial \psi_0^2} \right] + \ldots
\]

(3.37)

Similar to the outer expansion, we compare terms on the left and right hand sides of Eq. (3.37) order by order in terms of \(\epsilon\), which yield the following equations

\[
O(1) : \quad d^2 \frac{\partial^2 \psi_0}{\partial z^2} - \tilde{B} f(\psi_0) = d^2 \frac{\partial^2 \psi_0}{\partial z^2} - 4 \tilde{B} (\psi_0^2 - \psi_0) = 0,
\]

(3.38a)

\[
O(\epsilon) : \quad (\lambda \tau v - \kappa d^2) \frac{\partial \psi_0}{\partial z} = d^2 \frac{\partial^2 \psi_1}{\partial z^2} - \tilde{B} \psi_1 \frac{\partial f}{\partial \psi_0},
\]

(3.38b)

\[
O(\epsilon^2) : \quad \lambda \tau v \frac{\partial \psi_1}{\partial z} = \frac{\partial^2 \psi_2}{\partial z^2} + \kappa \frac{\partial \psi_1}{\partial z} + \frac{\partial^2 \psi_0}{\partial s^2} - \tilde{B} (\psi_2 \frac{\partial f}{\partial \psi_0} + \frac{1}{2} \psi_1^2 \frac{\partial^2 f}{\partial \psi_0^2}.
\]

(3.38c)

Next, we solve Eq. (3.38a), which is similar to Eq. (3.20) and therefore admits an exact solution that has the following form

\[
\psi_0 = \tanh \left( 2\sqrt{2\tilde{B}} \tilde{z} \right),
\]

(3.39)
where \( \tilde{z} = z/d \). As for Eq. (3.38b), multiplying both sides by \( \partial \psi_0/\partial z \) and integrating over the interface yield

\[
(\lambda \tau v - \kappa d^2) \int dz \left( \frac{\partial \psi_0}{\partial z} \right)^2 = d^2 \int \frac{\partial^2 \psi_1}{\partial z^2} \frac{\partial \psi_0}{\partial z} dz - \tilde{B} \int \psi_1 \frac{\partial \psi_0}{\partial z} \frac{\partial f}{\partial \psi_0} dz. \tag{3.40}
\]

The first term of the right hand side can be integrated by parts twice to give

\[
d^2 \int \frac{\partial^2 \psi_1}{\partial z^2} \frac{\partial \psi_0}{\partial z} dz = d^2 \int \psi_1 \frac{\partial}{\partial z} \frac{\partial^2 \psi_0}{\partial z^2} dz. \tag{3.41}
\]

Inserting Eq. (3.41) into Eq. (3.40) and using \( \partial f/\partial \psi_0 = (\partial z/\partial \psi_0)(\partial f/\partial z) \) yields

\[
(\lambda \tau v - \kappa d^2) \int dz \left( \frac{\partial \psi_0}{\partial z} \right)^2 = \int \left[ d^2 \psi_1 \frac{\partial^2 \psi_0}{\partial z^2} - \tilde{B} \psi_1 \frac{\partial \psi_0}{\partial z} \frac{\partial f}{\partial \psi_0} \frac{\partial}{\partial \psi_0} \right] dz \tag{3.42}
\]

\[
= \int \psi_1 \frac{\partial}{\partial z} \left( d^2 \frac{\partial^2 \psi_0}{\partial z^2} - \tilde{B} f \right) \frac{\partial}{\partial \psi_0} dz = 0, \tag{3.43}
\]

since the term in the parentheses satisfy Eq. (3.38a). Finally, the integral \( \int dz (\partial \psi_0/\partial z)^2 \) is non-zero since it is related to interfacial (grain-boundary) energy \(^{168}\); therefore, we get the following condition

\[
\lambda \tau v = \kappa d^2, \tag{3.44}
\]

which, after using \( \lambda = d^2/(\tau w^2 L) \), reduces to

\[
v = \frac{d^2}{\lambda \tau} \kappa = \frac{\tau w^2 L d^2}{\tau} \kappa = L w^2 \kappa, \tag{3.45}
\]

which indicates that the phase field framework utilizing Model A dynamics (Allen-Cahn equation) reduces to the sharp interface model for grain growth if \( w^2 L = M \gamma \). Within the phase field framework, \( w^2 \) is a factor that sets the interface energy and \( L \) is then a kinetic parameter that is proportional to interface mobility.
3.2 A Phase Field Model for the Microstructural Evolution in SOFCs

3.2.1 Theoretical Model

The theoretical model that is presented here is based on our work that was submitted for publication to the Journal of Power Sources and is currently under review [197]. In this Section, we present a phase field model to investigate Ni phase coarsening in solid oxide fuel cell (SOFC) anodes, and track the evolution of several microstructural attributes affecting electrochemical performance, such as three-phase boundary (TPB) lines, Ni phase contiguity and pore space microstructure. The model accounts for the polycrystalline nature of the Ni phase, i.e., Ni grain boundary (GB) energy, and is capable of capturing the interaction of Ni with the static YSZ backbone.

The starting point of our phase-field model is the introduction of order parameters for the phases in porous Ni/YSZ anodes. Additional structural order parameters are also introduced to represent the polycrystalline nature of the Ni phase and account for interfacial energies associated with Ni GBs. Next, a total free energy $F_{\text{tot}}$ that describes the state of anode system is constructed in terms of the order parameters and the dynamics of the system follow from the minimization of $F_{\text{tot}}$. Consistent with experimental observations [34, 38], a static, or non-evolving, order parameter $\theta(\mathbf{r})$ is assigned to the YSZ phase, reflecting its microstructural stability. In contrast, the evolution of the Ni phase is tracked with the aid of an order parameter $c(\mathbf{r},t)$ in combination with structural order parameters $\{\eta_i(\mathbf{r},t), i = 1, ..., n_\eta\}$ that describe the shape and crystallographic orientation of the Ni grains. Here, $n_\eta$ is the number of structural order parameters needed to resolve the texture of the Ni phase. The order parameters are chosen such that: (a) in the YSZ phase $(\theta, c) = (1, -1)$, (b) in the Ni phase $(\theta, c) = (0, +1)$, and (c) in the pore space $(\theta, c) = (0, -1)$. Furthermore, $\theta(\mathbf{r}) \in (0, 1)$ and $c(\mathbf{r},t) \in (-1, 1)$ define YSZ and Ni interfaces, respectively. For the
Figure 3.6: A schematic illustrating (a) the order parameters used in the phase field model and their equilibrium values in the bulk, and (b) typical equilibrium profiles of the order parameters, where they take on constant values in the bulk and vary rapidly but smoothly across interfaces. $\eta_m$ and $\eta_n$ are the structural order parameters used to track Ni grains $m$ and $n$, where $m$ and $n$ are grain labels.

As in standard Ginzburg-Landau formalism and motivated by the work of Wang [198] on solid-state sintering, the following total chemical free energy is employed for an SOFC anode system

$$F_{tot}[c, \theta, \{\eta_i\}] = \int dr \left[ f_{bulk} + \frac{w^2}{2} |\nabla c|^2 + \frac{1}{2} \sum_{i=1}^{n} k_i^2 |\nabla \eta_i|^2 + f_{wett} \right], \quad (3.46)$$

where $w$ and $k_i$ are the gradient energy coefficients employed to tune the Ni surface and grain boundary energies. The first term on the right hand side, $f_{bulk}$, is a fourth-order Landau polynomial that defines the homogeneous bulk free energy associated
with the Ni phase and multiple Ni grains. In particular, \( f_{\text{bulk}} \) is constructed such that the equilibrium values for the order parameters, i.e., \( \partial f_{\text{bulk}}/\partial c = \partial f_{\text{bulk}}/\partial \eta_i = 0 \), are \( (c = -1, \eta_i = 0, i = 1, ..., n_\eta) \) within non-Ni phases and \( (c = +1, \eta_i = +1, \eta_j \neq i = 0, i, j = 1, ..., n_\eta) \) within a Ni grain. A convenient form for \( f_{\text{bulk}} \) that satisfies these requirements is

\[
f_{\text{bulk}}(c, \{\eta_i\}) = m_H(c^2 - 1)^2 + A_H \left\{ \frac{1}{4} (c + 1)^2 + 3(1 - c) \sum_{i=1}^{n_\eta} \eta_i^2 - 2(3 - c) \sum_{i=1}^{n_\eta} \eta_i^3 + 3 \left[ \sum_{i=1}^{n_\eta} \eta_i^2 \right]^2 \right\}, \tag{3.47}
\]

where \( m_H \) and \( A_H \) are parameters we employ to tune the interfacial energies and widths. In this work, it is assumed that GB interfaces are isotropic, yielding \( k_i = k \).

The last term, \( f_{\text{wett}} \), on the right hand side of Eq. (3.46) accounts for the interaction between the Ni and YSZ phases, and the resulting wetting angle at triple junctions. In this work, \( f_{\text{wett}} \) is written as

\[
f_{\text{wett}}(c, \theta) = -\xi_1 c |\nabla \theta|^2 + \xi_2 \theta (c - c^3 / 3), \tag{3.48}
\]

where \( \xi_1 \) and \( \xi_2 \) are model parameters employed to tune the equilibrium Ni-YSZ wetting angle, experimentally observed to be \( \gtrsim 117^\circ \). \[118\]

With the proposed total chemical free energy functional in Eq. (3.46) and following the treatment of Cahn and Hilliard \[168\], the interfacial energies and widths can be evaluated analytically. In particular, we obtain the Ni surface energy \( \gamma_s \approx 4w\sqrt{2m_H/3} + k\sqrt{A_H/3} \) and interfacial width \( \delta_s \approx 2w/\sqrt{2m_H} \), while Ni GB energy \( \gamma_{GB} \approx 2k\sqrt{A_H/3} \) and its width \( \delta_{GB} \approx k/\sqrt{A_H} \). Therefore, the phase field model parameters \( w, m_H, A_H \) and \( k \) are uniquely determined from the Ni phase interfacial and GB energies and widths. Detailed derivations of interfacial (surface and GB) energies are presented in Appendix A.1.
Within the Ginzburg-Landau formalism and with the aid of variational derivatives, the governing equations for the evolution of \( c(\mathbf{r},t) \) and \( \{\eta_i(\mathbf{r},t), i = 1, \ldots, n_\eta\} \) for \((\mathbf{r},t) \in V \times [0,T] \subset \mathbb{R}^3 \times \mathbb{R}\), where \( V \) is the domain volume and \( T \) is the final time, can be stated respectively as

\[
\frac{\partial c}{\partial t} = \nabla \cdot \left[ M \nabla \left( \frac{\delta F_{\text{tot}}}{\delta c} \right) \right], \quad (3.49a)
\]

\[
\frac{\partial \eta_i}{\partial t} = -L_i \frac{\delta F_{\text{tot}}}{\delta \eta_i}, i = 1, 2, \ldots, n_\eta, \quad (3.49b)
\]

where \( M \) denotes the Ni phase mobility function and \( L_i \) is a kinetic parameter associated with Ni GB mobility, where under the isotropy assumption of GB interfaces, \( L_i = L \). At SOFC operating temperatures, Ni bulk self diffusion \( \sim 10^{-16} \text{ m}^2\text{s}^{-1} \) \cite{115}, whereas Ni surface self diffusion \( D_{Ni} \sim 10^{-11} \text{ m}^2\text{s}^{-1} \) \cite{116}. We also note that the \( Zr^{4+} \) surface diffusion coefficient in YSZ is \( \sim 10^{-18} \text{ m}^2\text{s}^{-1} \) \cite{117}, justifying the assumption that YSZ particles do not significantly evolve during Ni coarsening. Since Ni diffusivity along YSZ interfaces is not well characterized, it is assumed that the coarsening of Ni in Ni/YSZ cermet anodes is dominated by Ni surface diffusion along Ni-pore interfaces. In this work, Ni phase mobility has the general form \( M = M_{Ni}Q(c, \nabla c, \theta, \nabla \theta) \), where \( M_{Ni} \) is the Ni phase atomic mobility, and the detailed form of the dimensionless function \( Q \) is given below in Eq. (3.52).

The spatio-temporal evolution equations for \( c(\mathbf{r},t) \) and \( \eta_i(\mathbf{r},t) \) are made non-dimensional by introducing non-dimensional spatial coordinates \( \tilde{r} = r/d_o \) and time \( \tilde{t} = t/\tau \), where \( d_o \) and \( \tau \) denote the characteristic length (voxel edge length) and time scales, respectively. For convenience, we also introduce the non-dimensional quantities \( \tilde{w}^2 = m_H/(2E) \), \( \tilde{m}_H = m_Hd_o^2/(\delta_s^2E) \), \( \tilde{A}_H = A_Hd_o^2/(\delta_s^2E) \), \( \tilde{\xi}_1 = \xi_1/(E\delta_s^2) \), and \( \tilde{\xi}_2 = \xi_2d_o^2/(E\delta_s^2) \), where \( E \) is a reference energy density. Ni mobility can be written as \( M_{Ni} = D_{Ni}/(\partial^2 F_{\text{bulk}}/\partial c^2)_{ceq} = D_{Ni}/(\partial^2 f_{\text{bulk}}/\partial c^2)_{ceq} \). Therefore, the characteristic time
τ can be expressed as

$$\tau = \frac{m_H d_0^4 (\partial^2 f_{\text{bulk}}/\partial c^2)_{c=0}}{E D_{Ni} \delta_s^2} \approx \frac{16 \tilde{w}^2 d_o^4}{D_{Ni} \delta_s^2}. \quad (3.50)$$

For the systems we examine in this work, where \(d_o \sim 60\, \text{nm}, \delta_s \sim 1\, \text{nm}, D_{Ni} \sim 10^{-11} \, \text{m}^2\, \text{s}^{-1}\), the resulting characteristic time \(\tau \sim 40\, \text{s}\). As in standard phase field approaches, where a diffuse description for interfaces is utilized, microstructure evolution due to propagating fronts (i.e., Ni interfaces and grain boundaries) is captured without tracking phenomena occurring within the numerical interfaces. As for the governing equations for the non-conserved parameters, we introduce the non-dimensional \(\tilde{L} = \tau LE \delta_{GB}^2/d_o^2\) and \(\tilde{k}^2 = k^2/ (E \delta_{GB}^2)\). Similar to the treatment in Section 3.1.1.2 and more specifically, Eq. (3.45), GB mobility, \(M_{GB}\), and energy, \(\gamma_{GB}\), are related to the model parameters through

$$Lk^2 = M_{GB} \gamma_{GB} = \frac{\tilde{L} \tilde{k}^2 d_o^2}{\tau} \approx \frac{\tilde{L} \tilde{k}^2 D_{Ni} \delta_s^2}{16 \tilde{w}^2 d_o^2}, \quad (3.51)$$

where Eq. (3.50) has been employed in the last step.

The resulting non-dimensional spatio-temporal evolution equations for \(c(r, t)\) and \(\eta_i(r, t)\) have the same form as the original ones. For the remainder of this paper, we drop the tildes on all parameters for notational convenience. The reader is referred to Appendix A.2 for the derivation of the non-dimensional form of the governing equations. Finally, the form that is used for the Ni phase mobility

$$M = M_{Ni} \left[ (1.0 - \tanh(|\nabla \theta|^2/h_1)) \tanh (|\nabla \hat{c}|^2/h_2) + \right. \quad (3.52)$$

$$\left. M^* \tanh (|\nabla \theta|^2/h_1) \right],$$

where \(\hat{c} = \tanh(c/h_3)\). The model parameters \(h_1, h_2\) and \(h_3\) are employed to tune the range of \(c\) and \(\theta\) values that contribute to the mobility function, while \(M^*\) defines
a mobility contribution for Ni diffusing along Ni-YSZ interfaces. In this work, it is assumed that diffusion along Ni-pore interfaces is the dominant mass transport mechanism.

### 3.2.2 Numerical Implementation

Various numerical schemes exist for the solution of phase field equations, such as finite differencing [199], spectral [200], finite volume [161] or finite element methods [201]. The simulation of Ni coarsening in SOFC anodes that is reported in this thesis adopts a finite-difference approximation for both temporal and spatial derivatives. Before we present the numerical scheme and the computer implementation, let us first point out the following about the resulting phase field equations, Eq. (3.49): i) The governing equation for $c(\mathbf{r}, t)$ is a fourth order nonlinear diffusive partial differential equation. The numerical stiffness associated with this equation arises from a disparity in the length scale between the interfacial width and domain size. ii) The governing equations for the structural order parameters $\{\eta_i(\mathbf{r}, t), i = 1, ..., n_\eta\}$ are second order diffusive partial differential equations. We note here that a governing equation is to be solved for each structural order parameter used in the simulation. In the coarsening work presented in this thesis, we use $n_\eta = 10$ structural order parameters. iii) Therefore, the spatio-temporal evolution of the Ni phase in SOFC anodes involves the simultaneous numerical solution of 11 partial differential equations [including the one for $c(\mathbf{r}, t)$].

Based on the aforementioned observations, we require that the proposed numerical scheme be simple, fast and robust in order to handle the extensive calculations needed to track the evolution of the Ni phase in SOFC anodes. Therefore, we adopt an explicit Euler finite different scheme, where a forward Euler representation is used for the time derivative and a central difference stencil is used for the spatial derivatives. To overcome stability restrictions on the time step that are associated with explicit
schemes, we utilize distributed computing, where Message Passing Interface (MPI) libraries are used to divide the simulation box into smaller subdomains that are then assigned to different processors to perform the calculations. In general, phase field equations are local in nature, i.e., the solution at one point is dependent on the immediate environment only. Therefore, parallelization using MPI suits the phase field equations. First, the governing equations that we seek to solve for \( c(\mathbf{r}, t) \) and \( \{\eta_m(\mathbf{r}, t), m = 1, ..., n_\eta\} \) for \( (\mathbf{r}, t) \in V \times [0, T] \subset \mathbb{R}^3 \times \mathbb{R} \), where \( V \) is the domain volume and \( T \) is the final time, can be stated respectively as

\[
\frac{\partial c}{\partial t} = \nabla \cdot \left( M \nabla \mu_c \right) = \nabla \cdot \left( M \nabla \left( \frac{\delta F_{\text{tot}}}{\delta c} \right) \right),
\]

and

\[
\frac{\partial \eta_m}{\partial t} = -L_m \mu_{\eta_m} = -L_m \frac{\delta F_{\text{tot}}}{\delta \eta_m}, m = 1, 2, ..., n_\eta.
\]

In the scheme presented in this Section, the order parameters are defined on a mesh, or grid, where \( i \in [1, N_x] \), \( j \in [1, N_y] \) and \( k \in [1, N_z] \) are the grid points, and \( N_x, N_y \) and \( N_z \) are the total number of grid points along the x, y and z, respectively, with the corresponding grid point spacing being \( \Delta x, \Delta y \) and \( \Delta z \). Also, we introduce a time step, \( \Delta t \), where time is given by

\[
t = n \Delta t,
\]

where \( n = 0, ..., N_t \) is the time step number, or time iteration, and \( N_t \) is the total number of time steps. Therefore, the order parameters are defined on discrete points within the domain and at discrete points in time, i.e., \( c_{i,j,k}^n \) is the value of \( c \) at a grid point \( (x, y, z) = (i, j, k) \) and time step \( n \). Next, explicit forward Euler is used for the time derivative as

\[
\frac{\partial c}{\partial t} \approx \frac{c_{i,j,k}^{n+1} - c_{i,j,k}^n}{\Delta t},
\]
and a similar expression for the structural order parameters \( \{ \eta_m(\mathbf{r}, t), m = 1, ..., n_\eta \} \).

