THE REDUCTION OF NICKEL DOPED
FLUORITE AND PEROVSKITE
STRUCTURED OXIDES

by

Amy Morrissey
A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

Golden, Colorado

Date __________________________

Signed: _________________________
Amy Morrissey

Signed: _________________________
Dr. Ivar E. Reimanis
Thesis Advisor

Golden, Colorado

Date __________________________

Signed: _________________________
Dr. Ivar E. Reimanis
Professor and Interim Department Head
Department of Metallurgical and Materials Engineering
ABSTRACT

A powerful technique for preparing metal-oxide nanocomposites is internal reduction. The selective reduction of the least redox stable species creates a distribution of fine metallic precipitates in the microstructure, resulting in unique electrochemical and functional properties. Transition metal dopants, when added to fluorite and perovskite structured zirconia-based ceramics, reduce more easily in low oxygen partial pressure than constituents of the parent lattice. Nickel oxide (NiO) dopant is commonly added to ceramics that are used in fuel cells, catalysis, nanoionic devices, and many other electrochemical applications to aid microstructure development. An improved understanding of the mechanism for internal reduction of NiO-doped oxides will enable greater nanostructural control and will lead to smart engineering of nanoionic and catalytic devices.

Specifically the studies in this dissertation evaluate the microstructural influences on the overall internal reduction mechanism and reaction kinetics. Microstructural features have unique local chemistry compared to the bulk which can influence the mass transport by creating chemical and electrical gradients. The baseline microstructures are heavily characterized by this work to understand the distribution of NiO dopant prior to internal reduction. The current model describing the mechanism of internal reduction only explains mass transport in single crystals, neglecting space charge effects, and assumes that oxygen species are immobile. To overcome these limitations, internal reduction mechanisms are evaluated in polycrystalline NiO-doped YSZ with some porosity. It is possible to distinguish stages of reduction as they relate to microstructural features through systemic experimentation by varying temperature, oxygen partial pressure, and soak time. Each stage is described by distinct kinetics and magnetic signatures, showing that it is possible to tailor metal-oxide nanocomposites with nanoscale control of features. Redox cycling is performed to describe the reversibility and stability of the reduced microstructure.

The solubility of NiO dopant in BZY powders and pellets was examined prior to reduction studies. As a result, this dissertation characterizes the distribution and excess barium nickel oxide phases in NiO-doped BZY. Reduction experiments on NiO-doped BZY powders are used to show that chemical segregation during particle growth leads to selective reduction behavior. By varying the amount of NiO dopant, it is possible to ratchet the amount of excess barium nickel oxide in powders. Although the internal reduction mechanism is not described by this work, a foundation for magnetic characterization of NiO-doped BZY is provided for future studies.
# TABLE OF CONTENTS

ABSTRACT ........................................................................................................................................ iii  
LIST OF FIGURES ........................................................................................................................... viii  
LIST OF TABLES ............................................................................................................................. xiv  
LIST OF SYMBOLS ........................................................................................................................ xvi  
LIST OF ABBREVIATIONS ................................................................................................................ xviii  
ACKNOWLEDGMENTS ......................................................................................................................... xix  
DEDICATION .................................................................................................................................... xxi  

## CHAPTER 1 GENERAL INTRODUCTION ...................................................................................... 1  
1.1 Nickel Oxide Additions in YSZ ................................................................................................. 3  
1.2 Nickel Oxide Additions in BZY ............................................................................................... 5  
1.3 Motivation for Reduction Studies ............................................................................................ 6  
1.4 Overview of Thesis Layout ....................................................................................................... 6  

## CHAPTER 2 BACKGROUND ........................................................................................................ 8  
2.1 Reduction-Oxidation Reactions ............................................................................................... 8  
2.1.1 Conservation Rules ............................................................................................................ 8  
2.1.2 Model of Oxidation ........................................................................................................... 9  
2.1.3 Models of Internal Reduction ........................................................................................... 11  
2.2 Thermodynamic Considerations for Reduction of NiO ............................................................ 14  
2.3 Kinetic Considerations for Reduction of NiO .......................................................................... 18  
2.4 Defect Equilibrium and Kinetics ............................................................................................ 20  
2.5 Mass Transport During Reduction of NiO-doped YSZ ............................................................ 24  
2.5.1 Chemical Potential .......................................................................................................... 27  
2.5.2 Electrical Potential .......................................................................................................... 28  
2.6 Magnetic Properties .............................................................................................................. 29  
2.6.1 Paramagnetism .............................................................................................................. 30
2.6.2 Ferromagnetism ................................................................. 30
  2.6.2.1 Magnetic Domains .................................................... 31
2.6.3 Superparamagnetism .......................................................... 32

2.7 Characterization Techniques .................................................. 33
  2.7.1 Focused Ion Beam (FIB) Milling ....................................... 33
  2.7.2 Transmission Electron Microscopy (TEM) Micrograph Analysis .... 34
  2.7.3 Laser Atom Probe Tomography (APT) Analysis .................... 34
  2.7.4 Inductively Coupled Plasma (ICP) Analysis ....................... 35
  2.7.5 Principles of SQUID Magnetometry ................................... 35
    2.7.5.1 DC Susceptibility .................................................. 36
    2.7.5.2 AC Susceptibility .................................................. 36