In this work, we employ an explicit scheme, which indicates that the right hand side of Eq. (3.53) is evaluated at the current time step, or time iteration \( n \). We note that both chemical potentials for \( c \) and \( \eta_i \) involve Laplacian operators, refer to the expression for the total energy functional in Eq. (3.46). We adopt a central difference scheme, which is second order accurate, for the spatial derivatives. Figure 3.7 is a schematic illustrating the numerical stencil that is used to approximate the spatial derivatives. So, for the Laplacian operator for \( c \) we have

\[
\nabla^2 c^n_{i,j,k} \approx \frac{c^n_{i+1,j,k} - 2c^n_{i,j,k} + c^n_{i-1,j,k}}{(\Delta x)^2} + \frac{c^n_{i,j+1,k} - 2c^n_{i,j,k} + c^n_{i,j-1,k}}{(\Delta y)^2} + \frac{c^n_{i,j,k+1} - 2c^n_{i,j,k} + c^n_{i,j,k-1}}{(\Delta z)^2}, \tag{3.56}
\]

Figure 3.7: The numerical stencil that is used for the spatial derivatives of the \( c \) field. For example, the numerical representation of \( \nabla^2 c \) at a grid point \((i, j, k)\) would depend on its left and right neighbors along the \( x, y \) and \( z \) directions. In this case, a seven-point stencil is used for the Laplacian operator in three dimensions.
and for the structural order parameter $\eta$, we have

$$\nabla^2 \eta_{i,j,k}^n \approx \frac{\eta_{i+1,j,k}^n - 2\eta_{i,j,k}^n + \eta_{i-1,j,k}^n}{(\Delta x)^2} + \frac{\eta_{i,j+1,k}^n - 2\eta_{i,j,k}^n + \eta_{i,j-1,k}^n}{(\Delta y)^2} + \frac{\eta_{i,j,k+1}^n - 2\eta_{i,j,k}^n + \eta_{i,j,k-1}^n}{(\Delta z)^2}. \tag{3.57}$$

Next, Ni phase mobility $M$ is a function of the order parameters; therefore, it cannot be pulled out of the divergence operator in Eq. (3.53). We adopt the scheme detailed in [202], where we center everything appropriately and we have the following numerical scheme for the governing equation of the $c(r,t)$ phase field

$$\frac{c_{i,j,k}^{n+1} - c_{i,j,k}^n}{\Delta t} = M_{i+1/2,j,k}^n \left( \mu_{i+1,j,k}^n - \mu_{i,j,k}^n \right) - M_{i-1/2,j,k}^n \left( \mu_{i-1,j,k}^n - \mu_{i,j,k}^n \right) + \frac{M_{i,j+1/2,k}^n \left( \mu_{i,j+1,k}^n - \mu_{i,j,k}^n \right) - M_{i,j-1/2,k}^n \left( \mu_{i,j-1,k}^n - \mu_{i,j,k}^n \right)}{(\Delta y)^2} + \frac{M_{i,j,k+1/2}^n \left( \mu_{i,j,k+1}^n - \mu_{i,j,k}^n \right) - M_{i,j,k-1/2}^n \left( \mu_{i,j,k-1}^n - \mu_{i,j,k}^n \right)}{(\Delta z)^2}, \tag{3.58}$$

where $\mu = \mu_c = \delta F_{tot}/\delta c$, while $M_{i+1/2,j,k} = (1/2) \left[ M(c_{i+1,j,k}^n) + M(c_{i,j,k}^n) \right]$, $M_{i-1/2,j,k} = (1/2) \left[ M(c_{i-1,j,k}^n) + M(c_{i,j,k}^n) \right]$ and similar expressions in the y and z directions. Given the value of $c$ everywhere in the domain at time step $n$, the update formula in Eq. (3.58) can be used to obtain the phase field $c$ at time step $n+1$. As for the structural order parameters $\{\eta_m(r,t), m = 1, \ldots, n_\eta\}$, we have the following for a phase field $\eta$

$$\frac{\eta_{i,j,k}^{n+1} - \eta_{i,j,k}^n}{\Delta t} = -L\mu_{i,j,k}^n, \tag{3.59}$$

where $\mu = \mu_\eta = \delta F_{tot}/\delta \eta$. Again, given the value of $\eta$ everywhere in the domain at time step $n$, the update formula in Eq. (3.59) can be used to obtain the phase field $\eta$ at time step $n+1$. 

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It is well established that explicit Euler schemes for diffusive differential equations suffer from strict stability requirements for the time step $\Delta t$. For the numerical scheme of the $c(r,t)$ phase field and assuming a constant mobility $M$ and letting $\Delta y = \Delta z = \Delta x$, von Neumann eigenmodes analysis yields the following stability criterion:

$$\frac{8M\Delta t}{(\Delta x)^4} \lesssim 1.$$  \hfill (3.60)

To overcome small time steps that are associated with explicit schemes, distributed computing, where Message Passing Interface (MPI) libraries, are utilized to implement the numerical scheme, Eqs. (3.58) and (3.59), in parallel. One characteristic property of phase field equations is that they are local in nature, which indicates that the solution at a point in the domain is dependent on its immediate neighbors. Therefore, numerical implementations utilizing MPI are well suited for this class of problems. Within this implementation, the simulation domain is divided into subdomains, where each subdomain is passed to a computing processor. Then, each processor performs the numerical computations on the section of the simulation domain (subdomain) that is passed to it. For a given processor, if additional data are needed for grid points outside its assigned domain, they are passed to it from the processor operating on the subdomain that is neighboring to the original one. By utilizing the MPI parallel implementation, numerical simulations can be carried out for longer times thereby overcoming small time steps associated with explicit schemes. The numerical computations were conducted on the Princeton University supercomputing center using Della clusters. For the Ni coarsening analysis that is presented in this thesis, 24 to 36 processors were typically utilized for the computations.
Finally, periodic boundary conditions in all directions are assumed for the order parameters. For example, for the $c$ phase field along the $x$ direction we have

$$c_{N_x+1,j,k} = c_{1,j,k},$$

$$c_{0,j,k} = c_{N_x,j,k},$$

and similar expressions apply along the $y$ and $z$ directions and for the structural order parameters $\eta_i$. As for the initial conditions, synthesized “virtual” anode microstructures are employed, where the $c(r,t)$ and $\{\eta_m(r,t), m = 1, ..., n_\eta\}$ phase fields are initially assigned, i.e., they are known at $t = 0$.

### 3.3 A Continuum Model for the Redox Instability and Mechanical Damage in SOFC Anodes

#### 3.3.1 Theoretical Model

In this Section, we present a continuum model to investigate the development of mechanical stresses and subsequent damage to the YSZ phase due to Ni phase reduction-oxidation (redox) cycles. The theoretical and computational frameworks presented in this Section are based on our work [203, 204].

The reaction $\text{Ni} + 1/2\text{O}_2 \rightarrow \text{NiO}$ is a complex kinetic process, the details of which are currently not well-understood. From a mechanistic perspective, however, the most critical feature of this reaction is the large bulk volume changes associated with it. More specifically, the ratio of NiO to Ni molar volume is $\sim 1.66$ [39], which implies that for one mole of Ni, the volumetric strain $\epsilon_v$ due to complete oxidation is

$$\epsilon_v = \epsilon_{kk} = \frac{\Delta V}{V_o} = \frac{V_{\text{NiO}} - V_{\text{Ni}}}{V_{\text{Ni}}} = 1.66 - 1.0 = 0.66,$$

$$3.63$$
where the repeated indices imply summation. Figure 3.8 is a schematic that illustrates the expansion of a Ni particle (Ni swelling) due to re-oxidation, and the development of mechanical stresses in the YSZ. Localization of deformation occurs because the local porosity in SOFC anodes is incapable of accommodating the Ni to NiO transformation strain. In the theoretical treatment presented here, the following assumptions are made: i) All Ni particles can be taken to undergo the transformation to NiO at the same rate. Thus, at any given instant in time during the re-oxidation process, the degree of Ni oxidation $\Phi_{NiO}$ is the same for all Ni particles. This implies that one can effectively substitute the degree of Ni oxidation for physical time. ii) To connect the degree of Ni oxidation to the effective expansion of the Ni particles, we will assume that their volumetric expansion is uniformly distributed within each particle and directly proportional to the degree of oxidation, such that complete transformation to NiO ($\Phi_{NiO} = 1$) corresponds to a volumetric strain $\epsilon_v \approx 0.66$.

Given the above considerations, the starting point of our theoretical treatment is the introduction of a deformation energy that accounts for the large bulk expansion strains due to redox reactions and the evolution of interfacial stresses and the sub-
sequent mechanical damage in the YSZ phase. The deformation energy is written in terms of the spatial derivatives of the displacement field \( \mathbf{u} = (u_x, u_y, u_z) \). Therefore, we start by introducing the total strain tensor that admits an additive decomposition as

\[
\varepsilon_{ij} = \varepsilon^e_{ij} + \varepsilon^*_{ij},
\]

(3.64)

where the infinitesimal definition for strain is adopted here, such that \( \varepsilon_{ij} \equiv (u_{ij} + u_{ji})/2 \) and \( u_{ij} \equiv \partial u_i / \partial x_j \). \( \varepsilon^e_{ij} \) is the elastic component of the strain, whereas \( \varepsilon^*_{ij} \) is a transformation (eigen) strain tensor that is introduced to account for Ni bulk volume changes that occur due to redox. Frameworks incorporating eigen strains have been used to model nonelastic strains, such as thermal expansion, phase transformations and misfit strains [205]. In this work, the eigen strain tensor is hydrostatic, or only diagonal, and is written as

\[
\varepsilon^*_{ij} = \frac{\alpha(r)}{3K_{\text{NiO}}} \delta_{ij},
\]

(3.65)

where \( K_{\text{NiO}} \) is the bulk modulus for NiO and \( \delta_{ij} \) is the standard kronecker delta operator. \( \alpha(r) \) is a spatially dependent parameter that controls Ni bulk expansion strains due to redox. Here, \( \alpha = \alpha_o \) within the Ni/NiO domains and zero elsewhere.

We also define the redox strain, or the total volumetric transformation strain as the trace of the eigen tensor, i.e., \( \varepsilon^* = \varepsilon^*_{ii} \), and is written as

\[
\varepsilon^* = \frac{\alpha(r)}{K_{\text{NiO}}}.
\]

(3.66)

With this mechanistic description of the total strains that develop in Ni/YSZ porous anodes due to redox cycles, the total deformation energy \( F_{\text{def}} \) for a general state of deformation can be decomposed into an elastic and redox components, such
that

\[ F_{\text{def}} = \int d\mathbf{r} \ f_{\text{tot}} = \int d\mathbf{r} \ [f_{\text{elastic}} + f_{\text{redox}}]. \] (3.67)

As in standard elasticity formalism and under the isotropy assumption of the constituent phases, the elastic component is decomposed into hydrostatic (spherical) and deviatoric (pure shear) parts [206]. Therefore, in terms of the spatial derivatives of the displacement field \( \mathbf{u} = (u_x, u_y, u_z) \) the total deformation energy \( F_{\text{def}} \) is written as

\[ F_{\text{def}} = \int d\mathbf{r} \left[ \frac{1}{2} K(r) \Psi(r) \epsilon_{nn}^2 + \mu(r) \Psi(r) \left( \epsilon_{ij} - \frac{1}{3} \delta_{ij} \epsilon_{nn} \right)^2 - \alpha(r) \epsilon_{nn} \right], \] (3.68)

where, in Einstein notation, repeated indices imply summation. \( K(r) \) and \( \mu(r) \) denote the phase-dependent bulk and shear moduli, respectively. The first two terms on the right hand side of Eq. (3.68) denote the spherical and deviatoric parts of the elastic energy and the last term is the redox component of the energy, which accounts for the volumetric expansion of Ni particles due to NiO formation. To account for the damage accumulation in the YSZ phase, we introduce the damage field \( \Psi(r, \alpha) \), such that for a given \( \alpha \), or degree of Ni oxidation

\[ \Psi(r, \alpha) = \begin{cases} 
0, & \text{YSZ damaged regions,} \\
1, & \text{elsewhere.}
\end{cases} \] (3.69)

Within this framework, the binary description for the YSZ damage field indicates that the relaxation of \( \Psi \) is instantaneous. Frameworks involving damage fields with various relaxation dynamics have been used to model softening in materials systems [207]. We also note that the parameter \( \alpha \) is directly linked to the degree of Ni oxidation \( \Phi_{\text{NiO}} \) by realizing that for a complete transformation of a Ni particle to NiO, the redox strain \( \epsilon^* \sim 0.66 \) and \( \alpha = \alpha_0 = 0.66 K \Phi_{\text{NiO}} \) within the Ni/NiO domains and zero elsewhere.
Now, at a given state of redox strain that is controlled by \( \alpha \), mechanical equilibrium in the absence of body forces (balance of internal mechanical stresses) is written as \[195, 206\]

\[
\frac{\delta F_{\text{def}}}{\delta u_i} = -\frac{\partial}{\partial x_j} \left( \frac{\partial f_{\text{tot}}}{\partial u_{ij}} \right) = -\frac{\partial}{\partial x_j} \left( \frac{\partial f_{\text{tot}}}{\partial \epsilon_{ij}} \right) = -\frac{\partial \sigma_{ij}}{\partial x_j} = 0. \tag{3.70}
\]

To achieve equilibrium at a given redox state, or \( \alpha \) value, the displacement field has to be equilibrated, which can be achieved computationally in many ways. In this work, we utilize a dynamic relaxation scheme in which a damped wave equation is solved, where the driving force (source term) is the variation of the deformation energy with respect to the displacement field. Therefore, the effective dynamics for the displacement field can be written as

\[
\frac{\partial^2 u_i}{\partial t^2} + \left( \eta^* - \xi^* \nabla^2 \right) \frac{\partial u_i}{\partial t} = -\Gamma^* \frac{\delta F_{\text{def}}}{\delta u_i} = \Gamma^* \frac{\partial \sigma_{ij}}{\partial x_j}, \quad i = x, y, z, \tag{3.71}
\]

where the first term on the left hand side is the inertial term. We introduce the damping operator \( (\eta^* - \xi^* \nabla^2) \), where \( \eta^* \) is a parameter that provides linear damping to all modes, whereas \( \xi^* \) heavily damps modes with small wave lengths. In Fourier space, \( -\xi^* \nabla^2 \partial u_i/\partial t \rightarrow -\xi^* (ik)^2 \partial \hat{u}/\partial t = \xi^* k^2 \partial \hat{u}/\partial t \), so modes with the largest wave numbers \( (k \text{ values}) \), i.e., smallest wave lengths \( \lambda \) since \( \lambda = 2\pi/k \), are damped the heaviest and \( \xi^* \) controls this term. The right hand side is the forcing term and \( \Gamma^* \) effectively controls the effective elastic wave speed. Note that the steady-state solutions of Eq. \((3.71)\) by construction satisfy the mechanical equilibrium equations \( \partial \sigma_{ij}/\partial x_j = 0 \). Furthermore, the parameters \( \eta^*, \xi^* \) and \( \Gamma^* \) are chosen such that the simulated SOFC composite anode is maintained in the quasi-static regime. Thus, Eq. \((3.71)\) should be viewed as a “fictitious” time integration scheme, where the right hand side constitutes the driving force, employed to find the steady-state solution (equilibration of the displacement field) at a given \( \alpha \).
Importantly, our theoretical framework also incorporates a micro-cracking and mechanical damage criterion. More specifically, the YSZ is treated as a brittle ceramic \cite{129}; therefore the maximum principal (normal) stress failure criterion is a reasonable method of choice for the fracture of the YSZ phase \cite{208}. In our work, this criterion is implemented as follows. At a given instantaneous transformation strain $\alpha_0$ and a given distribution of Ni particles, the displacement field is equilibrated using Eq. (3.71). According to the thermodynamic energy functional in Eq. (3.68), the stress tensor is the thermodynamic conjugate to strain and, with the aid of variational derivatives, evaluates to

$$\sigma_{ij} = \frac{\delta F_{\text{def}}}{\delta \epsilon_{ij}} = \left(K(r)\epsilon_{kk} + \alpha(r)\right)\delta_{ij} + 2\mu(r) \left(\epsilon_{ij} - \frac{1}{3}\delta_{ij}\epsilon_{kk}\right). \quad (3.72)$$

Next, principal, or normal, stresses $(\lambda_1, \lambda_2, \lambda_3)$, which are the eigen values of the stress tensor are computed by finding the roots of the characteristic polynomial of the stress tensor that has the form \cite{206}

$$\lambda^3 - I_1\lambda^2 + I_2\lambda - I_3 = 0, \quad (3.73)$$

where $I_1, I_2$ and $I_3$ are the invariants of the stress tensor and are written as

$$I_1 = \sigma_{ii},$$

$$I_2 = \frac{1}{2}(\sigma_{ii}\sigma_{jj} - \sigma_{ij}\sigma_{ji}),$$

$$I_3 = \det \sigma_{ij}, \quad (3.74)$$

where “det” indicates the determinant. When the maximum principal stress $\sigma_{\text{max}} = \max\{\lambda_1, \lambda_2, \lambda_3\}$ in a given volume element within the YSZ phase exceeds its ultimate strength $F_{\text{tu}}$, the damage field $\Psi$ is set to zero locally, and Eq. (3.71) is again employed to relax the displacement field. If no additional fracture events occur, $\alpha_0$ is incre-
Figure 3.9: A schematic showing an anode system with (a) an epitaxial condition for
the Ni/YSZ interface, where displacements normal, $\vec{u}_\perp$, and parallel, $\vec{u}_\parallel$, to Ni/YSZ
interfaces are continuous, and (b) a slip condition where a thin region is defined
at Ni/YSZ interfaces whose shear modulus $\mu \to 0$. Displacements normal, $\vec{u}_\perp$, to
Ni/YSZ interfaces are continuous, whereas parallel components, $\vec{u}_\parallel$, develop a discon-
tinuity.

Finally, motivated by both the atomistic Ni oxidation mechanism proposed by
Jeangros et al. [125] indicating the presence of only partially coherent NiO/YSZ in-
terfaces and the lack of detailed experimental characterization of said interfaces, two
extreme cases of interfaces will be considered to assess the role of interface coherency
on redox stress generation. The first is an epitaxial NiO/YSZ interface, where co-
herency is always maintained during the transformation of Ni to NiO via a continuity
of the displacement field across the Ni/YSZ interface. Within our formalism, this
epitaxial condition for a NiO/YSZ interface, or simply an epitaxial condition, is nat-
urally implemented when both bulk and shear moduli at NiO/YSZ interfaces are
non-zero and finite, refer to Fig. 3.9(a) for a schematic. In this case, both normal
and shear tractions at the NiO/YSZ interface are in general non-zero and continuous,
implying that the displacements (both normal and parallel to the interface) are also
continuous.

The second type of NiO/YSZ interface we consider is one where only the normal
traction is allowed to be non-zero along the NiO/YSZ interface, while the shear trac-
tion vanishes identically along said interface. We refer to this interface condition as a
slip condition, since the vanishing of the shear tractions on either side of the interface
implies that the displacement field parallel to the interface in general develops a jump
discontinuity. Formally, such a slip condition for the interface can be conveniently
incorporated by introducing a narrow boundary region along NiO/YSZ interfaces
and letting the shear modulus $\mu \to 0$ within these regions, refer to Fig. 3.9(b) for a
schematic. In physical terms, the slip condition facilitates the relaxation of expansion
strains parallel to NiO/YSZ interfaces, while the expansion strains perpendicular to
such interfaces will impart stresses within the YSZ regions. We expect real physical
systems to fall somewhere in between the two extreme cases discussed above.

3.3.2 Numerical Implementation

In this Section, we discuss the numerical scheme that is used to solve the dynamical
equations for the displacement field $\mathbf{u} = (u_x, u_y, u_z)$. A dynamic relaxation scheme
is utilized to equilibrate the displacement field at a given applied redox, or transfor-
mation, strain. We start by the mathematical description of the problem. Given an
applied redox strain that is dictated by the parameter $\alpha$, we seek a compatible, or
equilibrium, displacement field, which follow from

$$
\frac{\partial^2 u_i}{\partial t^2} + (\eta^* - \xi^* \nabla^2) \frac{\partial u_i}{\partial t} = -\Gamma^* \frac{\delta F_{def}}{\delta u_i} = \Gamma^* \frac{\partial \sigma_{ij}}{\partial x_j}, \quad i = x, y, z,
$$

(3.75)
where $\mathcal{F}_{def}$ is the total deformation energy given in Eq. (3.68). The above set of equations, Eq. (3.75), are classified as second order, constant coefficient hyperbolic partial differential equations. Such equations appear in structural dynamics and wave phenomena in solids [209]. In this work, we are interested in the quasi-static solution, where $\partial \sigma_{ij} / \partial x_j = 0$. To achieve this equilibrium state, the first and second terms on the left hand side, which represent inertial and damping forces, are introduced and the equations are solved dynamically. Therefore, these equations can be viewed as a numerical marching technique that is used to arrive at the equilibrium state.