CHAPTER 3 EXPERIMENTAL .......................................................... 38
  3.1 Synthesis ................................................................. 38
  3.2 Reduction Furnace Assembly .............................................. 38
  3.3 Calibration of Oxygen Sensor ............................................ 39
  3.4 Calibration of Mass Flow Rate .......................................... 42
  3.5 Reduction ................................................................. 44
  3.6 Reduction-Oxidation (Redox) Cycling .................................... 46
  3.7 Characterization ........................................................... 46
    3.7.1 Inductively Coupled Plasma (ICP) Analysis ...................... 46
    3.7.2 Transmission Electron Microscopy (TEM) Analysis ............. 47
    3.7.3 Atom Probe Tomography (APT) Analysis .......................... 47
    3.7.4 SQUID Magnetometry ................................................ 48
      3.7.4.1 Direct Current (DC) Measurements ............................. 48
      3.7.4.2 Alternating Current (AC) Measurements ...................... 48
  3.8 Geometric Model of the Extent of Reaction ............................ 48
| Figure 2.1 | Illustration of Carl Wagner’s model of oxidation | 9 |
| Figure 2.2 | Proposed mechanism of internal reduction in oxide solid solutions as described by Schmalzried and Backhaus-Ricoult | 12 |
| Figure 2.3 | Proposed mechanism of internal reduction in an oxide solid solution as described by Ostyn and Carter | 13 |
| Figure 2.4 | Proposed mechanism of internal reduction in polycrystalline NiO-doped 10YSZ as described by White et al. | 14 |
| Figure 2.5 | Ellington-Richardson diagram with oxygen isobars for the oxidation reaction | 15 |
| Figure 2.6 | Ellingham-Richardson diagram with \( P_{H_2O}/P_{H_2} \) isobars for the reduction reaction | 16 |
| Figure 2.7 | Oxidation and reduction zones as a function of percent hydrogen, percent humidity, and temperature | 17 |
| Figure 2.8 | Plot showing the competition between the energy needed to nucleate a volume of a new phase and the associated interfacial energy | 19 |
| Figure 2.9 | A depiction of the contact angle for heterogeneous nucleation (a) on a free surface and (b) on a grain boundary | 19 |
| Figure 2.10 | Representative curves for (a) zero order reactions, (b) first order reactions, and (c) second order reactions | 19 |
| Figure 2.11 | A general depiction of the Brouwer diagram, for which the majority carrier can be segmented by oxygen partial pressure: low (n-type defects dominate), medium (intrinsic defects dominate), and high (p-type defects dominate) | 21 |
| Figure 2.12 | Brouwer diagram solved for YSZ showing how the defect concentration varies over oxygen partial pressure. In the selected conditions, the extrinsic defects introduced by the drop in oxygen partial pressure are less than the intrinsic oxygen vacancy concentration due to the dopant | 25 |
| Figure 2.13 | The effect of particle size on the magnitude of coercivity, where MD is multidomain particles, SD is single domain particles, and SP is a superparamagnetic particles | 32 |
| Figure 3.1 | Flow diagram of reduction build | 40 |
| Figure 3.2 | Dedicated furnace assembly for reduction runs | 40 |
| Figure 3.3 | Itemized build list for reduction furnace | 41 |
| Figure 3.4 | Photograph showing the (a) internal reference for in-situ measurement and (b) external oxygen sensors for ex-situ calibrations | 42 |
| Figure 3.5 | Micropoas internal reference oxygen sensor calibration data | 43 |
Figure 3.6 Plot showing oxygen partial pressure versus percent hydrogen for isotherms of 600°C, 800°C, and 1000°C.

Figure 3.7 A two-dimensional illustration of the the extent of reaction zone for polycrystalline cross-sections, considering only the extent of reaction from one external surface.

Figure 4.1 SEM micrograph showing the as-sintered polycrystalline microstructure of 0.5 molar % Ni-doped 10YSZ that contains average grains approximately 5 µm and approximately 5 % pre-existing porosity.

Figure 4.2 TEM micrograph showing pre-analysis representative APT specimen prepared from grain interior region of as-sintered pellet and reconstructions showing only Ni²⁺ species in characterized volume of 1.3 million atomic counts. A side and top view of reconstructions for only Ni²⁺ species shows a random distribution in the grain interior.

Figure 4.3 TEM micrograph showing pre-analysis representative APT specimen prepared from grain boundary region of as-sintered pellet and reconstructions showing only Ni²⁺ species in characterized volume of 3.5 million atomic counts. A side view of the reconstruction might appear to show higher counts at the grain boundary; however, a top view reconstruction shows no segregation along the grain boundary. The concave curvature of the grain interior with higher counts and the conical shape of the specimen produces a larger volume at greater depths and increased Ni²⁺ count density.

Figure 4.4 Optical micrographs of cross-sectioned 1000°C, $P_{O_2} \sim 10^{-15}$ atm (wet) reduced pellets. The reaction front moves inward from the exterior surfaces and results in a color change in the cross-section (tan to gray) as metallic Ni⁰ particles form. The extent of reduction is shown for various soak times: (b) 0.5 h, (c) 5 h, (d) 10 h, (e) 25 h, and (f) 50 h when the reaction front has swept the entire cross-sectional thickness.

Figure 4.5 Plot of the square extent of reaction versus time for the various experimental conditions: 1000°C, Dry $P_{O_2} \sim 10^{-19}$ atm, 900°C, Dry $P_{O_2} \sim 10^{-19}$ atm, 1000°C, Dry $P_{O_2} \sim 10^{-15}$ atm, and 1000°C, Wet $P_{O_2} \sim 10^{-15}$ atm. The thickness of the reaction layer squared varies linearly as a function of reduction time, indicating that the reaction is diffusion limited (parabolic kinetics). As expected, the highest rate (steepest slope) occurs in the 1000°C $10^{-19}$ atm reduced pellet. The error bars represent a 95% confidence interval.

Figure 4.6 TEM micrographs of reduced specimen after 5 h at 1000°C in 2% H₂ showing faceted metallic Ni⁰ particle in pre-existing pore that is representative of stage 1 reduction.

Figure 4.7 Magnetization versus field curves taken at 100 K showing the magnetic saturation for reductions at various times in 1000°C, Dry $P_{O_2}$ $10^{-19}$ atm. The magnitude of magnetic saturation correlates to the mass of metallic Ni⁰ due to reduction. As more Ni⁰ particles form with longer soak times the magnetic saturation increases. The precision of the SQUID magnetometry measurement is represented by the size of the data points.

Figure 4.8 Plot showing the percent of reduced metallic Ni⁰ versus soak time calculated from the saturation of mass magnetization for various reduction treatments. The pellets reduced at 1000°C, $P_{O_2} \sim 10^{-19}$ atm show deviation from a linear trends as soak times increase indicating there is a change in reduction kinetics. A linear trend is observed for the other experimental conditions which did not show microstructural features associated with stage 3 reduction at these soak times. The precision of the SQUID magnetometry measurement is represented by the size of the data points.
Figure 4.9 TEM micrographs of reduced specimen after 25 h at 1000°C, $P_{O_2} \sim 10^{-19}$ atm showing (a) YSZ grain boundary with coarsened metallic Ni$^0$ particles and increased strain contrast representative of late stage 2 reduction and (b) interior of YSZ grain with superparamagnetic Ni$^0$ particles in voids representative of stage 3 reduction.

Figure 4.10 Real $\chi'$ and imaginary $\chi''$ components of the AC susceptibility for 5, 10, 25, and 50 h soak times. The $\chi'$ for the 5 h soak shows a combination of Ni$^{2+}$ and large metallic Ni$^0$ particles (gradual increase after 100 K). The maximum in $\chi'$ is indicative of Ni$^0$ particle size, where lower temperatures correspond with superparamagnetic Ni$^0$ particles. The peak at 11 K in the 10 h soak shifts to higher temperatures as soak time increases, indicative of metallic Ni$^0$ particle growth. Note that the scale of the Y-axis is 10 times larger in the 25 and 50 h soak times than the 5 and 10 h soak times. The precision of the SQUID magnetometry measurement is represented by the size of the data points.

Figure 4.11 Schematic of the stages of reduction in polycrystalline Ni-doped 10YSZ at 1000°C. Electronic defects are introduced at the surface. In stage 1 (a) oxygen vacancies and electrons diffuse along the grain boundaries as charge neutral species and react with Ni$^{2+}$ in pre-existing pores. In stage 2 (b) Ni$^{2+}$ on Zr$^{4+}$ sites diffuse to the grain boundaries where it reacts with electrons to form metallic Ni$^0$ and drives a counter flux of zirconium and oxygen vacancies into the grain interiors. In stage 3 (c) superparamagnetic Ni$^0$ forms due to the increased concentration of vacancies in the grain interiors that lower the nucleation energy by creating a free surface (void) and coarsen with longer times. The shaded region around the grain boundary indicates the space charge layer.

Figure 4.12 Cross-sectioned pellets stood on edge, comparing as-sintered 10YSZ and 66 h reduced 10YSZ pellets. The 66 h reduced pellet shows darkening in the interior.

Figure 4.13 TEM micrographs showing features of the unreduced microstructure (a) a pre-existing pore, (b) a triple boundary, and (c) a single grain boundary at higher magnification.

Figure 4.14 TEM micrographs showing Run 2742 pre-run APT run analysis.

Figure 4.15 Run 2742 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.16 TEM micrographs showing Run 2745 pre-run APT run analysis.

Figure 4.17 Run 2745 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.18 TEM micrographs showing Run 2744 pre-run APT run analysis.

Figure 4.19 Run 2744 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.20 TEM micrographs showing Run 2746 pre-run APT run analysis.

Figure 4.21 Run 2746 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.22 TEM micrographs showing Run 2747 pre- and post-run APT run analysis.
Figure 5.2 Plots of AC susceptibility showing the real $\chi'$ and imaginary $\chi''$ components for (a) reduction 1, (b) oxidation 1, (c) reduction 2, and (d) oxidation 2. The temperature for which the peak in $\chi'$ occurs corresponds to particle size. The growth of Ni$^{0}$ particles from reduction 1 to 2 is observed by the peak shift to higher temperature. The peak in oxidation 1 and 2 is equivalent to reduction 1, and indicates the size of superparamagnetic Ni$^{0}$ particles in the reduced core volume is stable after redox cycling. 

Figure 5.3 TEM micrographs showing (a) a metallic Ni$^{0}$ particle at a grain boundary and associated strain contrast, (b) absence of metallic Ni$^{0}$ and strain contrast at the grain boundary after oxidation 1, (c) as-reduced microstructure with metallic Ni$^{0}$ particles that have nucleated in voids in a grain interior during internal reduction, and (d) oxidation 2 microstructure having voids filled with NiO in the grain interior after the second redox cycle.

Figure 5.4 A summary of the microstructure features is illustrated for each pellet. As-sintered pellets contain pores and grain boundaries with even Ni$^{2+}$ distribution. Reduction 1 has a distribution of Ni$^{0}$ form with sizes depending on location: $\sim 200$ nm in pores, $\sim 30$ nm along grain boundaries, and $\sim 5$ nm is grain interiors. Oxidation 1 converts the Ni$^{0}$ in grain interiors to NiO, while Ni$^{0}$ in pores and grain boundaries dissolve in the oxidation front. This is not the case for the reduced core, where $\sim 5$ nm Ni$^{0}$ remain and all the Ni$^{0}$ in pores and grain boundaries has converted to NiO. Reduction 2 results in a distribution of Ni$^{0}$ particle sizes similar to reduction 1, with exception that Ni$^{0}$ particles in the grain interiors grow. Oxidation 2 follows the trend of oxidation 1.

Figure 5.5 Optical micrographs showing an as-sintered pellet and the top view of redox cycled pellets.

Figure 5.6 Optical micrographs showing the extent of the reaction front for redox cycled pellets after (a) one cycle and (2) cycles.