We start by defining the displacement field on a mesh, or grid, where $i \in [1, N_x]$, $j \in [1, N_y]$ and $k \in [1, N_z]$ are the grid points, and $N_x, N_y$ and $N_z$ are the total number of grid points along the x, y and z, respectively, with the corresponding grid point spacing being $\Delta x, \Delta y$ and $\Delta z$. Also, we introduce a time step, $\Delta t$, where time is given by

$$t = n \Delta t,$$ (3.76)

where $n = 0, ..., N_t$ is the time step number, or time iteration, and $N_t$ is the total number of time steps. Therefore, displacements are defined on discrete points within the domain and at discrete points in time, i.e., $u^n_{i,j,k}$ is the value of $u$ at a grid point $(x, y, z) = (i, j, k)$ and time step $n$. In this work, we develop an explicit scheme, where the right hand side of Eq. (3.75) is evaluated at the current known time step, or time iteration $n$. The governing equations involve first and second order derivatives in time, which are approximated for a displacement component $u = [u_x, u_y, u_z]$ as

$$\frac{\partial u}{\partial t} \bigg|_{n,i,j,k} \approx \frac{u^n_{i,j,k} - u^{n-1}_{i,j,k}}{\Delta t},$$ (3.77a)

$$\frac{\partial^2 u}{\partial t^2} \bigg|_{n,i,j,k} \approx \frac{u^{n+1}_{i,j,k} - 2u^n_{i,j,k} + u^{n-1}_{i,j,k}}{(\Delta t)^2},$$ (3.77b)
where a first order accurate backward Euler is used for $\partial u / \partial t$ and second order central differencing is used for $\partial^2 u / \partial t^2$. As for the spatial derivatives, first order derivatives and the Laplacian operator are approximated as

$$\frac{\partial u}{\partial x} \bigg|_{i,j,k} \approx \frac{u_{i+1,j,k}^n - u_{i-1,j,k}^n}{2\Delta x}, \quad (3.78a)$$

$$\nabla^2 u \bigg|_{i,j,k} \approx \frac{u_{i+1,j,k}^n - 2u_{i,j,k}^n + u_{i-1,j,k}^n}{(\Delta x)^2} + \frac{u_{i,j+1,k}^n - 2u_{i,j,k}^n + u_{i,j-1,k}^n}{(\Delta y)^2} + \frac{u_{i,j,k+1}^n - 2u_{i,j,k}^n + u_{i,j,k-1}^n}{(\Delta z)^2}, \quad (3.78b)$$

where first order derivatives along the y and z directions are computed similar to Eq. (3.78a). If a displacement component $u$ is defined on the entire domain at time step $n$, the numerical update formula at grid $(i, j, k)$ becomes

$$u_{i,j,k}^{n+1} - 2u_{i,j,k}^n + u_{i,j,k}^{n-1} \frac{(\Delta t)^2}{(\Delta t)^2} + (\eta^* - \xi^* \nabla^2) \frac{u_{i,j,k}^n - u_{i,j,k}^{n-1}}{\Delta t} = -\Gamma^* \frac{\delta F_{\text{def}}}{\delta u} \bigg|_{i,j,k}^n \quad (3.79)$$

where the Laplacian operator is calculated according to Eq. (3.78b). Finally, if we let $\Delta x = \Delta y = \Delta z$ for the sake of simplicity, the solution at grid $(i, j, k)$ at time step $n + 1$ can be computed according to

$$u_{i,j,k}^{n+1} = 2u_{i,j,k}^n - u_{i,j,k}^{n-1} - \eta^* \Delta t \left( u_{i,j,k}^n - u_{i,j,k}^{n-1} \right) + \frac{\xi^* \Delta t}{(\Delta x)^2} \left( u_{i+1,j,k}^n + u_{i,j+1,k}^n + u_{i,j,k+1}^n - 6u_{i,j,k}^n + u_{i-1,j,k}^n + u_{i,j-1,k}^n + u_{i,j,k-1}^n \right) - \Gamma^* \frac{\delta F_{\text{def}}}{\delta u} \bigg|_{i,j,k}^n \quad (3.80)$$

One final note regarding boundary conditions. In the redox analysis of SOFC anodes that is presented in this thesis, fixed (i.e., “clamped”) displacement conditions
are applied at domain boundaries. These boundary conditions were applied directly after each time update by assigning \( \{u(\mathbf{r}) = 0 \mid \mathbf{r} \in S \subset \Omega \} \), where \( S \) and \( \Omega \) define the domain boundaries and domain volume, respectively. As for initial conditions, the system is assumed to be at rest initially, where \( \{u(\mathbf{r}, t=0) = 0, (\partial u(\mathbf{r}, t)/\partial t)_{t=0} = 0 \mid \mathbf{r} \in \Omega \} \).

### 3.4 Continuum Modeling of BMG Systems

#### 3.4.1 Theoretical Model

In this Section, we present a diffuse-interface mesoscale model for the highly localized deformation mechanisms and shear banding in BMGs. The model phenomenologically accounts for the structural heterogeneity of monolithic BMGs and BMG composites, and captures the fundamental aspects of plastic deformation in such systems. In monolithic BMGs, the model is capable of examining the role of internal microstructure, characterized by rigid/soft SRO, on the deformation behavior, while for BMG composites, the model is tuned to examine the role of ductile particle size, morphology and area fraction on the overall ductility.

The theory may be developed as follows. As in conventional shear transformation zone (STZ) approaches, we assume that every volume element in the BMG is susceptible to a localized “slip” event in a direction dictated by the (unit) vector \( \hat{n}(\mathbf{r}) \) and the plane, where atomic re-arrangements take place, is defined via the normal vector \( \hat{m}(\mathbf{r}) \). Figure 3.10 is a schematic of a BMG volume element showing the unit vectors \( \hat{n} \) and \( \hat{m} \). Within this framework, spatial variations in \( \hat{n} \) reflect the structural heterogeneity in the disordered material.

In this research effort, we focus on two-dimensional (2D) systems under simple shear loading, where extension to three dimensions is straightforward. Similar to the continuum framework that is developed in Section 3.3 for the mechanical deformation
Figure 3.10: A schematic illustrating atomic re-arrangements during a plastic event in a BMG material. The unit vector $\vec{n}$ points in the preferential direction for such re-arrangement, while $\vec{m}$ is a unit vector normal to the plane where the re-arrangement takes place.

In SOFCs due to redox cycles, the starting point is the definition of the infinitesimal strain tensor $\epsilon_{ij}$ in terms of the displacement vector $\mathbf{u} = (u_x, u_y, u_z)$ as

$$\epsilon_{ij} = \frac{1}{2} (u_{ij} + u_{ji}),$$  \hspace{1cm} (3.81)

where $u_{ij} = \partial u_i / \partial x_j$. Additionally, we define the following strain measures in 2D [210]

$$e_1 = u_{xx} + u_{yy},$$
$$e_2 = u_{xx} - u_{yy},$$
$$e_3 = u_{xy} + u_{yx},$$ \hspace{1cm} (3.82)

where $e_1$, $e_2$ and $e_3$ represent dilation, tetragonal and shear strains respectively [210].

Next, a volume element, whose preferential direction for atomic re-arrangements (plastic event) is given by the unit vector $\hat{\mathbf{n}}$, will define a “primed” frame that makes an angle $\theta$ with respect the reference frame, refer to Fig. 3.11(a) for a schematic. The
strain tensor in the primed reference can be expressed in terms of the reference frame via \( \epsilon'_{ij} = \Lambda_{ik} \epsilon_{jm} \Lambda_{km} \). (b) The energy landscape for a BMG material based on Eq. (3.88). \( \Delta \) sets the shear strain needed for a transition to a slipped state and it also controls the energy barrier needed for such a transition.

\[
\epsilon'_{ij} = \Lambda_{ik} \epsilon_{jm} \Lambda_{km},
\]

where \( \Lambda_{ij} \) is a \( 2 \times 2 \) orthogonal matrix and is written in terms of the angle \( \theta \) as

\[
[\Lambda_{ij}] = \begin{bmatrix}
\cos \theta & \sin \theta \\
-\sin \theta & \cos \theta 
\end{bmatrix}.
\]

The dilation \( \epsilon'_1 \), tetragonal \( \epsilon'_2 \), and shear \( \epsilon'_3 \) strain measures in the primed coordinate
are written as follow

\begin{align}
  e'_1 &= e_1, \\
  e'_2 &= e_2 \cos(2\theta) + e_3 \sin(2\theta), \\
  e'_3 &= e_3 \cos(2\theta) - e_2 \sin(2\theta),
\end{align}  \tag{3.85}

where as expected, the dilation strain is invariant under rotations \[206\]. Assuming that a BMG element has a preferential direction for atomic re-arrangement “slip” that makes an angle \( \theta \) with the global reference frame [cf. Fig. 3.11(a)] and motivated by the treatment of crystal plasticity by Onuki [212], we introduce a local nonlinear deformation energy density, which is multi-valued in the shear strain along \( \hat{n} = [\cos \theta(r), \sin \theta(r)] \) (and thus allows for slip events [210]), in terms of the spatial derivatives of the displacement field \( u(r,t) \)

\[
  \mathcal{E}(r) = \frac{K(r)}{2} e'^2_1 + \frac{\mu(r)}{2} \left[ e'^2_2 + \frac{\Delta^2(r)}{2\pi^2} \left( 1 - \cos \left( \frac{2\pi e'^3_3}{\Delta(r)} \right) \right) \right], \tag{3.86}
\]

where \( K(r) \) and \( \mu(r) \) denote the elastic moduli, which generally vary within the microstructure and are deformation history-dependent [213, 214]. We note that the expression in Eq. (3.86) approximates the standard quadratic elastic energy density in the small strain limit [206].

In this work, we examine BMG systems under simple shear, where active STZs are oriented such that \( \theta = 0 \) or \( \pi/2 \), and \( e'_1 = e_1, e'_2 = e_2 \) and \( e'_3 = e_3 \). Based on these assumptions, the total deformation energy of a BMG system is comprised of two components as

\[
  \mathcal{F}_{BMG} = \int \mathbf{dr} f_{tot} = \int \mathbf{dr} \left[ \mathcal{E}(r) \right]_{\theta=0} + f_{int}, \tag{3.87}
\]
where the first term on the right hand side is the elastic energy density given in Eq. (3.86) evaluated at \( \theta = 0 \). As in standard phase field methods, an interfacial energy term \( f_{\text{int}} \) is introduced that penalizes the formation of interfaces. The total deformation energy of a BMG system is then given by

\[
\mathcal{F}_{\text{BMG}} = \int dr \left[ \frac{K(r)}{2} e_1^2 + \frac{\mu(r)}{2} \left[ e_2^2 + \frac{\Delta^2(r)}{2\pi^2} \left( 1 - \cos \left( \frac{2\pi}{\Delta(r)} e_3 \right) \right) \right] \right] + \frac{W^2}{2} \int dr \left[ (\nabla u_{xx})^2 + (\nabla u_{yy})^2 + 4(\nabla \epsilon_{xy})^2 \right],
\]

(3.88)

where, according to conventional phase field methods, the last integral in Eq. (3.88) contains higher order gradients in the displacement field, and is invoked to regularize strain gradients on scales \( \lesssim W/\sqrt{\mu} \), where \( W \) represents an effective interfacial energy. The deformation energy functional in Eq. (3.88) incorporates a state variable \( \Delta(r) \) that effectively accounts for the structural heterogeneity in glass. \( \Delta(r) \) can be interpreted in two equivalent ways: It sets the local shear strain that each element has to experience in order to undergo a phase transition between an unslipped and slipped states, and it also controls the energy barrier associated with such a “slip” event. Therefore, the deformation energy presented in Eq. (3.88) treats plasticity in a BMG material as a phase transition between unslipped (pristine) and slipped states, where the energy barrier for such a transition is \( \mu(r)\Delta^2(r)/(4\pi^2) \) and the distance between these states along the reaction coordinate (shear strain) is simply \( \Delta(r) \). This can be clearly seen by examining Fig. 3.11(b), where the deformational energy \( \mathcal{F}_{\text{BMG}} \) is plotted vs. shear strain.

With the aid of the field \( \Delta \), the model is capable of describing the deformation in both monolithic BMGs and BMG composites. In the glassy (disordered) phase, structural heterogeneity can be incorporated by assuming that \( \Delta(r) \) is a quenched, Gaussian random field with average \( \langle \Delta(r) \rangle = \Delta_0 \) and a two-point correlation function \( \langle |\Delta(r) - \Delta_0| |\Delta(r') - \Delta_0| \rangle = \sigma^2 \exp(-|r - r'|/l) \), where \( \sigma^2 \) and \( l \) denote the variance...
of the distribution and a structural correlation length, respectively. In monolithic BMGs, $\Delta(r)$ is used as a descriptor that distinguishes between domains of rigid (large CN) and soft (low CN) SRO. To account for the soft crystalline particles in BMG composites, $\Delta(r)$ in these domains is constant to reflect the periodicity of crystalline materials \cite{210}. In a mean-field study of plasticity in monolithic BMGs, Johnson and Samwer \cite{215} used $\Delta = \text{const.}$; within mean-field theory, the local strain at the onset of global shear banding is given by $\langle \Delta \rangle_{BMG}/4$.

Within the continuum framework presented here and in the absence of body forces, mechanical equilibrium requires \cite{195, 206}

$$\frac{\partial \sigma_{ij}}{\partial x_j} = 0, \quad (3.89)$$

where repeated indices imply summation. The displacement field is equilibrated computationally by utilizing a dynamic relaxation scheme in which a damped wave equation is solved, where the driving force (source term) is the variation of the deformation energy with respect to the displacement field. The numerical marching scheme that is used here to equilibrate the displacement field has the same exact form to the one used in Section 3.3 to equilibrate displacements due to redox cycles in SOFCs. Therefore, we briefly discuss the dynamics and the reader is referred to Section 3.3 for more details on the scheme. The effective dynamics for the displacement field follow from

$$\frac{\partial^2 u_i}{\partial t^2} + \left( \eta^* - \xi^* \nabla^2 \right) \frac{\partial u_i}{\partial t} = -\Gamma^* \frac{\delta F_{\text{def}}}{\delta u_i} = \Gamma^* \frac{\partial \sigma_{ij}}{\partial x_j}, \quad i = x, y, z, \quad (3.90)$$

where the first term on the left hand side is the inertial term. $\eta^*$ is a parameter that provide linear damping to all wave lengths, whereas $\xi^*$ heavily damps modes with small wave lengths. The right hand side is the forcing term and $\Gamma^*$ controls the effective elastic wave speed. Note that the steady-state solutions of Eq. (3.90) by construction satisfy the mechanical equilibrium equations $\partial \sigma_{ij}/\partial x_j = 0$. Furthermore,
the parameters \( \eta^*, \xi^* \) and \( \Gamma^* \) are chosen such that displacements relax effectively instantaneously relative to the externally imposed (dimensionless) strain rate. Finally, length scales are measured in terms of the structural correlation length \( l \sim O(nm) \), while units of stress are measured in terms of a representative shear modulus of the ductile phase that is used to form BMG composites.

### 3.4.2 Numerical Implementation

The analysis of BMG microstructures that is presented in this thesis assumes two dimensional systems, where the displacement field \( \mathbf{u} = (u_x, u_y) \) is evaluated at every point within the BMG domain during the coarse of simulations. The numerical scheme that is used to solve the effective dynamical equations for the displacement field in BMG systems has the same exact form to the one used to equilibrate the displacement field in SOFC anodes under mechanical deformation due to redox cycling. The reader is referred to Section 3.3.2 for implementation details. Therefore, in this Section, we only discuss the boundary conditions that are applied to BMG systems that are under applied shear strain.

For a BMG system under simple shear loading, fixed “clamped” displacement conditions are applied at the bottom edge of the simulation box, such that \( \{ \mathbf{u}(\mathbf{r}) = 0 \mid \mathbf{r} \in \mathcal{L}_{bott} \subset \Omega \} \), where \( \mathcal{L}_{bott} \) and \( \Omega \) define the bottom edge and domain region, respectively. Furthermore, at a given time \( t \), the displacement along the \( x \) direction is prescribed at the top edge of the simulation box, such that \( \{ u_x = u_o(t) \mid \mathbf{r} \in \mathcal{L}_{top} \subset \Omega \} \), where \( \mathcal{L}_{top} \) defines the top edge of the simulation box. Periodic boundary conditions are assumed lengthwise, which are implemented as follows. Let a BMG system be represented using a set of discrete grid points, where \( i \in [1, N_x] \), \( j \in [1, N_y] \) define the grid points along the \( x \) and \( y \) directions, respectively. \( N_x \) and \( N_y \) are the total number of grid points along the \( x \) and \( y \) directions, respectively, with the corresponding grid point spacing being \( \Delta x \) and \( \Delta y \). Therefore, \( u_{x,i,j} \) represents the
value of the displacement along the $x$ direction $u_x$ at a grid point $(i,j)$. Based on the above domain discretization, periodic boundary conditions for $u_x$ imply

\begin{align}
    u_{x_{N_x+1,j}} &= u_{x_{1,j}}, \\
    u_{x_{0,j}} &= u_{x_{N_x,j}}.
\end{align}

As for the initial conditions, the system is assumed to be at rest initially, where
\[ \{ u(r, t = 0) = 0, \ (\partial u(r, t) / \partial t)_{t=0} = 0 \mid r \in \Omega \}. \]
Chapter 4

Mesoscale Modeling of Solid Oxide Fuel Cells

In this Chapter, we present our work on the theoretical and computational modeling of degradation mechanisms in solid oxide fuel cells (SOFCs). For clarity, simulation results are divided into two sections. Section 4.1 focuses on performance degradation mechanisms due to the morphological evolution “coarsening” of Ni phase and the role of microstructure, characterized by particle size and ratio of Ni and YSZ phases, on the evolution of several attributes that affect the electrochemical performance. In Section 4.2, we focus on the mechanical degradation of SOFC anode systems due to the redox instability, and the role of anode microstructure and coarsened state on the development of mechanical stresses and damage accumulation in these systems.

4.1 Ni Coarsening in SOFC Anodes

The research findings presented in this Section were submitted for publication to the Journal of Power Sources and is currently under review [197]. In this work, we focus, in a parametric study, on the role of anode microstructure on the topological evolution of SOFC anodes and its impact on electrochemical performance. More specifically, we
collaborated with the research group of professor R. M. McMeeking at the University of California at Santa Barbara (UCSB) to develop an integrated modeling approach to examine the impact of Ni phase coarsening in Ni/YSZ cermet anodes on the performance of SOFC cells. In this approach, several representative anode microstructures with tunable features (such as phase volume fractions and particle sizes) are first generated “virtually”. Then, the diffuse-interface model, developed in Section 3.2 which is capable of capturing Ni phase coarsening and Ni/YSZ interaction, and accounting for the polycrystalline nature of Ni, is employed to quantitatively investigate the coarsening of Ni phase particles in said microstructures. Then, time-dependent, effective morphological parameters are extracted from the simulations and employed as inputs to a macroscale electrochemical cell level model that was developed by the group at UCSB to quantitatively evaluate the time-dependent electrochemical performance \([216, 217]\). It is worth noting here the electrochemical modeling effort was conducted by the group at UCSB and will not be reported in this thesis. The reader may refer to Refs. \([197, 216]\) for more details on the electrochemical modeling.

First, we demonstrate that the developed phase field model is capable of capturing a wide range of Ni/YSZ wetting and Ni dihedral angles. To this end, we simulated the evolution of a Ni spherical droplet on a YSZ substrate. The results are shown in Fig. 4.1 where the model parameters \(\xi_1\) and \(\xi_2\) set the wetting angle of Ni (orange)
on a non-evolving YSZ (grey) substrate. Next, we demonstrate the capability of the model to simulate a wide range of dihedral angles that form when a Ni grain boundary (GB) meets a free surface. We simulated a neck growth of two spherical Ni particles, where the grain boundary separating them leads to equilibration of the dihedral angle. As is shown in Fig. 4.2, a wide range of angles can be attained by tuning the model parameters \( k, w \) and \( m_H \), which ultimately set the interfacial (i.e., Ni surface and grain boundary) energies.

Parameters of the phase field model were chosen such that they mimic the behavior of real SOFC anodes. First, the parameters of the mobility function, given in Eq. (3.52), were set to: \( M_{Ni} = 1.0, M^* = 0.01, h_1 = 0.01, h_2 = 0.005 \) and \( h_3 = 0.20 \), which ensure that transport mechanisms controlling Ni phase coarsening are dominated by Ni diffusion along Ni-pore interfaces. Young’s equation relates surface and grain boundary energies to the dihedral angle at junc-

Figure 4.2: Simulation of a neck growth of two spherical Ni particles and the resulting dihedral angle \( \Psi \). (a) Initial configuration, and equilibrium profile for (b) \( k = 3.0, w = 0.316, m_H = 0.05 \) and \( \Psi \sim 81^\circ \), (c) \( k = 3.0, w = 1.0, m_H = 0.5 \) and \( \Psi \sim 134^\circ \), and (d) \( k = 3.0, w = 1.414, m_H = 1.0 \) and \( \Psi \sim 155^\circ \).

Figure 4.3: Balance of surface \( \gamma_s \) and grain boundary (GB) \( \gamma_{GB} \) tensions at the intersection of a GB with a free surface. The resulting dihedral angle \( \Psi \) is determined by Young’s equation.
Figure 4.4: Illustration of the Ni dihedral and Ni/YSZ wetting angles used in the coarsening analysis of SOFC anode microstructures. (a) Neck growth of two Ni spherical grains and a dihedral angle $\sim 155^\circ$. Note that each Ni grain is assigned a unique color (grain 1 in purple and grain 2 in green) and the overlap in the two colors represents the grain boundary region. The solid black line defines the boundary of the Ni domains. (b) Evolution of a Ni droplet on a YSZ substrate and a wetting angle of $\sim 123^\circ$. Note that a wetting angle has been established and the profile continues to evolve to the equilibrium shape of a spherical cap.