Figure 5.7 Optical micrographs showing the extent of the oxidation front for redox cycled pellets (oxidation 1) after (a) 0.5 h, (b) 5 h, (c) 10 h, and (d) 25 h.

Figure 5.8 Optical micrographs showing the extent of the reduction front for redox cycled pellets (reduction 2) after (a) 0.5 h, (b) 5 h, (c) 10 h, and (d) 25 h.

Figure 5.9 Plot showing the squared extent of reaction squares versus time for the reduction 1 and reduction 2 reaction fronts.

Figure 6.1 Powder X-ray diffraction patterns for various nickel content in BZY15 powders calcined at 900°C for 10 h shows no impurity peaks and matches cubic phase BZY.

Figure 6.2 Powder X-ray diffraction patterns for various nickel content in BZY15 powders calcined at 950°C for 10 h shows impurity peaks at $\theta$ equals $\sim 23$ and $\sim 34$ degrees for all powders.

Figure 6.3 Powder X-ray diffraction patterns for various nickel content in BZY15 powders calcined at 1000°C for 10 h shows impurity peaks at $\theta$ equals $\sim 23$ and $\sim 34$ degrees for all powders.

Figure 6.4 M(T) curves for powders calcined at 900°C for 10 h shows all Ni dopant levels follow the same linear slope.
| Figure 6.5 | Mass magnetization versus nickel concentration curves measured at 5K for fresh/aged powders and sintered pellets. | 106 |
| Figure 6.6 | M(T) curves for pellets sintered at 1600°C for 24 h show very different slopes, particularly for higher Ni dopant concentrations. The data presented for 4.0 molar % Ni and 8.0 molar % Ni cannot be used to quantify excess phases because the pellets melted during sintering. | 108 |
| Figure 6.7 | TEM micrograph showing partially sintered 4.0 molar % Ni-doped BZY15 nano powders reduced at 600°C for 30 minutes having ±10 nm superparamagnetic metallic Ni particles on the surface (circled). | 110 |
| Figure 6.8 | TEM micrograph showing partially sintered 4.0 molar % Ni-doped BZY15 nano powders reduced at 900°C for 5 h having ±30 nm ferromagnetic metallic Ni particles on the surface (circled). | 110 |
| Figure 6.9 | TEM micrograph showing 4.0 molar % Ni-doped BZY15 (a) as-calcined, (b) after reduction at 600°C for 30 minutes, and (c) after reduction at 900°C for 5 h. The BaNiO_x layer and nodules that are visible in as-calcined powders decreases after reduction at 600°C for 30 minutes, and is completely reduced at 900°C after 5 h leaving pristine crystalline surfaces. | 111 |
| Figure 6.10 | Magnetization versus field at T = 100 K for 4.0 molar % Ni powders reduced at 600°C, 30 min or 900°C, 5 hours. The units are emu/g-sample and note the right hand scale (600°C sample) is 1/10th the left hand scale (900°C sample). | 111 |
| Figure 6.11 | AC susceptibility versus temperature curves for 900°C, 5 h reduced 4.0 molar % Ni powders. | 112 |
| Figure 6.12 | AC susceptibility versus temperature curves for 600°C, 30 min reduced 4.0 molar % Ni powders. | 112 |
| Figure 6.13 | Schematic describing the mechanism of excess BaNiO_x phase formation during decomposition of char precursor. | 114 |
| Figure 6.14 | A model was applied to determine the molar % Ni that can be accommodated as a monolayer based upon particle size. | 115 |
## LIST OF TABLES

| Table 2.1 | The calculated values of the concentration of oxygen vacancies and electrons determined from the Brouwer diagram for various oxygen partial pressures. | 24 |
| Table 2.2 | A summary of bulk diffusion coefficient and activation energies of species in NiO-doped 10YSZ. | 27 |
| Table 3.1 | Experimental mixtures of Ar and H$_2$ used to calibration the external oxygen sensor. | 44 |
| Table 3.2 | Summary of experimental conditions for reduction. | 45 |
| Table 4.1 | A summary of the observed blocking temperatures with calculated particle diameter shows coarsening of superparamagnetic metallic Ni$^0$ particles. | 62 |
| Table 4.2 | A summary of the parabolic rate of stage 1 reduction, comparing the measured rate to the corrected rate that accounts for the extra distance that oxygen vacancies diffuse along porosity. | 62 |
| Table 4.3 | Summary of atom probe tomography runs for grain interior and grain boundary. | 71 |
| Table 4.4 | Summary of atom probe tomography runs for grain interior and grain boundary of reduced specimens. | 76 |
| Table 4.5 | The diffusion distance due to a concentration gradient is compared to the radius of a sphere of YSZ needed to produce an equivalent amount of nickel ions to explain coarsening of superparamagnetic Ni$^0$ particles. | 87 |
| Table 5.1 | Summary of the total Ni$^0$ measured in pellet sections from each redox step. | 92 |
| Table 6.1 | Summary of characterized powders categorized by calcination and characterization date to define fresh versus aged designation. | 102 |
| Table 6.2 | The measured spins per Ni ion at low temperature for various BaNiO$_x$ type phases. The reference is spins per Ni for fresh powders only. | 105 |
| Table 6.3 | The spins per Ni ion measured at 5 K for various Ni dopant levels in fresh/aged powders and sintered pellets. The aged powders are in close agreement to theoretical predicted value of 2.83 Bohr magnetons for high spin Ni$^{2+}$. All powders were measured at NIST. | 107 |
| Table 6.4 | Crystallite size determined by Rietveld refinement using GSAS and results listed are for 900°C-10 hour calcined powders. | 109 |
| Table 6.5 | Summary of the calculated molar % of Ni dopant in BZY char. | 117 |
| Table 6.6 | Summary of nitrogen physisorption measurements taken on the 4.0 molar % Ni doped BZY powders reduced at 600°C for 30 minutes. | 118 |
| Table B.1 | Thermal gas properties for mass flow controller gas GCF calculations. | 144 |
Table D.1  Summary of NiO-doped 10YSZ specimens and run number. (X) indicates that the tip was liberated during the run.  . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . 151
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a$</td>
<td>Activity</td>
</tr>
<tr>
<td>$C_M$</td>
<td>Molar concentration</td>
</tr>
<tr>
<td>$C_S$</td>
<td>Surface molar concentration</td>
</tr>
<tr>
<td>$C_X$</td>
<td>Equilibrium molar concentration</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Initial molar concentration</td>
</tr>
<tr>
<td>$c_i$</td>
<td>Carrier concentration</td>
</tr>
<tr>
<td>$D$</td>
<td>Diffusivity</td>
</tr>
<tr>
<td>$D_0$</td>
<td>Diffusion coefficient</td>
</tr>
<tr>
<td>$E$</td>
<td>Voltage</td>
</tr>
<tr>
<td>$E_{act}$</td>
<td>Activation energy</td>
</tr>
<tr>
<td>$e$</td>
<td>Charge of an electron</td>
</tr>
<tr>
<td>$F$</td>
<td>Faraday’s constant</td>
</tr>
<tr>
<td>$\Delta G$</td>
<td>Gibbs free energy</td>
</tr>
<tr>
<td>$H$</td>
<td>Applied magnetic field</td>
</tr>
<tr>
<td>$\Delta H$</td>
<td>Change in enthalpy</td>
</tr>
<tr>
<td>$J$</td>
<td>Molar flux</td>
</tr>
<tr>
<td>$j$</td>
<td>Flux</td>
</tr>
<tr>
<td>$k$</td>
<td>Parabolic rate constant</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$L$</td>
<td>Thickness</td>
</tr>
<tr>
<td>$M$</td>
<td>(Mass) magnetization</td>
</tr>
<tr>
<td>$M_{sat}$</td>
<td>Magnetization saturation</td>
</tr>
<tr>
<td>$N$</td>
<td>Number of sites</td>
</tr>
<tr>
<td>$P$</td>
<td>Partial pressure</td>
</tr>
<tr>
<td>$Q$</td>
<td>Activation energy</td>
</tr>
</tbody>
</table>
LIST OF ABBREVIATIONS

Atom Probe Tomography .................................................. APT
Yttria-doped Barium Zirconate ....................................... BZY
Focused Ion Beam .............................................................. FIB
Inductively Coupled Plasma ............................................... ICP
Transmission Electron Microscopy ..................................... TEM
Super Conducting Quantum Interference Device .................. SQUID
X-Ray Diffraction ............................................................ XRD
Yttria-stabilized Zirconia .................................................. YSZ
ACKNOWLEDGMENTS

First, I would like to thank my advisor Ivar Reimanis. I am very fortunate for the opportunity to work and learn with you throughout this project that is funded by the National Science Foundation, Ceramics Program, Grant Number DMR 1003030. Thank you to my other committee members: Brian Gorman, Jianhua Tong, Jim O’Brien, and Neal Sullivan. I have tremendous respect for you all as scientists, and thank you for keeping me accountable in your respective fields of expertise. I am grateful for each of you throughout the years for your support and encouragement.

I cannot continue without thanking Dave Diercks. You are a big part of my microscopy success, from teaching me atom probe specimen preparation on the FIB through operating the atom probe. I am grateful for your patience and the opportunity to learn from one of the best. I’d also like to give thanks to Gary Zito for all that you do to keep the TEM up and running (or very timely updates when things were not up and running).

Thank you Mike Sanders. You deserve this whole paragraph. I might be years behind where I am at now without your experience with electronic communications, electrical wiring, LabView, etc. (the list goes on) during the fabrication and assembly of Skippy the Wonder Cart (Skippy wouldn’t even have a name!). You have always pointed me in the right direction, whether in personal or academic affairs. You are a great friend and I promise to never forget your birthday.

A big thanks to my peers in CCAC for impromptu hallway conversations, coffee runs, laughs, and empathy. Specifically, I want to thank Taylor Wilkinson. You are a tremendous friend and I know we will keep in touch in the years to come. I also want to thank my research group members and office mates Yachao Chen and Jaya Dorsey for your encouragement at the end. There are too many more of you to name and I hope our paths cross in the future.

Thank you to Foothills Running and Cycling Club (FRCC) for helping me achieve a side goal, running my first marathon. If you’re reading this as a PhD student, please know that I do not recommend running your first marathon while pursuing a PhD. I skipped a lot of training runs that made for a difficult race day but I never skipped Saturday morning endurance runs with FRCC. I wish to mention that running a marathon is the best mental training for the rigor and endurance needed to pursue a PhD. I won’t mention names for fear I will neglect to mention someone, but I thank you for camaraderie on runs.

I’ve saved the best for last. Thank you Mom and Dad for your “company” on my walks across campus to my car. Thank you for gift baskets, flowers, and the little things that have brightened many days. There are a very few people that know the challenges I’ve overcome. You have always believed in me. You have
instilled your values, strengths, and unique gifts that have brought me to this place. You are more than great parents, you are best friends.

Finally, I wish to thank my fiancé, Dan Holsey. You asked me not to dedicate my PhD thesis to you. Still I want you and anyone else reading this to know that you are integral to my success. I couldn’t afford to pay the bills without you but even if I could I probably wouldn’t remember to pay them, especially these last few months. Thank you for your tremendous sacrifices and support. Thank you for taking care of Eira. Since we made it through this, I believe we can make it through anything. I will never find the right words to tell you how incredibly grateful I am that you have endured this journey with me. I can only hope to repay you someday.
This thesis is dedicated in loving memory of William D. Morrissey.