... where grain boundaries meet free surfaces [32]. Figure 4.3 is a schematic of a dihedral angle at the intersection of a grain boundary with a free surface. For the configuration shown in Fig. 4.3, Young’s equation dictates that

$$\cos \left( \frac{\Psi}{2} \right) = \frac{\gamma_{GB}}{2\gamma_s}. \quad (4.1)$$

At SOFC operating temperatures, the ratio of Ni grain boundary to surface energy $\gamma_{GB}/\gamma_s \simeq 0.25$ to 0.5 [218], which yields dihedral angles ranging between $150^\circ$ to $165^\circ$. Therefore, based on the simple analytical expressions relating the phase field model parameters to interfacial energies, which are derived in appendix A.1, we set: $k = 3.0$, $w = \sqrt{2}$, $m_H = 1.0$ and $A_H = 1.0$, which yield $\gamma_{GB}/\gamma_s \sim 0.4$ and an equilibrium dihedral angle $\sim 155^\circ$. Ni phase grain boundary mobility $M_{GB}$ is temperature-dependent and can vary by orders of magnitude depending on the geometrical properties of the grain boundary and impurity content [219, 220]. In this work and based on Eq. (3.51), the kinetic coefficient $L = 1.0$, which corresponds to
Table 4.1: Phase field model parameters employed in the coarsening study.

<table>
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<th>Kinetic parameters</th>
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<th>Ni/YSZ wetting angle</th>
<th>Value</th>
<th>Interfacial energies and Ni dihedral angle</th>
<th>Value</th>
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</tbody>
</table>

Grain boundary mobility $M_{GB} \sim 10^{-11} m^4 s^{-1} J^{-1}$ typically found in metals [221, 222], was employed. Figure 4.4(a) is a simulation of neck growth and the resulting equilibrium dihedral angle $\sim 155^\circ$. Note that the structural order parameters $\eta_1$ and $\eta_2$ that identify Ni grains 1 and 2 are plotted, where each one is assigned a unique color, in order to show the overlap region, which represents the Ni grain boundary. Finally, the model parameters describing Ni/YSZ wetting angle were set to $\xi_1 = 5.0$ and $\xi_2 = 1.0$, which yield a wetting angle $\sim 123^\circ$. This is illustrated in Fig. 4.4(b) which shows the equilibrium configuration of a Ni droplet (orange) on a static YSZ substrate (grey) and the resulting equilibrium wetting angle. Phase field model parameters, which were used in the coarsening study that is presented in the following sections, are summarized in Table 4.1.
4.1.1 Virtual SOFC Anode Microstructures

Virtual random packing systems of spherical particles are utilized in the integrated modeling approach for the microstructural evolution of Ni/YSZ porous anodes and its impact on the electrochemical performance of SOFCs. Porous anodes are idealized as binary mixtures of electron and ion conducting particles. The influence of the local anode microstructure, characterized by Ni to YSZ particle size ratio, on the coarsening of Ni and the subsequent electrochemical performance is investigated.

We use the random close packing algorithm of Gan et al. [223, 224] to generate binary mixtures of spherical particles with periodic boundary conditions. Then, in order to numerically mimic the effect of sintering and enable the formation of connected particle clusters, overlap between the particles was generated by using the method described in Ref. [217]: The radii of all spheres were expanded uniformly and proportional to the radius while keeping the center of each sphere at a fixed position, until a desired densification was reached. Four virtual Ni/YSZ anodes were examined, denoted R1, R1.5, R2, R2.5, with Ni to YSZ particle radius ratio $R_{Ni}/R_{YSZ} = 1.0, 0.67, 0.50$ and 0.40, respectively. For all systems studied in this work, the resulting volume fractions of Ni, YSZ and pore phases were $30 \pm 2\%$, $45 \pm 2\%$, $25 \pm 2\%$, respectively, similar to experimentally characterized Ni/YSZ based cermet anodes [34, 35]. Furthermore, in this parametric study, the size of YSZ particles was kept constant. For a given SOFC anode system, or a given $R_{Ni}/R_{YSZ}$ ratio, the size and number of Ni particles were varied in order to attain the target volume fraction. Table 4.2 lists the Ni to YSZ particle size ratio, and the number of Ni and YSZ particles for each SOFC anode system used in this work. Perspective views of the R1, R1.5, R2 and R2.5 systems depicting Ni and YSZ particles and the resulting virtual anode microstructures are in turn shown in Fig. 4.5, where Ni and YSZ particles are colored in orange and blue, respectively. Finally, to account for sample-to-sample variations, coarsen-
Table 4.2: Properties of virtual SOFC anode systems considered in this study. The as-prepared anode active layer was idealized as a binary mixture of electron and ion conducting spherical particles with radii $R_{Ni}$ and $R_{YSZ}$, respectively. For all cases, the volume fractions of Ni, YSZ and pore phases were $30 \pm 2\%$, $45 \pm 2\%$, $25 \pm 2\%$, respectively.

<table>
<thead>
<tr>
<th>System Name</th>
<th>$R_{Ni}/R_{YSZ}$</th>
<th>Number of Ni particles</th>
<th>Number of YSZ particles</th>
</tr>
</thead>
<tbody>
<tr>
<td>R1</td>
<td>1.00</td>
<td>60</td>
<td>90</td>
</tr>
<tr>
<td>R1.5</td>
<td>0.67</td>
<td>206</td>
<td>92</td>
</tr>
<tr>
<td>R2</td>
<td>0.50</td>
<td>503</td>
<td>95</td>
</tr>
<tr>
<td>R2.5</td>
<td>0.40</td>
<td>1010</td>
<td>97</td>
</tr>
</tbody>
</table>

ing simulations on four ensembles for each SOFC anode system were performed and results were averaged for the use of the electrochemical performance analysis.

### 4.1.2 Microstructural Characterization

Several microstructural attributes were monitored during the course of Ni phase coarsening in the reactive anode layer. Of special interest are the effective material properties controlling the electrochemical performance: Percolation of Ni networks, TPB regions, pore space microstructure (average pore radius $R_{pore}$ and interfacial area), and the pore tortuosity factor $\alpha_\infty$, as well as the effective conductivities $\sigma_{eff}^{Ni}$ and $\sigma_{eff}^{YSZ}$. In accordance with the phase field model that is presented in Section 3.2, the fields $c(r,t)$ and $\theta(r,t)$ were extracted from the model at several time steps during the temporal evolution of anode systems, and used to describe the topology of three-phase anodes. Therefore, the extracted properties are time dependent, which make the electrochemical model a transient one. We note that this Section is focused on the topological evolution of Ni in porous Ni/YSZ anodes and the reader is referred to Ref. [197] for more on the electrochemical modeling results.
Figure 4.5: Perspective views of the virtual, as-prepared anode microstructures. Ni and YSZ particles are represented in orange and blue, respectively. (a) R1 system: $R_{Ni} = R_{YSZ}$, (b) R1.5 system: $R_{Ni} = 0.67 R_{YSZ}$, (c) R2 system: $R_{Ni} = 0.5 R_{YSZ}$, (d) R2.5 system: $R_{Ni} = 0.4 R_{YSZ}$. In all systems, the volume fractions of the Ni, YSZ and pore are 30%, 45%, 25%, respectively, with ±2% added to all fractions. Note that the YSZ particle size is fixed in all systems and only the number and size of Ni particles are varied.

4.1.2.1 Percolation and Three-phase Boundary

We define the percolation degree $P_D$ as the fraction of a phase that belongs to spatially contiguous clusters, i.e., percolating clusters that span the simulation box from end to end. For example, $P_D = 0.5$ indicates that 50% of the Ni phase belongs to Ni clusters that are spatially contiguous. Spatially isolated clusters are identified using the labeling algorithm developed by Hoshen and Kopelman [225]. It is worth
mentioning here that the YSZ phase in all anode systems used in this study is a non-evolving one with a constant percolation degree $\sim 99.5\%$. Therefore, it is sufficient to only monitor the temporal evolution of the Ni phase percolation degree $P_D$.

Junctions in the microstructure of the porous anode, where the Ni, YSZ and pore phases meet define the three-phase boundary, where electrochemical reactions take place. We distinguish between the total TPB, $\Lambda_{\text{tot}}^*$, which accounts for all junctions where the three phases meet, and the reactive TPB, $\Lambda_{\text{react}}^*$, which only accounts for the fraction of junctions where the Ni phase belongs to percolated clusters. The length of reactive TPB in porous SOFC electrodes represents an important parameter for the electrochemical performance as it dictates the overall charge transfer rate of the redox reactions.

**4.1.2.2 Pore Space Microstructure**

Serving as input parameters for modeling the diffusive gas transport through the pore network, the average pore radius, $R_{\text{pore}}$, and total pore space interfacial area, are extracted from the voxel discretized electrode microstructures. In order to determine $R_{\text{pore}}$, we first define the pore phase field $\Sigma(x,t)$, where $\Sigma = 1$ denotes the pore phase and zero elsewhere. Then, we compute the two-point correlation function $g_2(r,t) = \langle [\Sigma(r, t) - \langle \Sigma(r, t) \rangle][\Sigma(r', t) - \langle \Sigma(r, t) \rangle] \rangle / \mu$, where $\mu = \langle \Sigma^2(r, t) \rangle - \langle \Sigma(r, t) \rangle^2$ is the variance. The average pore radius $R_{\text{pore}}$ is defined as the full width at half maximum of $g_2(r,t)$ [189]. When considering the diffusion of fuel gas through porous media, the irregular geometry of the pore space shows a significant effect: Gas molecules are forced to follow tortuous pathways through the pore space, which slows down the rate of diffusional transport. The average pore radius $R_{\text{pore}}$ will predominantly influence electrochemical performance losses associated with the diffusive gas transport through the pore network.
4.1.3 Role of Ni Coarsening on Microstructural Features of SOFC Anodes

Having demonstrated that the model properly incorporates interfacial energetics, we start our exploration of the model by examining the virtual SOFC anode systems with various Ni to YSZ particle size ratios, or $R_{Ni}/R_{YSZ}$. Each virtual SOFC cermet anode was discretized to produce a simulation box of size $120 \times 120 \times 120$ voxels, where the voxel size is $\Delta x = \Delta y = \Delta z = 1.0$. Periodic boundary conditions in all three dimensions were used in the phase field simulations. First, we qualitatively investigate the morphological evolution due to Ni coarsening. For the R2.5 anode system, where $R_{Ni} = 0.4R_{YSZ}$, panels (a)-(c) of Fig. 4.6 depict the evolution of Ni phase spatially isolated clusters, where every Ni cluster is assigned a unique color at (dimensionless) coarsening times $0, 10^3$ and $10^4$, respectively. Initially, a single and highly intertwined cluster constituted most of the Ni phase. As the anode system evolved over time, parts of the Ni skeleton broke into smaller clusters, as can be seen in Figs. 4.6(b) and (c), which eventually led to loss of percolation degree $P_D$. This loss of percolation degree by fragmentation of large clusters into smaller ones will be discussed in more detail later in this Section.

Next, we examine the temporal evolution of the Ni phase morphology. Panels (d)-(f) of Fig. 4.6 depicts the temporal evolution of the grain morphology of the Ni phase for the R2.5 anode system. Initially, a collection of small spherical particles constituted the Ni phase. As the anode system evolved over time, Ni grain growth was observed, where the average size of grains increased and the number of Ni grains shrank. In addition to Ni coarsening, where the total interfacial energy is minimized, grain growth leads to reduction in the total interfacial energy associated with grain boundaries. To quantitatively examine Ni grain growth depicted in Figs. 4.6(d)-(f), we examine the temporal evolution of the average grain size of the Ni phase. First,
we define the field $\mathcal{H}$ as

$$\mathcal{H} = \sum_{i=1}^{n_H} \eta_i^2,$$  \hspace{1cm} (4.2)

which is used as a marker to track Ni interfaces. In this work, a Ni grain is assumed when $\mathcal{H} \geq 0.75$. Once Ni grains are identified using the $\mathcal{H}$ field, the cluster labeling algorithm of Hoshen and Kopelman [225] was used to calculate the volume and effective diameter of each Ni grain (assuming they are spherical in shape). Figure 4.7 is a plot of Ni phase average grain size as a function of coarsening time for all RCP systems, where it can be clearly seen that the average Ni grain size grows in time. By observing the trends in Fig. 4.7, it is evident that Ni grain growth (i.e., increase in
average grain size) proceeds at a slower rate at late times than initial ones. Furthermore, at late coarsening times, the average Ni grain for all RCP systems examined in this work was found to be similar in size. The trend observed in Fig. 4.7 is in agreement with experimental observations on Ni grain growth in SOFC anodes, where growth rates are high during initial times and become nearly zero at later coarsening times. In a study by Faes et al., they fit their experimental results for Ni growth in SOFC anodes to a constrained-growth charging capacitor model, where growth rates are nearly zero at late coarsening times.

We now turn our attention to several microstructural features affecting the electrochemical performance. We first start by examining the role of microstructure (Ni to YSZ particle size ratio) on the evolution of TPB regions. Within the phase field framework, TPB regions are defined as spatial regions where interfaces of all phase fields meet and overlap. Therefore, the total number of volume elements (voxels), where the Ni, YSZ, and pore phases meet, is regarded as a measure of total TPB, or $\Lambda_{tot}^*$. Figure 4.8(a) is a plot of $\Lambda_{tot}^*$ for all systems. It can be clearly seen that for a fixed YSZ particle size, systems with smaller initial Ni particles lead to higher $\Lambda_{tot}^*$. A quantity of critical importance when modeling electrochemical reactions is reactive TPB, or $\Lambda_{react}^*$, which is defined in this work as the total number of elements, where percolating Ni clusters meet the YSZ and pore phases. Figure 4.8(b) is a plot of the temporal evolution of $\Lambda_{react}^*$. At late coarsening times, systems with smaller initial Ni particles experience a sharper decrease in $\Lambda_{react}^*$. 

![Figure 4.7: Temporal evolution of the average grain size of the Ni phase.](image)
Figure 4.8: Temporal evolution of (a) total TPB $\Lambda_{\text{tot}}^*$ and (b) reactive TPB $\Lambda_{\text{react}}^*$. In both figures, TPB is measured by the voxel count of elements that are spatially located at Ni-YSZ-pore interfaces.

This is due to the loss of percolation of some Ni clusters, as will be shown later in this Section.

A close examination of Fig. 4.8(a) reveals a self similar behavior for the temporal evolution of $\Lambda_{\text{tot}}^*$ during Ni coarsening. Figure 4.9(a) is a log-log plot of $\Lambda_{\text{tot}}^*$ vs. time, where $\Lambda_{\text{tot}}^*$ is shown to be consistent with a power law of the form

$$\Lambda_{\text{tot}}^* = f \times t^\rho,$$

(4.3)

where the exponent $\rho = -0.16 \pm 0.02$ and $f = f(R_{\text{Ni}}/R_{\text{YSZ}})$ is a pre-factor, which encompasses the effects of anode microstructure. We expect $\rho$ to depend on the volume fractions of the Ni and YSZ phases, and Ni-YSZ wetting angle. We also note that other forms for the scaling of TPB have been proposed [35]. We have been unable to develop a physically-based argument which explains the observed value of the exponent $\rho$. Figure 4.9(b) in turn demonstrates the dependence of the pre-factor
Figure 4.9: (a) On a log-log scale, total TPB $\Lambda^\ast_{\text{tot}}$ vs. coarsening time. (b) The pre-factor $f = f(R_{Ni}/R_{YSZ})$, where $\Lambda^\ast_{\text{tot}}$ is assumed to follow: $\Lambda^\ast_{\text{tot}} = f(R_{Ni}/R_{YSZ})t^\rho$. The dashed line is drawn for clarity.

$f$ on the Ni to YSZ particle size ratio $R_{Ni}/R_{YSZ}$, where the dashed line is drawn as a guide to the eye.

Next, we examine the evolution of pore space during the microstructural evolution of SOFC anodes. Figure 4.10(a) is a plot of the average pore radius $R_{pore}$ normalized by the YSZ particle radius $R_{YSZ}$, which is constant (recall that YSZ is a non-evolving phase) and the same in all systems. In all SOFC anode systems, $R_{pore}$ increased during the evolution of Ni phase. We also notice that SOFC anode systems having larger initial Ni particles yielded larger pores $R_{pore}$. Figure 4.10(b) is a plot of the total pore space interfacial area (with both Ni and YSZ) $A_{pore}$ normalized by its initial value $A_{pore}(t = 0)$. All SOFC anodes experienced a continuous decrease in pore interfacial area with systems having smaller initial Ni particles experiencing a larger drop in pore interfacial area. At the end of coarsening simulations, the total decrease in pore interfacial area $\sim 25\%, 40\%, 50\%$ and $55\%$ for R1 ($R_{Ni} = R_{YSZ}$), R1.5 ($R_{Ni} = 0.67R_{YSZ}$), R2 ($R_{Ni} = 0.5R_{YSZ}$) and R2.5 ($R_{Ni} = 0.4R_{YSZ}$) anode systems, respectively. The decrease in total pore interfacial area is primarily due to
the temporal evolution of Ni-pore interfaces. By examining the evolution of pore space, it can be concluded that the pores grew in size [Fig. 4.10(a)], and evolved into more equiaxed shapes, or became more round, thus minimizing total interfacial area [Fig. 4.10(b)].

Finally, we examine the temporal evolution of Ni phase percolation degree $P_D$. Figure 4.11(a) is a plot of Ni phase percolation degree as a function of coarsening time. It can be clearly seen, that during Ni coarsening, systems with smaller initial Ni particles experienced the largest drop in Ni phase contiguity, i.e., decrease in percolation degree. A close examination of the Ni phase grain morphology reveals that the loss of percolation degree may be associated with the presence of Ni grain boundaries. The two panels in Fig. 4.11(b) depict a section of a Ni skeleton in the R2.5 anode system, where the top panel (early time) shows a connected Ni cluster. In the bottom panel (late time) of Fig. 4.11(b), it can be seen that a pinch-off effect along Ni grain boundaries caused the cluster to lose contiguity.
Figure 4.11: (a) Temporal evolution of Ni phase percolation degree $P_D$, which is a measure of percolating Ni clusters that span the simulation box. (b) For the R2.5 anode system, two panels; top (early time) and bottom (late time) showing a section of a Ni skeleton. Circles colored in red show a pinch-off effect at Ni grain boundary regions that leads to morphological instability. Grain boundaries are colored in black.

In more quantitative terms, the temporal evolution of Ni phase percolation degree $P_D$ can be cast in a functional form as follows

$$P_D(t) - P_D(0) = G_{ref}(t/t^*),$$  

(4.4)

where $t^* = t^*(R_{Ni}/R_{YSZ})$ denotes a characteristic time scale that controls the loss of percolation degree, while $G_{ref}$ is a reference functional form for the percolation degree $P_D$. The self-similar behavior of Ni phase percolation degree is depicted in Fig. 4.12(a), while the dependence of $t^*$ on the ratio $R_{Ni}/R_{YSZ}$ is in turn depicted in Fig. 4.12(b). The data can be reasonably well fit with a simple power law function of the form $t^* \sim (R_{Ni}/R_{YSZ})^\chi$, where $\chi \simeq 4.1 \pm 2.2$ denotes the effective scaling exponent.
Figure 4.12: (a) Self similar scaling of Ni phase percolation degree $P_D$ for all SOFC anode systems. (b) On a log-log scale, characteristic time $t^* = t^*(R_{Ni}/R_{YSZ})$ that sets the morphological instability vs. Ni to YSZ particle size ratio.

To rationalize this strong dependence of loss of percolation degree on initial Ni particle size, consider the following: If Ni particles in the initial stage are idealized as cylindrical morphologies with “beaded” structures, then the loss of Ni phase percolation degree can be related to the classic Rayleigh instability of inviscid liquid jets [226]. In this case, the cylindrical liquid jet is linearly unstable to perturbations with wavelengths greater than the circumference of the cylinder, and the presence of such perturbations eventually leads to the breaking of the jet into spherical droplets.

In the context of solid cylinders, McCallum et al. [227] examined analytically the stability of cylindrical islands on rigid substrates with various wetting angles and demonstrated that the characteristic time for the onset of morphological instability for the case of surface diffusion $\tau_s \sim L_d^4/b$, where $b$ is a parameter that encompasses various materials properties, such as diffusivity and surface tension, and $L_d$ is a length scale that characterizes the cross-sectional area of the unperturbed cylinder. In addition, we note that grain boundaries also play an important role in the loss of contiguity [cf. Fig. 4.11(b)]. In particular, during the late stages of the pinch-off process, grain
boundary grooving takes place [111]. By extending Mullins’s analysis for a cylindrical bi-crystal, it can be shown that the time to pinch-off displays a simple $R^4$ scaling form, where $R$ denotes the radius of the unperturbed cylinder. Both of these simple arguments thus suggest a $t^* \sim (R_{Ni}/R_{YSZ})^4$ scaling form for the characteristic time scale for the loss in Ni percolation degree, consistent with our numerical simulations.