Your two enduring words have resounded in my thoughts throughout this journey: *stay focused.*
CHAPTER 1
GENERAL INTRODUCTION

Interest in ionic transport in solids has grown since the early 1900s with the demonstration of the “Nernst glow”. Nernst used the passage of an electric current through zirconia, ZrO$_2$, doped with small amounts of yttria, Y$_2$O$_3$, to emit a bright white light. The glow was due to the conduction of oxygen ions, O$^{2-}$ [1].

The addition of Y$_2$O$_3$ dopant to ZrO$_2$ stabilizes the cubic phase at room temperature but also leads to the formation of vacancies, as presented in Kroger-Vink notation:

$$Y_2O_3 \rightarrow 2Y'/Zr + V^{\bullet\bullet}O + 3O_{\circ}$$  \hspace{1cm} (1.1)

where a net negative charge is represented by “’” and a net positive charge is represented by “••”. The extra charge created by the substitution of Y$^{3+}$ for Zr$^{4+}$ leads to the creation of oxygen vacancies, V$^{\bullet\bullet}O$. The vacant oxygen sites are the mechanism by which O$^{2-}$ ions move through the Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) lattice and conduct oxygen ions, O$^{2-}$.

In the mid-to-late 1900s, an increased fundamental understanding of electrochemistry led to the development of electrochemical devices, such as solid oxide fuel cells (SOFCs), for which YSZ is a common electrolyte [2–4]. A fuel cell is an oxide battery, comprised of an electrolyte between the anode and cathode. The addition of Y$_2$O$_3$ dopant creates more V$^{\bullet\bullet}O$ sites for O$^{2-}$ ions to hop. Ionic conduction, $\sigma_i$, is described by:

$$\sigma_i = c_iq_iu_i$$  \hspace{1cm} (1.2)

where the $c_i$ is carrier concentration, $q_i$ is charge of the ionic species, and $u_i$ is mobility. In addition, the Nernst-Einstein equation relates $u_i$ to the diffusion coefficient, $D_i$:

$$u_i = q_iD_i/k_BT$$ \hspace{1cm} (1.3)

where $k_B$ is Boltzmann constant and $T$ is temperature. Combining equations 1.2 and 1.3, it becomes evident that $\sigma_i$ depends on $T$. At temperatures below 800°C, O$^{2-}$ conduction in YSZ occurs in very low levels [2]. Increasing temperature results in increased O$^{2-}$ conduction because there is sufficient thermal energy to overcome energy barriers to mass transport. In addition to thermal energy barriers, research performed by Badwal on single-crystal and polycrystalline YSZ revealed that grain boundaries contribute significant resistance to O$^{2-}$ conduction [5, 6].

A brief overview of how O$^{2-}$ conduction is impacted by microstructural features is covered to provide a foundation for interpreting mass transport during reduction of polycrystalline YSZ. Grain boundary resis-
tance in YSZ has been supported by numerous, recent simulations [7–10]. It is known that the addition of $\text{Y}_2\text{O}_3$ dopant increases $\text{O}^{2-}$ conduction up to a point, after which further additions of $\text{Y}_2\text{O}_3$ decrease $\text{O}^{2-}$ conductivity. The optimum concentration of $\text{Y}_2\text{O}_3$ dopant is between 8 to 10 molar percent [11–13]. There are two main structural arguments to explain the conductivity ceiling: 1) the large size of $\text{Y}^{3+}$ cation compared to the $\text{Zr}^{4+}$ creates lattice strain that prohibits the movement of $\text{V}^{\bullet\bullet}_\text{O}$ [14, 15] and 2) defect complexes of $\text{Y}^{3+}$ to $\text{V}^{\bullet\bullet}_\text{O}$ decrease the amount of free $\text{V}^{\bullet\bullet}_\text{O}$ for conduction [9, 16, 17]. These theories both successfully explain the microstructural contribution of decreased $\text{O}^{2-}$ conductivity along the grain boundaries.

Coupled with the structural effects, grain boundaries exhibit local chemistry that differs from that in the grain interior. As the YSZ polycrystalline microstructure evolves, dopant or impurity ions segregate to grain boundaries [6, 18]. Dopant segregation to surfaces [19] and grain boundaries [20, 21] is energetically favorably. The large $\text{Y}^{3+}$ ion on the $\text{Zr}^{4+}$ site creates strain, and the difference in valency results in a negatively charged space charge layer at the grain boundary which limits $\text{O}^{2-}$ conduction. The $\text{Y}^{3+}$ ion also complexes with $\text{V}^{\bullet\bullet}_\text{O}$. Despite the large concentration of $\text{V}^{\bullet\bullet}_\text{O}$ that are present along grain boundaries, experimental work by De Souza et al find the boundaries do not act as fast diffusion paths due to cation dopant-vacancy complexing [22]. Essentially, the excess $\text{V}^{\bullet\bullet}_\text{O}$ present at grain boundaries are trapped because they are needed for charge neutrality, and they don’t participate in $\text{O}^{2-}$ conduction. The structural arguments for the conductivity ceiling in YSZ are active in grain boundary regions where local chemistry varies from the bulk. High purity synthesis techniques are shown to decrease impurities, thus diminishing impurity segregation effects [23]. Grain size and cooling rate are also shown to influence grain boundary conductivity [24]. Grain size effects are balanced between reducing the grain boundary area with large grains and reducing the concentration of impurities along the boundaries with fine grains. Quenching may also be used to limit diffusion time for impurity ions to segregate upon cooling after sintering.

Besides $\text{O}^{2-}$ conduction, mass transport of other species is reported in YSZ. In oxidizing environments, Kosaki et al. [25] have reported enhanced conductivity attributed to dissolved protons along grain boundaries [26–29]. Several researches show that a hydrogen or hydroxide ion is permeable in YSZ [30–32], specifically in open porosity or grain boundaries where it physisorbs or chemisorbs to surfaces. Any enhancement in conductivity due to physisorbed or chemisorbed water on conductivity is under debate [33, 34]. In reducing environments the conduction of electrons is studied. Karton et al. show that YSZ exhibits minimum electronic conduction in oxygen partial pressures between 100 atm or even as low as $10^{-20}$ to $10^{-25}$ atm [11]. In contrast, researchers have shown that electronic conduction is rapid in low oxygen partial pressures [35–37]. Electrons in YSZ can be trapped by $\text{V}^{\bullet\bullet}_\text{O}$ or can reduce the valence state of dopant or impurity ions; the preferred reaction depends on the concentration and electronegativity of the impurity [38].
The selection criteria for an electrolyte requires high ionic or protonic conductivity (in combination with low electronic conductivity), chemical stability, and mechanical durability under reducing and oxidizing environments at high operating temperatures. The ideal anode material must oxidize the fuel and act as a current collector. More recently perovskites are being investigated for use in SOFCs and as catalysts in electrochemical reactions. Yttria-doped barium zirconate (Y$_2$O$_3$-doped BaZrO$_3$ or BZY) is a widely studied ceramic proton/oxide/electronic hole conductor, depending on the environmental conditions. In particular, the chemical stability under reducing, oxidizing or carbon dioxide atmospheres enables a broad range of potential applications due to high proton conductivity at reduced operating temperatures compared with conventional solid oxide fuel cell (SOFC) electrolytes [39, 40]. The excellent coking resistance of BZY is ideal for electrochemical and catalysis applications [39–43]. A major drawback to using BZY is that high sintering temperatures are usually required to achieve full density [44], resulting in volatilization of barium and a loss in stoichiometry. Transition metal oxides are often added to BZY to improve sintering [45–47]. Specifically, the addition of NiO is shown to lower the sintering temperature, increase density, and increase electronic conductivity [48, 49]. Much like small amounts of Y$_2$O$_3$ dopant change mechanical and electronic properties of ZrO$_2$, this also occurs when a small amount of nickel oxide is added to YSZ or yttrium-doped barium zirconate (BZY). An overview of the effects of NiO dopant in YSZ and BZY is provided.

1.1 Nickel Oxide Additions in YSZ

Small amounts of NiO dopant are commonly added to promote sintering at lower temperature and accelerate densification and grain growth [50–53]. The mechanism is debated, but a common speculation is Ni$^{2+}$ reduces the surface energy or sintering activation energy [52–54]. The solubility of Ni$^{2+}$ ions in YSZ is between 1 to 2 molar percent [55–57]. It is generally accepted that Ni$^{2+}$ substitutes on Zr$^{4+}$ sites, as illustrated with Kroger-Vink notation:

$$\text{NiO} \rightarrow \text{Ni}^{2+}_{\text{YSZ}} + \text{V}^{\text{m}}_{\text{O}} + \text{O}^{\text{v}}_{\text{O}} \quad (1.4)$$

The atomic radius of Ni$^{2+}$ (0.069 nm) is small compared to Y$^{3+}$ (0.090 nm), however, the atomic radius of Ni$^{2+}$ is similar to Zr$^{4+}$ (0.072 nm). Research has shown NiO alone will not stabilize the cubic phase in YSZ [58] and the solution energy for Ni$^{2+}$ in YSZ is higher compared with other transition metals [59]. Above 2 molar percent, Ni-rich secondary phases, such as NiO, are commonly observed and accentuated with longer sintering times [55]. Higher nickel dopant in YSZ is commonly used in SOFC anode structures, which require tortuous and porous structures to increase surface area for electrochemical reactions to occur. In fact, higher NiO dopant concentrations can increase the prevalence of enclosed pores in grains due to the rapid grain growth [51–53].
Conductivity is an important measure of fuel cell anode performance. In oxidizing environments the conductivity performance of NiO-doped YSZ is similar to undoped YSZ [51, 60]. In reducing environments, NiO-doped YSZ is chemically unstable and significant degradation in conductivity and microstructure is reported [60–64]. Microstructural degradation includes a phase transformation from cubic to tetragonal that is common in 8YSZ and the exsolution of Ni$^{2+}$ resulting in metallic nickel particles [64–67]; both types of degradation can create significant lattice strains [62, 68]. To prevent phase transformation during reduction in order to study the evolution of metallic particles, 10YSZ was selected for this work because it is fully-stabilized, cubic structure at low and high temperatures [69].

The exact mechanism describing the nucleation of metallic nickel particles in reducing environments is not well understood. The Ellingham diagram is used to estimate equilibrium oxygen partial pressure, $P_{O_2}$, and shows that redox stability of NiO is around $10^{-12}$ to $10^{-14}$ atm for the temperature range of this study [61, 66]. The difference in oxygen activity from the ambient oxygen partial pressure compared with the fugacity of the oxide provides a thermodynamic driving force for the surface reaction:

$$\text{H}_2 + O_O^x \leftrightarrow 2e' + V_{O}^{**} + \text{H}_2\text{O} \quad (1.5)$$

A general description of the reduction mechanism is that electronic defects are introduced into the oxide and react with Ni$^{2+}$ to form metallic Ni$^0$ particles. Jeangros et al. speculate that H$_2$ absorbs and dissociates at Ni$^{2+}$ sites on the surface forming metallic Ni$^0$ which further enables the absorption of hydrogen and dissociation of water [70]. Saraf et al. report significant Ni$^{2+}$ surface migration in reducing environments [71]. The reaction rate of nickel reduction follows a parabolic rate law [72, 73], suggesting the reaction is diffusion limited by the reactant species moving through the bulk lattice. The discrepancy in reports provides evidence that clarification of Ni$^{2+}$ distribution and kinetics during reduction is needed by further research.