In summary, a mesoscale phase field model was developed that captures Ni coarsening in Ni/YSZ cermet anodes, accounts for Ni-YSZ interaction, and incorporates the polycrystalline nature of Ni. Several microstructural features that influence electrochemical performance were tracked as “virtual” anodes systems evolved over time. Our simulation results revealed simple scaling laws for the decrease in overall TPB length and loss in Ni percolation degree, or contiguity. A Ni phase size effect was revealed, such that systems with initially smaller Ni particles maintained higher density of TPBs but lost contiguity faster than the ones with large Ni particles.

In broader terms, our approach highlights the importance of the initial anode microstructure on the morphological stability of Ni phase. Several physical phenomena are identified as possible mechanisms that control Ni phase stability and coarsening rates in SOFC porous anodes. Our modeling approach, which is informed by the local microstructure, can be used as a design tool to investigate the following: i) Identify combinations of morphological parameters that yield anode systems with optimal characteristics for the microstructural stability and electrochemical performance of SOFCs, ii) utilize the trends and scaling laws for TPB, Ni contiguity and pore radius to predict the performance of SOFCs under extended use, and iii) explore other avenues aiming at stabilizing Ni phase coarsening, such as doping Ni to increase wettability with the YSZ backbone.
Table 4.3: Mechanical properties of Ni, NiO and YSZ employed in this work. $K$, $E$ and $\mu$ represent bulk, Young and shear moduli, respectively, while $F_{tu}$ denotes the ultimate strength.

<table>
<thead>
<tr>
<th>Material</th>
<th>$K$(GPa)</th>
<th>$E$(GPa)</th>
<th>$\mu$(GPa)</th>
<th>$F_{tu}$(GPa)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>210</td>
<td>220</td>
<td>83</td>
<td>1.00 (bulk)</td>
<td>[228, 229]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.50 (grain boundary)</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>166</td>
<td>200</td>
<td>77</td>
<td>-</td>
<td>[230]</td>
</tr>
<tr>
<td>NiO</td>
<td>193</td>
<td>220</td>
<td>84</td>
<td>-</td>
<td>[230]</td>
</tr>
</tbody>
</table>

4.2 Redox Instability and Mechanical Damage in Solid Oxide Fuel Cell Anodes

Next we investigate the redox instability, mechanical deformation, and heterogeneous damage accumulation in solid oxide fuel cell anodes. From a mechanistic perspective, the most critical feature of the re-oxidation reaction $\text{Ni} + \frac{1}{2}\text{O}_2 \rightarrow \text{NiO}$ is the large bulk volume changes associated with it. In the analysis presented here, the following assumptions were made: i) All Ni particles can be taken to undergo the transformation to NiO at the same rate. Thus, at any given instant in time during the re-oxidation process, the degree of Ni oxidation $\Phi_{\text{NiO}}$ is the same for all Ni particles. This implies that one can effectively substitute the degree of Ni oxidation for physical time. ii) To connect the degree of Ni oxidation to the effective expansion of the Ni particles, we will assume that their volumetric expansion is uniformly distributed within each particle and directly proportional to the degree of oxidation, such that for a Ni spherical particle, complete transformation to NiO ($\Phi_{\text{NiO}} = 1$) corresponds to a volumetric strain $\epsilon^* \sim 0.66$. To account for bulk volume changes due to NiO formation, $\alpha(r) = \alpha_0$ within the Ni/NiO domains and zero elsewhere, such that $\alpha_0 = 0.66K\Phi_{\text{NiO}}$ in terms of the degree of Ni oxidation $\Phi_{\text{NiO}}$. 

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To examine the development of stresses and evolution of mechanical damage due to Ni re-oxidation, the redox computational framework was implemented as follows: For a given $\alpha$ value, Eq. (3.71) was iterated until the displacement fields converged, and subsequently the stress tensor $\sigma_{ij}$ and its eigenvalues (i.e., principal stresses) were calculated for each volume element. In the YSZ phase, the max principal tensile stress $\sigma_{\text{max}}$ was then compared against $F_{tu}$ to determine whether a volume element fractured or not; in the former case, $\Psi$ was set to 0 locally, and Eq. (3.71) was iterated again. If no additional fracture events occurred, $\alpha_0$ was incremented and iterations were re-started. It is worth noting here that the failure criterion is not applied to the Ni phase due to its ductile nature and the large amount of intrinsic plasticity it can accommodate before fracture [231]. Table 4.3 lists the mechanical properties of the Ni, NiO and YSZ phases that were used in this work.

Two studies will be presented herein. The first one focuses on modeling the deformation and damage accumulation in a real experimentally obtained anode microstructure. The second study examines the role of microstructure, characterized by Ni to YSZ particle size ratio, and coarsening state on the redox instability and damage in SOFC anodes.

### 4.2.1 Experimentally Obtained Anode Microstructure

The research findings presented in this Section were published in the Journal of Applied Physics [203]. An experimentally obtained SOFC anode microstructure was provided by the research group of Professor W. Chiu from the University of Connecticut.

We study the redox behavior and mechanical damage evolution in experimentally obtained SOFC anode systems. Within our redox modeling framework, we define two continuum fields, $\theta(r)$ and $c(r)$, which distinguish between the constituent phases of the SOFC anode. In particular, $c = 1$ within the Ni/NiO particles and
$c = -1$ elsewhere, while $\theta = 1$ within the YSZ phase and zero elsewhere. In terms of these three fields, the bulk modulus is written 

$$K(r) = K_{Ni}[(1 + \tanh(c(r)/h))/2] + K_{YSZ}[\tanh(\theta(r)/h)],$$

with a similar expression for the shear modulus $\mu(r)$. Furthermore, we assume that $\alpha(r) = \alpha_0[(1 + \tanh(c(r)/h))/2]$, where $\alpha_0$ is increased in small steps in the simulations. Note that this form of $\alpha(r)$ ensures that it is non-zero only within the Ni particles.

The anode microstructure employed in the simulations is a representative volume element of a tape-cast Ni/YSZ anode support that was imaged using the transmission x-ray microscope at beamline 32-ID-C of the Advanced Photon Source. Three-dimensional microstructural and elemental data were obtained using x-ray nanotomography with absorption contrast imaging across the Ni k-absorption edge. This technique permits the segmentation, characterization, and analysis of the Ni, YSZ, and pore phases within the anode. Figure 4.13(a) is a perspective view of the anode microstructure using the raw data from x-ray nanotomography. In order to eliminate artificial stress concentration sites that arise due to the segmentation of experimental data ("wedding cake" interfaces), nanotomography data were mapped into a standard phase field formalism with "model B" dynamics, refer to Eq. (3.9), and evolved for a few time steps in order to obtain smooth interfaces. After the numerical smoothing step, the phase field model was mapped back into a sharp interface one, where the fields $\theta(r)$ and $c(r)$ were then extracted and used in the simulations presented in this work. Figure 4.13(b) is a perspective view of the numerically smoothed anode microstructure.

In the simulations, stresses and length scales were measured in terms of $K_{YSZ}$ and the spatial grid spacing $\approx 50$ nm, respectively. The dynamical equations for the displacement field, Eq. (3.71), were integrated on a $123 \times 123 \times 123$ uniform lattice with $\Delta x = \Delta y = \Delta z = 1.0$ and a "fictitious" time step $\Delta t = 0.002$. The SOFC composite anode was simulated with all displacement components fixed on all cube
Figure 4.13: (a) A perspective view of the original experimentally constructed and digitized anode system. (b) A perspective view of the numerically smoothed anode microstructure. In (a) and (b), Ni (orange), YSZ (green) and pores (white) form the constituent phases. (c) For the numerically smoothed system, iso-surface plot of $\Psi(r)$ at redox strain $\epsilon^* = 0.32$, where regions colored in blue represent fractured (i.e., damaged) YSZ volume elements.

faces. In the YSZ phase, $K = 1.0$, $\mu = 0.45$, while in the Ni/NiO, $K = 0.9$, and $\mu = 0.38$. Other parameters that were utilized in the simulations were set to $\eta^* = 0.00$, $\xi^* = 0.01$, $\Gamma^* = 1.0$, $F_{tu} = 0.08$, and $h = 0.01\Delta x$.

We first start by examining the spatial evolution of the damage field $\Psi$. Figure 4.13(c) is an iso-surface plot of $\Psi(r)$ for a redox strain $\epsilon^* = 0.32$ with fractured YSZ volume elements labeled in blue. We note that the damage accumulation is spatially heterogeneous, and strongly correlated with the local microstructure, as will be discussed next.

To gain a better understanding of the effect of local microstructure on the failure process of the YSZ phase, we have examined several two-dimensional section-cuts of the simulated SOFC anode in order to identify YSZ regions that are under high principal stresses $\sigma_{\text{max}}$, and correlate them to the local microstructure. To this end, Fig. 4.14(a) displays a close-up view of one of the examined section-cuts, where the highly intertwined nature of Ni (orange) and YSZ (green) domains can be clearly discerned. Figure 4.14(b) in turn displays a contour of $\sigma_{\text{max}}$ corresponding to the same close-up view at a redox strain $\epsilon^* = 0.16$. It is evident that YSZ regions, which
are highly constrained by the surrounding Ni/NiO clusters, tend to localize stresses. It is precisely these YSZ volume elements, which initiate the damage accumulation process, leading to the heterogeneous spatial distribution of fractured YSZ elements shown in Fig. 4.13(c).

Next, we quantify the effect of redox strain $\epsilon^*$ on the volume fraction $\phi$ of fractured YSZ elements. This data is shown in Fig. 4.15(a), where the results for the original system, without numerical smoothing, are plotted along with the numerically smoothed one for comparison. First, we note that there exists a threshold $\epsilon^* \sim 0.16$ below which no YSZ fracture is observed, while $\phi$ increases rapidly when $\epsilon^* \gtrsim 0.16$. Furthermore, at each value of $\epsilon^*$, we have also identified the volume fraction of fractured YSZ elements, $\phi_{int}$, that reside in the vicinity of NiO/YSZ interfaces. At the onset of the damage accumulation process, most fractured YSZ elements are located at NiO/YSZ interfaces. As $\epsilon^*$ increases, the overall volume fraction $\phi$ of fractured YSZ elements increases, while $\phi_{int}$ decreases. This implies that while the initial damage
accumulation occurs at NiO/YSZ interfaces, the subsequent damage accumulation process proceeds via the inward growth of fractured YSZ elements into the bulk YSZ phase. We also note that the numerical smoothing process of the original system leads to reduction in the volume fraction $\phi$ of fractured YSZ elements. This is due to the fact that numerical smoothing leads to reduction in artificial stress risers, which overestimate the stress levels.

Finally, to better characterize the degree of accumulated damage, we have calculated the damaged YSZ cluster size distribution using the cluster labeling algorithm detailed in Ref. [225]. To this end, Figure 4.15(b) displays a histogram of fractured YSZ clusters for $\epsilon^* = 0.22$, 0.29, and 0.44. It can be seen that initial damage accumulation occurs via the formation of small seed clusters, while increasing $\epsilon^*$ leads to the emergence of both more numerous small clusters and their coalescence into larger, spatially extended ones. According to our failure criterion, a local YSZ element is no longer a load bearing member when the max principal stress in the YSZ reaches $F_{tu}$. In dimensional units, if the YSZ bulk modulus $K \sim 210$ GPa [228, 229], then...
the principal stress in the YSZ that causes failure equals \( F_{tu} = 0.08K \sim 16 \text{ GPa} \). It should be noted that while the computed stress levels are influenced by the degree to which the microstructure has been resolved, improvements in the experimental resolution will lead to improved predictive capability of the method.

In summary, the mesoscale model presented in Section 3.3 was used to examine the redox instability, mechanical deformation and damage accumulation in an experimentally obtained anode system. The results presented here shed light on the critical role that the SOFC anode microstructure plays in the mechanical deformation behavior and failure of such materials. The close integration of experiments and simulations highlighted in this work opens new research avenues into the mechanical deformation behavior and stability within a broader range of materials for energy conversion and storage. While the results presented here examined a real anode microstructure, a parametric study is needed to explore the phase space of microstructural features affecting redox instability, and identify optimal combinations of these attributes, which yield anode systems that are more resistant to mechanical damage due to redox.

### 4.2.2 Role of Anode Microstructure and Ni Coarsening

Next we investigate the role of anode microstructure, characterized by Ni to YSZ particle size ratio, on the mechanical deformation and damage accumulation in porous Ni/YSZ cermets during redox cycling. Furthermore, we examine the impact of Ni phase coarsening and the accompanying topological changes to Ni networks in Ni/YSZ cermet anodes on the redox instability and damage accumulation in these systems. The research findings presented in this Section were submitted for publication to Journal of Applied Physics and is currently under review.

We utilize the same class of microstructures that was employed in Section 4.1 to investigate complex coarsening phenomena taking place in SOFC anode materials. A convenient feature of this class of binary random close-packed (RCP) systems of
Figure 4.16: Perspective views of the initial microstructures of the (a) R1 \((R_{Ni}/R_{YSZ} = 1.0)\), (b) R1.5 \((R_{Ni}/R_{YSZ} = 0.67)\), (c) R2 \((R_{Ni}/R_{YSZ} = 0.5)\), and (d) R2.5 \((R_{Ni}/R_{YSZ} = 0.4)\) anode systems. In the initial state, anode systems are idealized as binary mixtures of Ni (orange) and YSZ (grey) spherical particles. Representative cross-sectional views of the (e) R1, (f) R1.5, (g) R2, and (h) R2.5 anode systems, where orange (grey) domains represent Ni (YSZ) particles. YSZ grain boundaries are colored in red.

spherical particles is that critical microstructural parameters, such as number and size of particles, particle size ratios, and overall volume fractions of the solid and porous phases can be easily varied.

Four representative SOFC anode microstructures are examined, denoted R1, R1.5, R2, R2.5, with Ni to YSZ particle size ratios \(R_{Ni}/R_{YSZ} = 1.0, 0.67, 0.50\) and 0.40, respectively. The volume fractions of the constituent phases are chosen to be representative of experimentally characterized Ni/YSZ based porous anodes \[34, 35\], and are set to \(30 \pm 2\%\), \(45 \pm 2\%\), \(25 \pm 2\%\), for Ni, YSZ and pore phases, respectively. Moreover, in this parametric study, the size of YSZ particles is kept fixed. For a given SOFC anode system, or a given \(R_{Ni}/R_{YSZ}\) ratio, the size and number of Ni particles are varied in order to attain the target volume fraction. Table 4.2 lists the Ni to YSZ particle size ratios and the number of Ni and YSZ particles for each SOFC anode.
system employed in this study. Furthermore, the polycrystalline nature of YSZ and
the associated heterogeneity in mechanical properties are accounted for by assigning
an ultimate strength $F_{tu}$ at YSZ grain boundaries that is smaller than the one for
the bulk YSZ volume elements. This is motivated by experimental observations of
intergranular cracking along YSZ grain boundaries, which is a sign of low cohesive
strength, in Ni/YSZ cermets during redox cycles \[21\]. In our work, regions with low
$F_{tu}$ values act as seed points, or flaws, where the mechanical damage can potentially
start. The virtual anode systems are digitized to yield a $120^3$ uniform lattice with
a voxel size $\sim 30\text{nm}$. This digitization level is chosen such that the resulting YSZ
particle radius $R_{YSZ} \sim 0.35\mu m$ is comparable to the ones in typical SOFC anode
systems \[21\ \[35\]. It is important to note, however, that within our continuum elas-
ticity approach, the absolute particle size does not play any role in the evolution of
mechanical stresses, as the governing equations of linear elasticity do not contain any
length scales. Therefore, for a given volume fraction of the constituent phases and a
given arrangement of particles, it is the Ni to YSZ particle size ratio that will control
the redox instability in these systems.

Now, perspective views of the SOFC anode systems employed in this study are
shown in Fig. \[4.16\](a)-(d), where orange (grey) spheres represent Ni (YSZ) parti-
cles that were packed in a periodic box. Representative cross-sectional views of the
these anode systems, which reveal the local microstructure along with the YSZ grain
boundary network, are in turn shown in Fig. \[4.16\](e)-(f). These virtual anode systems
simulate the initial, or short-term, reduced state of a SOFC cell. In this work, the
anode systems that are depicted in Fig. \[4.16\] will be referred to as “initial” systems.

To examine the role of Ni phase coarsening on the redox stability of Ni/YSZ porous
anodes, coarsened microstructures from our previous simulations, which are presented
in Section \[4.1\] were employed as inputs in the present work. These coarsened mi-
crostructures were generated via large-scale simulations of a diffuse-interface model,
which incorporates the coarsening of Ni phase particles around a non-evolving YSZ network \[197\]. Perspective views of the SOFC anode microstructures at late stages of Ni phase coarsening are shown in Fig. 4.17(a)-(d), where Ni and YSZ domains are represented in orange and grey, respectively. The corresponding representative cross-sectional views of these anode systems are shown in Fig. 4.17(e)-(h), where the resulting coarser Ni networks can be clearly discerned. These systems represent anode microstructures at a late, or long term, reduced state of a SOFC cell. In this study, they will be referred to as “coarsened” systems.

With regard to the role of the NiO/YSZ interface coherency (or lack thereof) on redox stress development, volume elements that belong to Ni/YSZ interfaces are identified and assigned a shear modulus $\mu \rightarrow 0$. Figure 4.18 is a representative cross-sectional view of an anode system, where orange (maroon) denote shear modulus
Figure 4.18: A shear modulus contour of a representative cross-sectional view of the coarsened R2.5 anode system, where orange (maroon) denote the shear modulus of Ni (YSZ), under (a) epitaxial and (b) slip interfacial conditions for Ni/YSZ interfaces. Regions with zero shear modulus are colored in white.

In Fig. 4.18(a), an epitaxial interface is assumed, where the shear modulus is interpolated smoothly between YSZ (maroon) and Ni (orange), resulting in a non-zero shear modulus along the interface. In Fig. 4.18(b), on the other hand, a slip interfacial condition has been implemented by assigning a zero shear modulus to the volume elements residing along the Ni/YSZ interface.

In the simulations to be reported below, Units of stress and length scales were measured in terms of the bulk modulus of the YSZ phase and voxel size, respectively. The dynamical equations for the displacement field were numerically integrated with $\Delta x = \Delta y = \Delta z = 1.0$ and $\Delta t = 0.01$. The virtual RCP Ni/YSZ anode systems were simulated with all displacement components fixed, or clamped, along all cube faces. In the YSZ phase, $K = 1.0$ and $\mu = 0.4$, while in Ni/NiO, $K = 0.92$ and $\mu = 0.4$. Furthermore, $F_{tu} = 0.005$ and 0.0025 in the YSZ bulk and grain boundary regions, respectively. Other parameters that were utilized in the simulations were set to $(\eta^*, \xi^*, \Gamma^*) = (2.0, 0.001, 400.0)$.

We begin our exploration of the simulation results by highlighting some of the salient features and observations for the coarsened R2.5 anode system ($R_{Ni}/R_{YSZ} = 0.4$). To this end, Figure 4.19 displays results for this system under both epitaxial
Figure 4.19: Stress development and damage accumulation behavior for the coarsened R2.5 anode system under epitaxial [(a)-(c)] and slip conditions [(d)-(f)]. (a) and (d): Max principal stress at a redox strain of $\epsilon^* = 1.6\%$. Solid black (green) lines define boundaries of YSZ (Ni) domains. Regions in red denote max normal stress $\approx F_{tu}$. (b) and (e): At a redox strain $\epsilon^* = 6.4\%$, a perspective view of the YSZ skeleton with the damage field $\Psi(r)$ colored in blue. (c) and (f): On a semi-log scale, total damage (voxel count) of YSZ domains as a function of redox strain for the R2.5 system in the initial and coarsened configurations.

[panels (a)-(c)] and interfacial slip [panels (d)-(f)] conditions. Under epitaxial conditions, Fig. 4.19(a) displays a contour of the max principal stress $\sigma_{\text{max}}$ at a redox strain $\epsilon^* = 1.6\%$, where regions colored in red represent stresses $\approx F_{tu}$. It can be clearly seen that $\sigma_{\text{max}}$ accumulates at Ni/YSZ interfaces and within the YSZ bulk phase. At even larger redox strain values, these regions with high $\sigma_{\text{max}}$ values develop microcracks. This is illustrated in Fig. 4.19(b), which displays a perspective view of the YSZ skeleton with the damage field $\Psi(r)$ shown in blue at a redox strain $\epsilon^* = 6.4\%$. 
To quantify the damage accumulation behavior, the total damage (in voxel count) is shown in Fig. 4.19(c) for the YSZ phase for both the initial and coarsened R2.5 anode systems under epitaxial conditions. It can be clearly seen that at a given redox strain level, the initial R2.5 anode system is more resistant to mechanical damage than the coarsened one. This is an indication that the anode microstructure indeed plays a critical role in the deformation and damage accumulation during redox cycles.

Panels (d)-(f) of Fig. 4.19 in turn demonstrate the response of the R2.5 coarsened anode system under the slip condition for Ni/YSZ interfaces, where a contour of max principal stress at a redox strain $\epsilon^* = 1.6\%$ is shown in panel (d), perspective view of the damage field $\Psi(r)$ at a redox strain $\epsilon^* = 6.4\%$ in panel (e), and plot of total damage vs. redox strain in panel (f). The anode system with the slip condition for Ni/YSZ interfaces exhibits a similar overall trend to the one with the epitaxial interfacial condition. It can be seen, however, that localization of the max normal stress and damage accumulation levels are lower for the anode system with the slip interfacial condition in comparison with the epitaxial system. This is expected, as relaxation of expansion strains parallel to the Ni/YSZ interfaces results in smaller effective load transfer to the YSZ phase.

Next, we examine the role of YSZ grain boundaries on damage localization and accumulation. To this end, we identify the fraction of damaged elements $\phi_{GB}$ that are spatially located within YSZ grain boundaries as a function of redox strain $\epsilon^*$. Panels (a) and (b) of Fig. 4.20 display graphs of $\phi_{GB}$ vs. $\epsilon^*$ for the initial and coarsened R2.5 anode system under epitaxial and slip conditions, respectively. For this anode system, a peak in the $\phi_{GB}$ curve can be observed at redox strain values corresponding to the onset of damage accumulation, which indicates that YSZ grain boundaries act as initiation sites. At larger redox strains, $\phi_{GB}$ curves experience a continuous drop as a function of redox strain indicating that damage is no longer confined within the YSZ grain boundary regions.
Figure 4.20: Fraction of damaged elements, $\phi_{GB}$, that are located within YSZ grain boundaries as a function of redox strain $\epsilon^*$ under (a) epitaxial and (b) slip conditions for Ni/YSZ interfaces for the initial and coarsened R2.5 anode systems.

The same process of simulating the R2.5 anode system under both epitaxial and slip conditions for Ni/YSZ interfaces was repeated for the other remaining anode systems R1, R1.5 and R2 as well. The results are summarized in Fig. 4.21 which displays plots of total damage in voxel count vs. redox strain $\epsilon^*$ for all anode systems in the initial and coarsened configurations under both epitaxial and slip interfacial conditions. As is clearly evidenced in panels (a) and (c), initial anode systems exhibit a Ni particle size effect such that smaller particles yield microstructures that are more resistant to mechanical damage during re-oxidation. A stronger dependence on Ni particle size is observed for systems under epitaxial interfacial conditions. For example, for the initial anode systems under epitaxial interfacial conditions [cf. Fig. 4.21(a)] and at a redox strain of $\epsilon^* = 12\%$, the R2.5 anode system with $R_{Ni}/R_{YSZ} = 0.4$, yields total damage that is roughly two orders of magnitude lower than the R1 system with $R_{Ni}/R_{YSZ} = 1.0$. This is an indication that introducing fine features (i.e., smaller Ni particles compared to the YSZ ones) can yield microstructures that are initially more tolerant to mechanical damage due to redox strains. This trend is in qualitative agreement with experimental results of Fouquet et al. [21], who observed a positive correlation between the increase in NiO particle size at a fixed YSZ particle
Figure 4.21: On a semi-log scale, total damage (in voxel count) vs. redox strain $\epsilon^*$ for the SOFC anode systems: Under the epitaxial condition for the (a) initial and (b) coarsened systems. Under the slip condition for the (c) initial and (d) coarsened systems. Note (1) the strong Ni particle size dependence for the initial, “as-synthesized”, systems with larger Ni particles rendering the systems more susceptible to damage accumulation during re-oxidation, and (2) disappearance of the size effect for coarsened systems.

Importantly, for the coarsened systems, there appears to be a loss of the size effect observed earlier for the initial systems under both epitaxial and slip interfacial conditions, as shown in Fig. 4.21(b) and (d), respectively. That is, the benefits of introducing small Ni particles with regard to mechanical integrity are lost rapidly as coarsening proceeds during SOFC operation or reduction/oxidation. In passing, we
Figure 4.22: For the coarsened R2.5 system: Perspective views of the isolated damaged clusters with each cluster assigned a unique color at a redox strain $\epsilon^* = 3.61\%$ under (a) epitaxial and (c) slip conditions and $\epsilon^* = 6.19\%$ under (b) epitaxial and (d) slip conditions.

note that in the R1, R1.5, and R2 systems, damage distribution in terms of YSZ grain boundaries vs. bulk regions displays a quantitatively similar behavior as in the R2.5 system [cf. Fig. 4.20].

Next, we examine the role of spatial damage growth on the failure of SOFCs at the cell level. To this end, we employed the labeling algorithm by Hoshen and Kopelman [225] to track spatially isolated clusters of damaged YSZ elements at each redox strain $\epsilon^*$. We start by qualitatively observing the spatial evolution of YSZ damage. For the coarsened R2.5 anode system under the epitaxial interfacial condition,
Figure 4.23: For the coarsened R2.5 system: On a semi-log scale, a histogram of spatially isolated damaged clusters at redox strains $\epsilon^* = 3.61\%$ and $6.19\%$ under (a) epitaxial and (b) slip conditions for Ni/YSZ interfaces.

Figs. 4.22(a) and (b) are perspective views of the damage clusters at $\epsilon^* = 3.61\%$ and $6.19\%$, respectively. In these views, each spatially isolated cluster can be identified due to its unique color. Mechanical damage in the YSZ phase starts with seed points that are spatially distributed [cf. Fig. 4.22(a)]. Then, a few damaged clusters continue to grow and extend spatially [cf. Fig. 4.22(b)]. Under the slip condition for Ni/YSZ interfaces, damaged YSZ clusters at $\epsilon^* = 3.61\%$ [cf. Fig. 4.22(c)] and $\epsilon^* = 6.19\%$ [cf. Fig. 4.22(d)] exhibit similar trends to the ones under the epitaxial condition. By examining the damaged clusters shown in Fig. 4.22, the anode system with the slip interfacial condition yields a less severe damage state (damage clusters appear smaller in size) than the one with the epitaxial interfacial condition.

To quantify this effect, a histogram of such mechanically damaged clusters is constructed in order to monitor the growth and coalescence of the damaged YSZ regions. Motivated by the experimental study of Bale et al. [233], who monitored *in situ* the time-dependent mechanical damage evolution and microcracking in ceramic systems under high temperatures, a redox-strain-to-failure $\epsilon_f$ is defined as the redox strain value where the size of the largest damage cluster is proportional to the YSZ particle size, and is employed as a quantitative metric of when the mechanical integrity of the system is compromised. For the coarsened R2.5 anode system under the epitaxial
interfacial condition, Fig. 4.23(a) displays a histogram of the spatially isolated YSZ damage clusters taken at two redox strains $\epsilon^* = 3.61\%$ and $6.19\%$, corresponding to before and after mechanical failure according to our strain-to-failure criterion, respectively. The dashed line in the histogram corresponds to the YSZ particle size. The trend observed in panels (a) and (b) of Fig. 4.22, where clusters grew in size as $\epsilon^*$ increases, can be clearly seen by examining the tail of the histogram in Fig. 4.23(a). A small number of large damaged YSZ clusters prevail at large redox strain values. The above process is then repeated for the slip interfacial condition. The histogram for this case is depicted in Fig. 4.23(b). At a redox strain of $\epsilon^* = 6.19\%$, the anode system with epitaxial interfaces [cf. Fig. 4.22(b)] yields more damaged YSZ elements than the system with slip ones [cf. Fig. 4.22(d)]. This is evidenced by comparing the tails of the cluster size distributions for the system under epitaxial [cf. Fig. 4.23(a)] and slip [cf. Fig. 4.23(b)] interfacial conditions.

Finally, the redox-strain-to-failure, $\epsilon_f$, is recorded for all initial and coarsened anode systems employed in this work under both epitaxial and slip conditions for Ni/YSZ interfaces. The data is shown in Fig. 4.24 as a function Ni to YSZ particle size ratio $R_{Ni}/R_{YSZ}$. It can be clearly seen that for the initial (i.e., as-synthesized) systems, reducing the Ni particle size increases the resistance of these systems to mechanical damage due to redox cycling. This trend is observed for initial anode systems under both epitaxial and slip conditions for Ni/YSZ interfaces. On the other hand, close inspection of the data shows that coarsened anode systems yield microstructures that are significantly less tolerant to mechanical damage accumulation within the YSZ phase, as the $\epsilon_f$ values for the coarsened systems are much less than those for the initial systems. Importantly, the redox-strain-to-failure $\epsilon_f$ in coarsened anode systems exhibits essentially no dependency on the initial Ni particle size for the systems examined in this work. Furthermore, while the loss of NiO/YSZ interface
Figure 4.24: Redox-strain-to-failure $\epsilon_f$ vs. particle size ratio $R_{Ni}/R_{YSZ}$ for both initial and coarsened anode systems under epitaxial and slip conditions for Ni/YSZ interfaces. Note the strong Ni particle size dependence of $\epsilon_f$ for the initial, as-synthesized, systems and the weak Ni particle size dependence for the coarsened ones. The lines are drawn as guides to the eye.

coherency increases the redox-strain-to-failure in comparison with the fully epitaxial case, this effect is rather small especially in the case of coarsened systems.

It is worth noting that the redox-strain-to-failure values obtained above ($\lesssim 14\%$) correspond to relatively small degree of Ni oxidation values at failure ($\Phi_{NiO} \lesssim 0.20$). This is not surprising, as the YSZ phase is treated as a simple linear-elastic brittle material in this work. Additionally, comparing our simulation results to what redox experiments reveal merits more detailed attention. First, in free-standing anodes that were oxidized in air, it was observed that mechanical damage and cracking occurred after oxidation of approximately 50% of the Ni, while for anodes that were oxidized electrochemically, cracking caused failure after only ca. 5% of the Ni was oxidized, mainly due to the non-uniform nature of oxidation in the SOFC anodes [45]. In a study by Laurencin et al. [43], Ni/YSZ anodes under direct oxidation in air developed cracks under a conversion degree of Ni into NiO ranging between 58 and 71%. Experimental observations of Sarantaridis et al. [234], on the other hand, paint a more nuanced picture. In particular, they have shown that a Ni/YSZ anode system can be
completely re-oxidized at 800°C after reduction without any noticeable (i.e., macroscopic) damage, even though the YSZ network is forced to accommodate a linear expansion strain of \( \sim 0.6\% \). This suggests that during Ni re-oxidation the YSZ network accommodates the expansion strains via creep deformation mechanisms. Hence, re-oxidation experiments carried out at lower temperatures (where creep in YSZ is negligible) should reveal the development of significant damage and microcracking in the brittle YSZ phase at the relatively small degree of Ni oxidation values reported in this work.

In summary, the hallmark of our microstructure-based modeling approach is the ability to track the spatial evolution of mechanical damage and capture the interaction of YSZ damaged regions with the local microstructure. In particular, our work focused on virtually-designed random close-packed (RCP) microstructures, and the role of coarsening of the metallic phase on redox behavior. Simulation results highlight the importance of the microstructure characterized by Ni to YSZ particle size ratio on the redox behavior and damage accumulation in as-synthesized SOFC anode systems.

In order to quantify the degree by which anode microstructures become more susceptible to mechanical damage due to redox cycling, a redox-strain-to-failure criterion was developed. According to this criterion, once the largest damage cluster exceeded the YSZ particle size, the mechanical integrity of the system was deemed compromised. Notably, the redox-strain-to-failure \( \epsilon_f \) in coarsened anode systems, that were examined in this work, exhibited essentially no dependency on the initial Ni particle size. This is in contrast to the as-synthesized anode systems, which displayed a strong Ni particle size dependence in qualitative agreement with experiments [21]. With regard to the effect of absolute particle size on redox stability, experiments of Waldbillig et al. [22] indicate that a fine structured Ni/YSZ anode is more susceptible to mechanical damage than a coarser one at fixed component volume fractions, in contrast with our results which do not display any such absolute
size dependence. It should be noted, however, that samples with finer structures are subject to larger thermodynamic forces which drive coarsening processes during both reduction and re-oxidation [197], resulting in microstructures that are more susceptible to redox damage accumulation than the as-sintered ones. Thus, we suspect that the morphological evolution due to Ni phase coarsening during reduction/oxidation may significantly affect experimental studies that focus on the size-dependent redox instability in SOFC anode systems.

We also quantified the role of coherency (or the lack thereof) of NiO/YSZ interfaces on redox stress generation. More specifically, two types of interfaces were considered, namely epitaxial ones, where coherency is always maintained during the transformation of Ni to NiO via a continuity of the displacement field across the Ni/YSZ interface, and ones where the displacement field parallel to the interface in general develops a jump discontinuity. These interfacial types represent extreme cases, with real physical systems falling somewhere in between. In physical terms, the slip condition facilitates the relaxation of expansion strains parallel to NiO/YSZ interfaces, while the expansion strains perpendicular to such interfaces impart stresses within the YSZ regions. Our results demonstrate that while the loss of NiO/YSZ interface coherency increases the redox-strain-to-failure in comparison with the fully epitaxial case, this effect is rather small especially in the case of coarsened systems.

The above observations for coarsened anode systems suggest that under high utilization of SOFC cells, the role of initial Ni particle size is not a critical factor in determining the mechanical stability of these systems, at least for the class of microstructures employed in this work. More generally speaking, the main design criterion for SOFC anode materials is thus given by electrochemical performance considerations, rather than mechanical ones.
Chapter 5

Mesoscale Modeling of Bulk Metallic Glasses and Composites

In this Chapter, we utilize the continuum model that was presented in Section 3.4 to explore inelastic deformation mechanisms in monolithic bulk metallic glasses (BMGs) and investigate the role of the ductile phase on the mechanical properties of BMG composites. Two separate studies will be presented here. The first deals with the interplay between rigid and soft short range order (SRO) and their impact on the deformation and overall ductility of monolithic BMGs. The second study explores the mechanical deformation of BMG composites and the role of soft crystalline phase, area fraction and morphology, on the overall ductility.

Before we start exploring the model, it is worth noting that the physical quantities in the simulations presented here were made non-dimensional. More specifically, length scales were measured in terms of the structural correlation length $l \sim \mathcal{O}(nm)$, while units of stress and elastic constants were measured in terms of a representative shear modulus of the ductile phase that is introduced to monolithic BMGs in order to form BMG composites. Finally, a dynamic relaxation scheme given by Eq. (3.90) was used to relax the displacement field at a given applied strain increment.
5.1 Inelastic Deformation in Monolithic BMGs

In this Section, we examine the effects of rigid/soft SRO distributions on the mechanical behavior of monolithic BMGs. The findings that are presented herein were published in Physical Review Letters [235].

From the mechanics points of view, monolithic BMGs are idealized as two phase microstructures, where regions of rigid and soft SRO form the constituent phases. Let \( \phi_r \) be the area fraction occupied by rigid SRO elements, while \( 1 - \phi_r \) is the fraction occupied by the soft SRO. Regions with full icosahedra constitute rigid SRO, which have higher shear transition barriers [143]; thus, they are assigned larger \( \langle \Delta(r) \rangle = \Delta_r^0 \) values than soft SRO domains, where \( \langle \Delta(r) \rangle = \Delta_s^0 \). In order to assess the role of structural heterogeneities on the deformation behavior of BMGs, \( \langle \Delta(r) \rangle \) values for rigid/soft SRO domains were varied such that the average \( \Delta(r) \) for the whole monolithic BMG system was set to 0.6. This condition can be written as

\[
\langle \Delta(r) \rangle_{BMG} = \phi_r \Delta_r^0 + (1 - \phi_r) \Delta_s^0 = 0.6. \tag{5.1}
\]

The spatial variations in \( \Delta \) were implemented as follow: i) Two distributions \( \Delta_r(r) \) and \( \Delta_s(r) \), corresponding to rigid and soft SRO domains, respectively, were generated. \( \Delta_r(r) \) and \( \Delta_s(r) \) have the same form for the two-point correlation function (with \( \sigma^2 = 0.0125 \)) but differ in \( \langle \Delta(r) \rangle \) as discussed above. Next, lattice sites, which add up to a fraction \( \phi_r \), were independently labeled as rigid SROs. Once a given lattice site was labeled rigid (soft), its \( \Delta \) value was set equal to the local \( \Delta_r \) (\( \Delta_s \)) value.

BMG systems were simulated under simple shear loading, where the top edge was displaced with respect to the bottom one, while periodic boundary conditions were used lengthwise. Elastic constants were set to \( K(r) = 2 \) and \( \mu(r) = 2 \), while \( l = 2.0 \) and \( W = 1.0 \). The dynamical equations for the displacement field were integrated on a \( 512 \times 512 \) uniform lattice with \( \Delta x = \Delta y = 1 \) and a “non-dimensional” time step
Figure 5.1: (a) Representative microstructure of BMG1, 90% area fraction of rigid SRO. Blue (white) domains represent regions of rigid (soft) SRO. Shear strain contours for BMG1 at (b) 8% and (c) 9% nominal strain. Notice that a single shear band has formed and propagated through the sample, which is a hallmark of strain localization in monolithic BMGs.

$\Delta t = 0.003$. Other parameters that were used ($\eta^*, \xi^*, \Gamma^*$) = (0, 80, 240), which were chosen, such that stresses relax effectively instantaneously relative to the externally imposed (dimensionless) strain rate, $2 \times 10^{-4}$, up until the propagation of incipient shear bands.

Several monolithic BMGs were examined, denoted BMG1, BMG2 and BMG3, with $\phi_r$ = 0.9, 0.6, and 0.4, respectively. For these cases, $\Delta^*_0$ = 0.65, 0.82, and 1.1 and $\Delta^*_s$ = 0.21, 0.27, and 0.27 in the rigid and soft regions, respectively. In BMG1 and BMG2, rigid SRO regions percolate, while in BMG3, rigid SRO sites form spatially disconnected regions. A representative microstructure and shear strain contours at 8% and 9% nominal strain for BMG1 are shown in Figs. 5.1(a)-(c). The non-uniform strain distribution seen in Fig. 5.1(b) arises from the structural heterogeneity associated with the rigid/soft SRO regions. Above 8.5% nominal strain, the deformation in BMG1 becomes highly localized in a single shear band. Shear stress-strain curves for the three monolithic BMGs are depicted in Fig. 5.2. Ductility is enhanced, while strength is reduced, as the fraction of rigid SRO $\phi_r$ decreases. This is an indication that if the composition of the constituent phases in monolithic BMGs is fine-tuned,
such that it promotes a larger fraction of the soft “fertile” SRO, the ductility of these systems can be increased. It is worth noting that the trend observed in Fig. 5.2 is in agreement with atomistic simulations of monolithic BMGs [87, 143], where more homogeneous deformation and increased ductility were observed as the fraction of rigid SRO was decreased.

Therefore, altering the fraction and spatial distribution of rigid/soft SRO directly affect the mechanical properties of monolithic BMGs. The high strength of BMGs is attributed to a backbone of rigid SRO, while overall ductility is controlled by soft SRO regions that are spatially distributed. The optimization of mechanical properties in monolithic BMGs can be achieved by fine-tuning the solute composition in the glassy alloy, which in turn affects the structure of SROs (i.e., coordination number, packing polyhedra, critical stress for slip events). At the mesoscopic level, the fraction of rigid/soft SRO in a BMG can be optimized to yield the desired properties.
5.2 Deformation in BMG Composites

In this Section, we examine the role of soft crystalline phase (area fraction and morphology) on the mechanical deformation and enhancement in ductility of BMG composites. The results presented herein have been published in Physical Review Letters [235] and Applied Physics Letters [236].

In this work, simple geometrical shapes were assumed for the soft crystalline domains. Virtual BMG composites were then formed by randomly placing the soft crystalline particles in the glassy matrix. The design parameters here are the area fraction $\phi$ of the crystalline phase, and the number and size of crystal particles. Let us first start by incorporating isotropic crystalline domains. To this end, BMG composite microstructures with mono-dispersed crystalline disks were generated. In the following simulations, $K(\mathbf{r}) = 2.0$ and $\mu(\mathbf{r}) = 2.0$ in the glassy phase, while in the ductile phase, $K(\mathbf{r}) = 1.0$ and $\mu(\mathbf{r}) = 1.0$. Also, $l = 1.0$ and $\sigma^2 = 0.08$.

Two BMG composites, each with 40% area fraction of crystalline phase but differing in the particle size $R$ ($R = 36.5$ and $R = 10.5$, respectively), were examined. Figure 5.3(a) shows a representative BMG composite with particle size $R = 36.5$. The glassy phase was assumed to be rich in rigid SRO with $\langle \Delta(\mathbf{r}) \rangle = 0.6$, while for the ductile phase and to reflect crystal periodicity, $\Delta(\mathbf{r}) = 0.2$. BMG systems were simulated under simple shear loading, where the top edge of the simulation box was displaced relative to the bottom one, while periodic boundary conditions were used lengthwise. The dynamical equations for the displacement field were integrated on a 512 $\times$ 512 uniform lattice with $\Delta x = \Delta y = 1$ and a “non-dimensional” time step $\Delta t = 0.003$. Other parameters that were used in the simulations were set to $(\eta^*, \xi^*, \Gamma^*) = (0, 80, 240)$. To account for sample-to-sample variations, results were averaged over ten runs.

To demonstrate the mechanical behavior of these virtually synthesized BMG composites, let us examine qualitatively the behavior of the BMG composite with
Figure 5.3: (a) Representative microstructure of a BMG composite with 40% area fraction of ductile phase and particle size $R = 36.5$. Blue (white) domains represent the glassy (ductile) phases. Shear strain contours for the BMG composite at (b) 8% and (c) 11% nominal strain. Plastic strain accumulates within the ductile particles prior to shear band formation.

$R = 35.6$. Panels (b) and (c) of Fig. 5.3 show shear strain contours at 8% and 11% nominal strains, respectively. The heterogeneous nature of the BMG composite microstructure leads to a non-uniform state of deformation, as can be seen in Fig. 5.3(b). Due to the low energy barrier to slip that is associated with the ductile particles, they readily accumulate localized plastic strain. Note that a shear band is starting to develop in the BMG composite at a later stage (11% nominal strain) than the monolithic counterpart (8% nominal strain). This is an indication that the addition of ductile particles mitigates shear banding in BMG systems. To quantify this effect, we have examined the stress-strain behavior for these BMG composites, shown in Fig. 5.4.

It can be seen that BMG composites are characterized by strain-induced hardening and large plastic strain-to-failure values. At 40% area fraction of the ductile phase, the BMG composite with smaller particle size ($R = 10.5$) exhibits more ductility and higher strength values than the larger one with $R = 36.5$. This is due to the presence of glass/crystalline interfaces along with the elastic mismatch, which enable plastic deformation to be globally distributed, thereby mitigating shear band nucleation.
Figure 5.4: Shear stress, $\sigma_{xy}$, vs. shear strain, $\gamma_{xy}$, curves for the BMG composites with particle sizes $R = 36.5$ and $10.5$ (40% area fraction of crystalline phase).

Next, we examine the ultimate strength, $\sigma_{UTS}$, and total strain-to-failure, $\gamma_f$, (peak point in the stress-strain curve) as a function of area fraction $\phi$ of ductile phase and crystal particle size. To this end, BMG composites with various area fractions for the ductile phase and several sizes for the mono-dispersed crystalline disks were generated. As depicted in Fig. 5.5(a), $\sigma_{UTS}$ of a composite decreases monotonically as the content of the crystalline phase increases. At a fixed $\phi$, composites with smaller particles exhibit higher strength values. In a study by Lee et al. [90], they observed a similar trend to the one shown in Fig. 5.5(a), where the compressive/tensile yield strengths are monotonically decreasing functions of the area fraction of the ductile phase. Furthermore, Fig. 5.5(b) shows the nonlinear behavior of $\gamma_f$ as a function of $\phi$. Small area fractions are ineffective in improving ductility, while larger area fractions lead to an increase in $\gamma_f$ over the monolithic BMG. At a fixed $\phi$, a large number of small crystalline domains is more effective in obstructing the extension of shear bands than a small number of large domains. At $\phi$ values above $\sim 40\%$, ductility increases rapidly for both BMG composites. The nonlinear dependence of $\gamma_f$ as a function of $\phi$ can be related to a percolation transition in the BMG composite [90].
Now, for a given area fraction of the ductile phase, let us examine the role of crystalline particle (disk) size on the overall ductility. To this end, several BMG composites with 35% area fraction of the ductile phase and various sizes for the crystal disks were generated. Fig. 5.5(c) shows the dependency of total strain-to-failure $\gamma_f$ on the crystalline particle size. The results suggest that $\gamma_f(R) \approx \gamma_f^0 + \text{const.}/R$, implying that ductility of BMG composites can be improved by introducing fine-scale microstructural features. These trends in the data can be explained by assuming that the shear band spacing $\lambda \sim R$, and further assuming that the plastic strain $\gamma_f \approx w_{SB}/\lambda$, in accordance with Ref. [152]. Our findings suggest that, in addition to the volume fraction of the ductile phase, the mechanical properties of BMG systems can be optimized with respect to the characteristic particulate length scales and morphology.

Next, let us explore the role of the morphology of ductile phase particles on the mechanical deformation and overall ductility of BMG composites. To this end, a crystalline dendrite was idealized as two perpendicularly intersecting ellipses, shown in Fig. 5.6(a), with the angle $\alpha$ representing the orientation of the dendrite. We note that the proposed dendrite morphology collapses to the case of circular disks when the major and minor axes ($L_a$ and $L_b$, respectively) of the intersecting ellipses
Figure 5.6: (a) Idealization of a crystalline dendrite in a BMG composite. $\alpha$ is the random orientation angle of the dendrite. (b) Two-point correlation function $G(r)$ and (c) shear stress-strain curves for the BMG composites, Comp1, Comp2, and Comp3, with 30% area fraction of the ductile phase.

are set equal. Realizations of BMG composite microstructures were generated by randomly placing the ductile dendrites with random orientations in the glassy matrix. Here, the design parameters are the total area fraction of the crystalline phase $\phi$ and the length scales $L_a$ and $L_b$ associated with the dendrites. In order to extract a characteristic length scale $R$ for the crystalline dendrites, the two-point correlation function $G(r) = \langle \Theta(r)\Theta(r') \rangle$ for the BMG composite was calculated, where $\Theta(r)$ is a local phase indicator with $\Theta(r) = 1.0$ in the dendritic phase and zero elsewhere. More specifically, $R \sim (L_aL_b)^{1/2}$ corresponds to the point of the first minimum in $G(r)$. The statistics of the $\Delta(r)$ field were implemented as follow: i) To reflect periodicity in the ductile phase, $\Delta(r) = \Delta_{\text{crystal}}$ is constant and was set to 0.2. ii) $\langle \Delta(r) \rangle = \Delta_0$ in the glassy phase and was set, such that the overall average $\langle \Delta(r) \rangle_{BMG}$ for the BMG composite was fixed to 0.6. This condition can be written as

$$\langle \Delta(r) \rangle_{BMG} = \phi\Delta_{\text{crystal}} + (1 - \phi)\Delta_0 = 0.6.$$  \hspace{1cm} (5.2)
In the ductile phase, $K(r) = 2.17$, $\mu(r) = 1.0$, while in the glassy matrix $K(r) = 4.33$, $\mu(r) = 2.0$. Also, $l = 2.5$, $\sigma^2 = 0.005$, and $W = 1.0$. Other numerical parameters that were used in this study were the same as the ones employed in the simulations of BMG composites with crystalline disks. To account for sample-to-sample variations, results were averaged over ten runs.

We begin our exploration of the model by examining the effects of dendrite morphology and the associated length scales on the deformation patterns of BMG composites. To this end, three BMG composites, Comp1, Comp2, and Comp3, each with $\phi = 0.3$ and $\Delta_0 = 0.771$ but differing in the characteristic length scales associated with the dendritic microstructure, were examined. Figure 5.6(b) displays $G(r)$ for Comp1, Comp2, and Comp3, for which $R \approx 82, 25, \text{ and } 14$, respectively. Figures 5.7(a)-(c) in turn show representative microstructures of Comp1, Comp2, and Comp3. In Comp1, dendrites are represented by mono-dispersed disks whereas in Comp2, the more ramified dendrites form spatially disconnected regions. Finally, in Comp3, the dendrites are highly stretched ellipses that form a connected framework. Contours of shear strain at 10\% nominal strain are shown in Figs. 5.7(d)-(f) for Comp1, Comp2, and Comp3, respectively. The non-uniform strain distribution is due to the heterogeneous nature of the microstructures. In Comp1, a shear band formed and started to extend throughout the sample while in Comp2, pockets of localized strain can be seen. Strain is more globally distributed in Comp3 with no signs of shear banding. Figures 5.7(g)-(i) show strain contours at 11.5\% nominal strain for Comp1, Comp2, and Comp3, respectively. A fully developed shear band can be seen in Comp1 while in Comp2, several shear bands started to form and propagate in the sample implying extensive plasticity prior to catastrophic failure. In Comp3, strain is still globally distributed with the appearance of pockets of localized strain.

To quantify the instance of shear banding, we examined shear stress-strain curves for these composites, shown in Fig. 5.6(c). In all composite systems, local slip events
occur at \( \sim 3\% \) nominal strain but the composites continue to strain harden until the ultimate strength is reached. The BMG composite with smaller dendrites, Comp3, exhibits more ductility (total strain to failure) and a higher strength value than the ones with larger dendrites, Comp1 and Comp2. Nominal strain at the onset of shear banding is \( \sim 9\%, 11\%, \) and \( 13\% \) for Comp1, Comp2, and Comp3, respectively.

Figure 5.7: Representative BMG composite microstructures for (a) Comp1, (b) Comp2, and (c) Comp3. Maroon (white) domains represent the glassy (ductile) phase. Shear strain contours at 10\% nominal strain for (d) Comp1, (e) Comp2, and (f) Comp3. Shear strain contours at 11.5\% nominal strain for (g) Comp1, (h) Comp2, and (i) Comp3.
Next, we quantify the microstructural effects by examining the total strain-to-failure \( \gamma_f \) and ultimate strength \( \sigma_{UTS} \) as a function of both the area fraction \( \phi \) and the characteristic length scale \( R \) associated with the dendritic particles. We simulated BMG composites with \( \phi \) ranging from 10\% to 40\%. For a given \( \phi \), several realizations of BMG composites were obtained spanning multiple length scales for the crystal domain size. Figures 5.8(a) and (b) show plots of \( \gamma_f \) and \( \sigma_{UTS} \), respectively, as a function of \( 1/R \). The results suggest that \( \gamma_f \) and \( \sigma_{UTS} \) scale with \( 1/R \sim (L_a L_b)^{-1/2} \), implying that, at a fixed \( \phi \), ductility and strength can be enhanced by tailoring the length scales associated with the dendritic particles. More specifically, for a fixed \( \phi \), BMG composites with fine-scale microstructural features exhibit better mechanical properties than the ones with coarser crystal domains. In particular, these results suggest that for dendritic morphologies, the relevant length scale for the overall mechanical properties of the composites is \( (L_a L_b)^{1/2} \), that is, the geometric mean of the dendrite arm length and width.
In summary, we demonstrated that the mesoscale model introduced in Section 3.4 accounts for the structural heterogeneity of monolithic BMGs and BMG composites, and captures the fundamental aspects of plastic deformation in such systems. The effect of internal structure, characterized by rigid/soft short range order (SRO), on the deformation behavior of monolithic BMGs was investigated, while for BMG composites, we examined the roles of ductile particle size, morphology, and area fraction in enhancing overall ductility. In the former case, we demonstrated that the connectivity of the rigid SRO regions plays a key role in the deformation behavior of monolithic BMGs, while in the latter case, it was shown that (a) the ductility of the composite is a non-linear function of the area fraction of the reinforcement phase and (b) ductility is inversely proportional to the crystalline particle size.
Chapter 6

Conclusion and Future Outlook

In this thesis, two heterogeneous materials systems were examined, namely solid oxide fuel cells (SOFCs) and bulk metallic glasses (BMGs). Theoretical and mesoscale computational models were developed to investigate two dominant degradation mechanisms in SOFC anode systems, namely, coarsening of Ni phase, and redox instability and mechanical damage. For the BMG project, a microstructure-based continuum model was developed to study inelastic deformation mechanisms and shear banding in monolithic BMGs, and examine the role of crystalline phase attributes on the enhancement in ductility in BMG composites. The theoretical and computational tools utilized in this thesis incorporate models from various scientific disciplines, such as phase field mathematical models from the condensed matter physics community, continuum and damage mechanics concepts and theory of elasticity commonly used by applied mechanicians, and numerical algorithms for solving differential equations that are common among applied mathematicians, astrophysicists and engineers.

Chapter 1 provided an overview of solid oxide fuel cells, how they operate, key advantages and the main degradation mechanisms that hinder their use in commercial applications. Furthermore, the concept of a metallic glass was introduced. Key mechanical properties of BMGs were highlighted along with the deformation mecha-
nisms observed in these systems. In Chapter 2, the published literature was surveyed for findings concerning the coarsening of Ni phase in SOFC anodes and its impact on the topological parameters affecting electrochemical performance. Research findings on the redox instability and mechanical damage in SOFC anodes were discussed. Furthermore, experimental and modeling observations concerning the inelastic deformation and shear banding in monolithic BMGs were presented. Finally, the role of soft crystalline phase microstructure on the enhancement in ductility in BMG composites was presented.

In Chapter 3, the theoretical and computational models used in this thesis were introduced. These models can be classified into two types: i) Phase field models and ii) computational mechanics frameworks. Two examples were provided to demonstrate the phase field method, namely, spinodal decomposition using a conserved phase field, and grain growth in metals using a non-conserved order parameter. Two models were introduced to examine degradation mechanisms in SOFC anodes. The first is a phase field model for the morphological evolution, or coarsening, of Ni phase in SOFC anodes. The model combines a conserved order parameter for the Ni phase with a set of non-conserved structural order parameters to account for the polycrystalline nature of Ni. The second is a continuum model, which incorporates a damage field, for the redox instability and mechanical deformation in SOFC anodes. The hallmark of this redox modeling approach is the ability to track the spatial evolution of mechanical damage and capture the interaction of damaged regions with the local microstructure. For the BMG project, a microstructure-based model was developed for the inelastic deformation in BMGs. The model incorporates an order parameter that accounts for the structural heterogeneity of monolithic BMGs and BMG composites, and is capable of capturing the fundamental aspects of plastic deformation in these systems.

Original results for SOFCs and BMGs were presented in Chapters 4 and 5. For clarity, each Section within these Chapters corresponds to a study that was published
or is currently under review. In Chapter 4, a phase field model was developed for the morphological evolution, or coarsening, of Ni phase in SOFC anodes. Several microstructural attributes, such as three phase boundary regions, Ni phase contiguity and pore space microstructure, that affect electrochemical performance were tracked as “virtual” porous anodes evolved over time. The role of anode microstructure on the evolution of these attributes was examined and several scaling laws that govern their evolution were suggested. It was shown that smaller Ni particles can optimize the microstructural features affecting electrochemistry provided Ni phase contiguity is maintained. Our simulation results revealed that the loss of contiguity of Ni clusters in SOFC anodes can be related to Rayleigh type instability that is assisted by thermal grooving.

Also, in Chapter 4, the continuum model for the redox instability in SOFC anodes was used to examine the mechanical deformation and damage in these systems. First, simulation results on an experimentally obtained anode system revealed the role of anode microstructure and spatial configuration of the constituent phases on the evolution of mechanical stresses and development of damage during redox cycles. Next, the roles of anode microstructure, characterized by particle size and ratio, and coarsened state on the evolution of mechanical damage due to redox were examined. Simulation results revealed that in the initial, as-sintered, state smaller Ni particles yield less damage than larger Ni domains. Additionally, coarsened, or aged, anodes were found to be less resistant to mechanical damage than the corresponding ones in the initial state.

In Chapter 5, the microstructure-based model for the inelastic deformation in BMG systems was used to examine the role internal structural heterogeneity, characterized by rigid/soft short range order (SRO), on the localized deformation mechanisms in monolithic BMGs. It was shown that ductility increases and more homogeneous deformation ensues as the fraction of BMG elements exhibiting rigid SRO
characteristics decreases. A large fraction of rigid SRO, while yielding high strength values, was found to cause localized deformation, where a single operating shear band accommodates the externally applied strain. As for BMG composites, the effective interaction between shear bands and the soft ductile domains was found to enhance overall ductility. It was revealed that the spatial distribution of soft crystalline domains yields a more homogeneous state of deformation. For a given area fraction of the ductile phase, a large number of small ductile domains was found to be more effective in enhancing the mechanical properties of BMG composites than a small number of large ductile particles.

For the SOFC project, we identify two avenues that can be utilized to enhance the models used to examine the degradation mechanisms in SOFC anodes. These are: i) The addition of more microstructural features that affect the behavior of SOFC anodes. For example, the existence of impurities affects boundary motion (Ni surface and grain boundary) which in turn impacts coarsening rates. Also, providing a feedback from electrochemistry to the morphological evolution model will have a direct impact on coarsening rates. Several kinetic parameters in our phase field model for Ni coarsening are influenced by the electrochemical reactions. For example, Ni mobility is highly dependent on the temperature and water content that are associated with these reactions. For the study of redox instability in SOFC anodes, the ceramic phase is expected to accommodate a fraction of the applied strain via creep mechanisms, especially at high temperatures. Therefore, the continuum model for redox instability can be further enhanced by allowing creep deformation to take place. ii) The next avenue to explore deals with the numerical implementation of the phase field model. To fully capture the role of Ni coarsening on performance, coarsening simulations of SOFC anodes have to effectively represent anodes that are under thousands of hours of operation. Our parallel phase field model can be made more efficient by utiliz-
ing a numerical scheme that allows for larger time steps. For example, semi-implicit schemes or multi-time stepping can be utilized to increase the efficiency of the model.

For the BMG project, the model can be further enhanced by extending it to three dimensions to account for full field effects and allow for various loading scenarios to be simulated. For BMG composites, hardening laws can be added to the model to allow for intrinsic plasticity in the ductile phase, which will affect the overall mechanical properties of these systems.
Appendix A

Appendix

A.1 SOFC Coarsening Model: Derivation of Interfacial Energies

In this Section and starting with our phase field model that is presented in Section 3.2, we derive simple analytical expressions, in terms of model parameters, for the Ni phase surface and grain boundary (GB) energies.

A.1.1 Ni Surface Energy

Without loss of generality, let an anode system consist of one Ni grain; therefore, two phase fields are needed to describe the state of the Ni phase, i.e., $c$ and $\eta$ fields. At a Ni surface, both order parameters $c$ and $\eta$ will vary smoothly across the interface. Therefore, Ni surface energy $\gamma_s$ has two contributions due to variations of both $c$ and $\eta$ and is written as

$$\gamma_s = \gamma_c + \gamma_\eta,$$

(A.1)

where $\gamma_c$ and $\gamma_\eta$ are the contributions from the $c$ and $\eta$ phase fields, respectively.
Let us start by calculating the interface energy contribution due to the $c$ phase field. Assuming a constant $\eta$, the energy contribution from the $c$ phase field is written as

$$ F = \int dr \left[ m_H f(c) + \frac{w^2}{2} |\nabla c|^2 \right] = \int dr \left[ m_H (c^2 - 1)^2 + \frac{w^2}{2} |\nabla c|^2 \right]. \quad (A.2) $$

Following the treatment of interfaces by Cahn and Hilliard [168], the equilibrium profile in a one dimensional system is attained by arriving at a stationary chemical potential, i.e., $\mu = 0$. This condition can be written as

$$ \mu = \frac{\delta F}{\delta c} = m_H \frac{\partial f}{\partial c} - w^2 \nabla^2 c = 4m_H (c^3 - c) - w^2 \nabla^2 c = 0. \quad (A.3) $$

The solution of the above second order differential equation along with the boundary conditions $c \rightarrow \pm 1$ as $x \rightarrow \pm \infty$, yield the equilibrium profile $c(x)$. To solve Eq. (A.3), we first multiply both sides with $c' \equiv dc/dx$ and letting $c'' \equiv d^2 c/dx^2$ for notational convenience.

$$ 4m_H (c' c^3 - c' c) - w^2 c' c'' = 4m_H \left[ \left( \frac{c^4}{4} \right)' - \left( \frac{c^2}{2} \right)' \right] - w^2 \left( \frac{c'^2}{2} \right)' = 0. \quad (A.4) $$

Next, we integrate the above equation and note that the constant of integration is found by applying the boundary condition $c \rightarrow +1$ and $c' \rightarrow 0$ as $x \rightarrow +\infty$. The result can be written as

$$ m_H (c^4 - 2c^2 + 1) = m_H f(c) = \frac{w^2}{2} c'^2. \quad (A.5) $$

By substituting Eq. (A.5) into Eq. (A.2), we arrive at

$$ F = \int dr \left[ m_H f(c) + \frac{w^2}{2} |\nabla c|^2 \right] = \int dr \ w^2 |\nabla c|^2 = \int dr \ 2m_H f(c). \quad (A.6) $$
Figure A.1: The equilibrium profile for the phase field $c$ given by Eq. (A.8). Note that the interface width is dictated by the factor $w/\sqrt{2m_H}$, where blue, red and green curves are for $w/\sqrt{2m_H} = 0.2, 1.0$ and $3.0$, respectively.

Next, we re-arrange Eq. (A.5) in order to separate variables

$$\frac{dc}{c^2 - 1} = -\frac{\sqrt{2m_H}}{w} dx,$$  

(A.7)

and integrate both sides to arrive at

$$c(x) = \tanh \left( \frac{x}{w/\sqrt{2m_H}} \right).$$  

(A.8)

It is worth noting here that the interface width $\delta_s$ is dictated by $w/\sqrt{2m_H}$. Figure A.1 displays plots of $c(x)$ for $w/\sqrt{2m_H} = 0.2, 1.0$ and $3.0$, where it can be seen that interfaces get wider as the value of $w/\sqrt{2m_H}$ increases. Next, the surface energy is defined as

$$\gamma_s = \int dx (\Delta f + \frac{w^2}{2} |\nabla c|^2),$$  

(A.9)

where $\Delta f$ is the difference between the energy of the system and that of the homogeneous one that is obtained by the double tangent construction. In this work and
based on Eq. (A.5), $\Delta f = m_H f = (w^2/2)|\nabla c|^2$ and the surface energy is simply

$$\gamma_s = w^2 \int dx |\nabla c|^2.$$  \hspace{1cm} (A.10)

By combining Eq. (A.8) and Eq. (A.10), we arrive at the following analytical expression for $\gamma_s$

$$\gamma_s = w^2 \int_{-\infty}^{+\infty} dx |\nabla c|^2 = 2m_H \int_{-\infty}^{+\infty} dx \text{sech}^4 \left( \frac{\sqrt{2m_H} w x}{w} \right) = \frac{4w}{3} \sqrt{2m_H}.$$

(A.11)

The next step is to derive the contribution to Ni surface energy due to spatial variations in the $\eta$ phase field. According to the bulk energy in Eq. (3.47), the total energy that is associated with $\eta$ is written as

$$\mathcal{F} = \int dr \left[ A_H g(\eta) + \frac{k^2}{2} |\nabla \eta|^2 \right] = \int dr \left[ A_H (6\eta^4 - 12\eta^3 + 6\eta^2) + \frac{k^2}{2} |\nabla \eta|^2 \right].$$

(A.12)

Here, we follow the same steps that were used to find $\gamma_s$ but with the boundary conditions of $\eta \to +1$ as $x \to +\infty$ and $\eta \to 0$ as $x \to -\infty$. The equilibrium profile is found when the chemical potential of $\eta$ is stationary

$$\mu = \frac{\delta \mathcal{F}}{\delta \eta} = A_H \frac{\partial g}{\partial \eta} - k^2 \nabla^2 \eta = 24\eta^3 - 36\eta^2 + 12\eta - k^2 \nabla^2 \eta = 0.$$  \hspace{1cm} (A.13)

Multiplying both sides by $d\eta/dx$, integrating once, and using the boundary condition at $x \to +\infty$, we arrive at

$$\frac{d\eta}{dx} = \frac{-2\sqrt{3A_H}}{k} \eta(\eta - 1).$$

(A.14)
With the aid of the boundary conditions, the above differential equation is solved for \( \eta(x) \), which has the following form

\[
\eta = \frac{1}{2} \left[ 1 + \tanh \left( \frac{\sqrt{3}A_H}{k} x \right) \right].
\]

(A.15)

As in standard phase field treatments, the energy contribution due to the \( \eta \) phase field is calculated using the equilibrium profile for \( \eta \) as follows

\[
\gamma_\eta = k^2 \int_{-\infty}^{+\infty} \left( \frac{d\eta}{dx} \right)^2 dx = k \sqrt{\frac{A_H}{3}}.
\]

(A.16)

### A.1.2 Ni Grain Boundary Energy

In this Section and with the aid of the free energy functional in Eq. (3.46), we develop a simple analytical expression for Ni grain boundary (GB) energy. The geometry used for the calculation is shown in Fig. A.2, where the GB is assumed when two semi-infinite grains meet. Based on this geometry, the following assumptions are made: (a) Two planar Ni grains with phase fields \( \eta_i \) and \( \eta_j \) describing grains \( i \) and \( j \), respectively, (b) the phase fields \( \eta_i \) and \( \eta_j \) are symmetric, such that \( \eta_i = 1 - \eta_j \) and \( d\eta_i/dx = -d\eta_j/dx \), and (c) \( \eta_i = 1, \eta_j = 0 \) as \( x \to -\infty \), \( \eta_i = 0, \eta_j = 1 \) as \( x \to +\infty \) and \( d\eta_i/dx = d\eta_j/dx = 0 \) as \( x \to \pm \infty \).

Figure A.2: A schematic illustrating two semi-infinite Ni grains (grain \( i \) and \( j \)) meeting at a grain boundary and the associated profiles for their \( \eta_i \) and \( \eta_j \) phase fields.
The starting point is the introduction of the total energy contribution due to the \( \eta_i \) and \( \eta_j \) phase fields, which is written as

\[
\mathcal{F} = \int d\mathbf{r} \left[ f(\eta_i, \eta_j) + \frac{k^2}{2} (|\nabla \eta_i|^2 + |\nabla \eta_j|^2) \right],
\]

where

\[
f(\eta_i, \eta_j) = A_H \left[ -4 (\eta_i^3 + \eta_j^3) + 3 (\eta_i^2 + \eta_j^2)^2 + 1 \right].
\]

Equilibrium profiles are attained at stationary chemical potentials for \( \eta_i \) and \( \eta_j \), such that

\[
\mu_{\eta_i} = \frac{\delta \mathcal{F}}{\delta \eta_i} = \frac{\partial f}{\partial \eta_i} - k^2 \nabla^2 \eta_i = 0,
\]

\[
\mu_{\eta_j} = \frac{\delta \mathcal{F}}{\delta \eta_j} = \frac{\partial f}{\partial \eta_j} - k^2 \nabla^2 \eta_j = 0.
\]

Multiplying Eq. (A.19a) by \( \partial \eta_i / \partial x \) and Eq. (A.19b) by \( \partial \eta_j / \partial x \) and adding them yield

\[
\frac{\partial f}{\partial \eta_i} \frac{\partial \eta_i}{\partial x} + \frac{\partial f}{\partial \eta_j} \frac{\partial \eta_j}{\partial x} - k^2 \left[ \frac{\partial}{\partial x} \left( \left( \frac{\partial \eta_i}{\partial x} \right)^2 \right) + \frac{\partial}{\partial x} \left( \left( \frac{\partial \eta_j}{\partial x} \right)^2 \right) \right] = 0.
\]

We integrate both sides and apply the boundary condition at \( x \to +\infty \) to arrive at

\[
f = \frac{k^2}{2} \left[ \left( \frac{\partial \eta_i}{\partial x} \right)^2 + \left( \frac{\partial \eta_j}{\partial x} \right)^2 \right],
\]

which after re-arrangement, can be written as

\[
\frac{\partial \eta_i}{\partial x} = - \sqrt{2f/k^2 \left( 1 + \left( \frac{\partial \eta_j}{\partial \eta_i} \right)^2 \right)}.
\]
Following the treatment of Ni surface energy in Section A.1.1 and with the aid of Eqs. (A.21) and (A.17), the Ni GB energy $\gamma_{GB}$ is calculated as

$$
\gamma_{GB} = k^2 \int_{-\infty}^{+\infty} 2f \, dx = 2 \int_{1}^{0} f \, \frac{dx}{d\eta_i} \, d\eta_i \\
= -2 \int_{1}^{0} d\eta_i \, f \sqrt{k^2 \left(1 + \left(\frac{\eta_j}{\eta_i} \right)^2\right)^2 / 2f} \\
= 2k \int_{0}^{1} d\eta_i \sqrt{f},
$$

(A.23)

where the symmetry condition, $\eta_j = 1 - \eta_i$, can be used to write $f = f(\eta_i, \eta_j(\eta_i))$, and the above integration yields the following for the Ni grain boundary energy

$$
\gamma_{GB} = \frac{2k}{\sqrt{3}} \sqrt{A_H}. 
$$

(A.24)

A.2 SOFC Coarsening Model: Non-dimensional Governing Equations

In this Section, we present the steps used to arrive at the non-dimensional governing equations for the phase field model that is presented in Section 3.2. Based on the total energy functional, Eq. (3.46), the governing equations for the $c$ and $\{\eta_i, i = 1, \ldots, n_\eta\}$ phase fields can be stated as follow

$$
\frac{\partial c}{\partial t} = \nabla \cdot M \nabla \frac{\delta F_{tot}}{\delta c}, \\
\frac{\partial \eta_i}{\partial t} = -L \frac{\delta F_{tot}}{\delta \eta_i},
$$

(A.25)
which yield

\[
\frac{\partial c}{\partial t} = \nabla \cdot M \nabla \left[ m_H \frac{\partial f_1}{\partial c} + A_H \frac{\partial f_2}{\partial c} - w^2 \nabla^2 c - \xi_1 |\nabla \theta|^2 + \xi_2 \theta (1 - c^2) \right],
\]

(A.26)

\[
\frac{\partial \eta_i}{\partial t} = -L \left[ A_H \frac{\partial f_2}{\partial \eta_i} - k^2 \nabla^2 \eta_i \right],
\]

(A.27)

where \( M = M_{Ni} Q(c, \nabla c, \theta, \nabla \theta) \) and \( M_{Ni} \) is the Ni phase atomic mobility. \( f_1 \) and \( f_2 \) take on the following forms

\[
f_1(c) = (c^2 - 1)^2,
\]

\[
f_2(c, \eta_i) = \frac{1}{4}(c + 1)^2 + 3(1 - c) \sum_{i=1}^{n_i} \eta_i^2 - 2(3 - c) \sum_{i=1}^{n_i} \eta_i^3 + 3 \left( \sum_{i=1}^{n_i} \eta_i^2 \right)^2.
\]

We start by defining the non-dimensional space and time as: \( \tilde{x} = x/d_o \) and \( \tilde{t} = t/\tau \) such that \( \partial c/\partial t = (1/\tau) \partial c/\partial \tilde{t} \) and \( \nabla c = (1/d_o) \nabla \tilde{c} \). The governing equations then become

\[
\frac{\partial \tilde{c}}{\partial \tilde{t}} = \frac{\tau}{d_o^2} \nabla \cdot \tilde{M} \nabla \left[ m_H \frac{\partial f_1}{\partial c} + A_H \frac{\partial f_2}{\partial c} - \frac{w^2}{d_o^2} \nabla^2 \tilde{c} - \frac{\xi_1}{d_o^2} |\nabla \tilde{\theta}|^2 + \xi_2 \tilde{\theta} (1 - c^2) \right],
\]

(A.28)

\[
\frac{\partial \tilde{\eta}_i}{\partial \tilde{t}} = -L \left[ A_H \frac{\partial f_2}{\partial \tilde{\eta}_i} - \frac{k^2}{d_o^2} \nabla^2 \tilde{\eta}_i \right],
\]

(A.29)

A simple way to relate Ni phase diffusivity to mobility is by assuming that the chemical potential \( \mu = \mu(c) \), such that

\[
\tilde{M} \nabla \mu = M \frac{\partial \mu}{\partial c} \nabla c = D \nabla \tilde{c},
\]

(A.30)

where Ni phase diffusivity can be expressed as

\[
D = M \frac{\partial \mu_c}{\partial c} \bigg|_{c=\pm1} \approx M m_H \frac{\partial^2 f_1}{\partial c^2} \bigg|_{c=\pm1} = 8M m_H.
\]
Based on the treatment of Ni interfacial energies that is presented in Section A.1, Ni surface energy $\gamma_s$ and GB energy $\gamma_{GB}$ along with Ni interface $\delta_s$ and GB $\delta_{GB}$ widths are expressed in terms of the model parameters as: $\gamma_s \approx (4w/3)\sqrt{2m_H}$, $\delta_s \approx \sqrt{2w/\sqrt{m_H}}$, $\gamma_{GB} \approx 2k\sqrt{A_H}$ and $\delta_{GB} \approx k/\sqrt{A_H}$. We also introduce $E$ as a reference energy density scale. The governing equations then become

$$\frac{\partial c}{\partial t} = \tau D \vec{\nabla} \cdot \vec{Q} \vec{\nabla} \left[ m_H \frac{\partial f_1}{\partial c} + A_H \frac{\partial f_2}{\partial c} - \frac{m_H \delta_s^2}{2d_o} \vec{\nabla}^2 c \right. \left. - \frac{\xi_1}{d_o^2} |\vec{\nabla} \theta|^2 + \frac{\xi_2}{E} \theta (1 - c^2) \right],$$

(A.31)

$$\frac{\partial \eta_i}{\partial t} = -\tau L \left[ \frac{A_H}{E} \frac{\partial f_2}{\partial \eta_i} - \frac{A_H \delta_{GB}^2}{d_o^2} \vec{\nabla}^2 \eta_i \right].$$

By factoring out $E\delta_s^2/d_o^2$ and $E\delta_{GB}^2/d_o^2$ from the $c$ and $\eta_i$ governing equations, respectively, we arrive at

$$\frac{\partial c}{\partial t} = \tau E \delta_s^2 \vec{\nabla} \cdot \vec{Q} \vec{\nabla} \left[ m_H d_o^2 \frac{\partial f_1}{E \delta_s^2} + A_H d_o^2 \frac{\partial f_2}{E \delta_s^2} - \frac{m_H}{2E} \vec{\nabla}^2 c \right. \left. - \frac{\xi_1}{E \delta_s^2} |\vec{\nabla} \theta|^2 + \frac{\xi_2 d_o^2}{E \delta_s^2} \theta (1 - c^2) \right],$$

(A.32)

$$\frac{\partial \eta_i}{\partial t} = -\tau L_e \frac{E \delta_{GB}^2}{d_o^2} \left[ \frac{A_H}{E} \frac{d_o^2}{\delta_{GB}^2} \frac{\partial f_2}{\partial \eta_i} - \frac{A_H}{E} \vec{\nabla}^2 \eta_i \right].$$

Finally, if we introduce the following non-dimensional model parameters: $\tau = (8d_o^4m_H)/(DE\delta_s^2)$, $\tilde{m}_H = (m_H d_o^2)/(E \delta_s^2)$, $\tilde{A}_H = (A_H d_o^2)/(E \delta_s^2)$, $\tilde{w}^2 = (m_H)/(2E)$, $\tilde{\xi}_1 = \xi_1/(E \delta_s^2)$, $\tilde{\xi}_2 = (\xi_2 d_o^2)/(E \delta_s^2)$, $\tilde{k}^2 = A_H/E = k^2/(E \delta_{GB}^2)$, and $\tilde{L} = (\tau L E \delta_{GB}^2)/d_o^2$ and further assume that $\delta_s \approx \delta_{GB}$, we arrive at the non-dimensional governing
equations for $c$ and $\eta_i$

$$\frac{\partial c}{\partial t} = \tilde{\nabla} \cdot Q(c, \theta) \tilde{\nabla} \left[ \tilde{m}_H \frac{\partial f_1}{\partial c} + \tilde{A}_H \frac{\partial f_2}{\partial c} - \tilde{w} \tilde{\nabla}^2 c - \tilde{\xi}_1 |\tilde{\nabla} \theta|^2 + \tilde{\xi}_2 \theta (1 - c^2) \right],$$

$$\frac{\partial \eta_i}{\partial t} = -\tilde{L} \left[ \tilde{A}_H \frac{\partial f_2}{\partial \eta_i} - \tilde{k} \tilde{\nabla}^2 \eta_i \right].$$

(A.33)

### A.3 Redox Transformation Strains: An Analytical Treatment

In this Section, we develop a closed-form solution for the mechanical stresses and strains that develop in the Ni and YSZ phases, when a Ni transformation strain develops due to a redox reaction. The following assumptions are made for the geometry and boundary conditions: i) A one-dimensional Ni/YSZ system is assumed, where $\phi_{Ni}$, and $\phi_{YSZ} = 1 - \phi_{Ni}$ denote the fraction of Ni, and YSZ in the system, respectively, ii) the Ni/YSZ anode system is clamped at both ends, such that the displacement is set to zero, and iii) the Ni transformation strain that is associated with the redox reaction is $\epsilon^*$. A schematic representation of the Ni/YSZ anode system is shown in Fig. [A.3].

First, for a given Ni transformation strain $\epsilon^*$, the net macroscopic strain is zero since the system is clamped at both ends. Using the rule of mixtures, we can write this condition as

$$\epsilon_{tot} = \phi_{YSZ} \epsilon_{YSZ} + \phi_{Ni} \epsilon_{Ni} = 0,$$

(A.34)

where $\epsilon_{Ni}$ and $\epsilon_{YSZ}$ are the strains that develop in the Ni and YSZ phases, respectively.
due to the transformation strain \( \epsilon^* \). Elastic stresses are expressed as

\[
\sigma_{YSZ} = E_{YSZ}\epsilon_{YSZ},
\]
\[
\sigma_{Ni} = E_{Ni}(\epsilon_{Ni} - \epsilon^*),
\]

where \( E_{Ni} \) and \( E_{YSZ} \) are Young’s moduli of the Ni and YSZ phases, respectively.

Equilibrium of adjacent Ni and YSZ volume elements imply that the stress in the Ni phase \( \sigma_{Ni} \) and the one in the YSZ \( \sigma_{YSZ} \) are equal, which yields

\[
\epsilon_{YSZ} = \frac{E_{Ni}}{E_{YSZ}}(\epsilon_{Ni} - \epsilon^*).
\]

Combining Eqs. (A.37) and (A.34) yields the following compatibility equation

\[
\epsilon_{tot} = \phi_{YSZ} \left[ \frac{E_{Ni}}{E_{YSZ}} (\epsilon_{Ni} - \epsilon^*) \right] + \phi_{Ni} \epsilon_{Ni} = 0,
\]

which can be re-arranged in order to arrive at the following expression for the strain in the Ni

\[
\epsilon_{Ni} = \frac{\phi_{YSZ} E_{Ni}}{\phi_{YSZ} E_{YSZ} + \phi_{Ni}} \epsilon^*.
\]

Next, we substitute Eq. (A.39) into Eq. (A.36) in order obtain the following expression for the stress in the Ni phase in terms of the transformation strain

\[
\sigma_{Ni} = E_{Ni}(\epsilon_{Ni} - \epsilon^*) = \frac{-\phi_{Ni} E_{Ni}}{\phi_{YSZ} E_{YSZ} + \phi_{Ni}} \epsilon^*.\]
Figure A.4: For a one-dimensional Ni/YSZ system: A comparison between the analytical solution and simulation results assuming $E_{Ni} = 1.0, E_{YSZ} = 2.0, \phi_{Ni} = 1/3, \phi_{YSZ} = 2/3$ and $\epsilon^* = 0.5$. The length of the Ni/YSZ anode is assumed 1.0.

In summary, for a transformation strain $\epsilon^*$ in the Ni phase due to a redox reaction, the mechanical stress and strain in the Ni are given by

\begin{align}
\sigma_{Ni} &= -\phi_{Ni} E_{Ni} \frac{E_{Ni}}{\phi_{YSZ} E_{YSZ} + \phi_{Ni}} \epsilon^*, \\
\epsilon_{Ni} &= \phi_{YSZ} E_{Ni} \frac{E_{Ni}}{\phi_{YSZ} E_{YSZ} + \phi_{Ni}} \epsilon^*,
\end{align}

(A.41)  
(A.42)

whereas the stress and strain the YSZ phase are given by

\begin{align}
\sigma_{YSZ} &= -\phi_{Ni} E_{Ni} \frac{E_{Ni}}{\phi_{YSZ} E_{YSZ} + \phi_{Ni}} \epsilon^*, \\
\epsilon_{YSZ} &= -\phi_{Ni} E_{Ni} \frac{E_{Ni}}{\phi_{YSZ} E_{YSZ} + \phi_{Ni}} \epsilon^*.
\end{align}

(A.43)  
(A.44)
Finally, we employ the continuum model for redox instability in SOFC anodes, which in presented in Section 3.3, to simulate a one-dimensional Ni/YSZ anodes system with a prescribed Ni transformation strain $\epsilon^*$. The results are then compared to the exact solutions, Eqs. (A.42) and (A.44), in order to demonstrate that the numerical scheme, presented in Section 3.3.2, leads to convergent results. For example, in terms of non-dimensional units for the length scale and stress, we let: $E_{Ni} = 1.0, E_{YSZ} = 2.0, \phi_{Ni} = 1/3, \phi_{YSZ} = 2/3, \epsilon^* = 0.5$, while the length of the Ni/YSZ system is assumed 1.0. Parameters of the numerical scheme were set to $(\eta^*, \xi^*, \Gamma^*, \Delta t) = (50.0, 0.0, 100.0, 0.001)$. Figure A.4 shows our simulation result for the one-dimensional Ni/YSZ stack along with the exact solution that is obtained from Eqs. (A.42) and (A.44). It can be clearly seen that the dynamic relaxation scheme that is presented in Section 3.3.2 yields results that are in excellent agreement with the closed-form solutions for the case of a one-dimensional Ni/YSZ system under a prescribed Ni transformation strain.
Bibliography


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