Blackening of NiO-doped YSZ occurs, most likely due to Mie scattering or absorption from the formation of metallic nickel particles [61, 64, 66, 73, 74]. It is unlikely the color change results only due to the formation of electronic defects and zirconium vacancies, $V_{Zr}^{iii}$ [75]. Briefly, blackening in undoped YSZ is due to color centers created by a Y$^{3+}$ complexed with $V_O^{**}$, yielding the association ($Y'_ZrV_{O}^{**}$)$^*$ with a net positive charge, and a single, trapped electron, 2e’, which causes a shift in adsorption edge energy [76, 77]. The interface between reduced (black) and unreduced (white) YSZ has a local electrical potential [78, 79] which creates a driving force for the reaction. The contribution of an electrical potential on the internal reduction mechanism of NiO-doped YSZ has not been discussed in literature.

The microstructural features affect where metallic Ni$^0$ particles form during the reduction reaction. It is widely reported that metallic Ni$^0$ particles form first along grain boundaries. When metallic Ni$^0$ particles form in the grain interior, Kondo et al. report that the metallic Ni$^0$ particles are observed in pores [65].
The generation of porosity is attributed to a difference in lattice parameter between NiO (0.418 nm) and metallic nickel (0.368 nm). Since SOFCs are redox cycled the reversibility of the reduced microstructure is also of interest in this work. Redox experiments involving NiO-doped YSZ show that re-oxidation occurs rapidly in SOFC anodes containing high NiO dopant concentrations [80–83], above the solubility limit. It is expected that the metallic Ni\(^0\) particles will directly reduce to form NiO. Klemenso et al. observed oxide growth on metallic Ni\(^0\) particles [83]. Upon a re-reduction, the structure and distribution of the metallic Ni\(^0\) particles does not match the original microstructure. Zhang et al. report a spongy metallic Ni\(^0\) particles in anodes [81]. Sumi et al. report a refined metallic Ni\(^0\) structure having smaller particle sizes [80]. All of the redox experiments in literature have been reported on 50% NiO-doped 8YSZ, but show that microstructure has irreversible changes. The stability and reversibility of the internally reduced microstructure is of interest for a variety of nano-ionic applications.

1.2 Nickel Oxide Additions in BZY

BZY is a widely studied proton conducting ceramic exhibiting high protonic/ionic/electronic conductivity at reduced operating temperatures. High sintering temperatures are required to achieve full density in BZY which often results in astoichiometry. The volatility of Ba\(^{2+}\) results in the formation of low melt phases like BaCO\(_3\) [84]. The astoichiometry enhances hydration of the BZY, which ultimately degrades the mechanical properties [85]. Astoichiometry is mitigated by lowering the sintering temperature and by the addition of transition metal oxides [45–47]. The addition of NiO is shown to lower the sintering temperature needed to achieve full densification and increase the electronic conductivity [49, 86].

The mechanism by which NiO additions aid densification is not understood. A common hypothesis is that transition metal dopants form low melting point phases, resulting in liquid phase sintering [87, 88]. The addition of NiO is reported to lead to the formation of Y\(_2\)BaNiO\(_5\) or other phases that host unincorporated Ni\(^{2+}\) ions [86, 87]. How much NiO dopant is incorporated into BZY depends upon the solid solution limit of Ni\(^{2+}\) in BZY. Ricote and Bonanos show with lattice parameter measurements that the solubility of Ni\(^{2+}\) is BZY is likely less than 1 molar percent [49]. An improved understanding of the solubility of Ni\(^{2+}\) in BZY and the stoichiometry of the excess nickel phases is necessary to eliminate second phases that form during processing. Alternatively, improved understanding of the process conditions that lead to excess Ni\(^{2+}\) phases in BZY powders could enable the ability to selectively reduce excess nickel phases to prepare nanocomposites for catalytic and electrochemical applications.
1.3 Motivation for Reduction Studies

It is clear from the previous discussion that the reduction of NiO-YSZ and its influence on the microstructure is connected with the mechanical durability and conductivity. The ability to model and predict the internal reduction mechanism is desirable to enable microstructure design of heterogeneous metal-ceramic nanocomposites and electrochemical devices. The original model for reduction was based upon single crystal or amorphous materials with very low $O^{2−}$ conductivity [89–91]. Internal reduction studies in polycrystalline systems suggest that grain boundaries act as fast diffusion paths for transporting species [92], however, the reduction front is shown to progress along the grain boundaries in NiO-doped YSZ [93]. The current model for internal reduction has three major limitations when applied to this work: 1) the assumption that oxygen ions are immobile in the lattice when YSZ is an $O^{2−}$ conductor, and 2) the model is constructed for single crystal but most structural applications are polycrystalline, and 3) the model only considers diffusion due to chemical potential gradients and not electrical potential gradients. The present study aims to improve understanding of how the microstructure affects the kinetics of internal reduction and redox cycling. An improved understanding of the reduction mechanism can lead to nanostructural control and the ability to engineer catalytic devices [94, 95], nanomagnetic devices [96], metal-ceramic reinforced composites [97], and redox stable anodes [98]. Insights from the reaction kinetics could enable prediction of grain boundary diffusivity of the rate limiting species and an improved understanding of how Ni$^{2+}$ is distributed in the 10YSZ lattice.

In addition, this work provides the foundation to perform reduction studies of internal reduction in NiO-doped BZY by using magnetic characterization to study how nickel is incorporated into powders and pellets. Identifying the formation of excess phases in BZY powders is a promising approach to understand the mechanism by which NiO acts a sintering aid. Alternatively, reduction of powders with excess Ni phases enables synthesis of nanocomposites for catalysts directly from powders [99, 100]. Mixed ionic and protonic conducting oxides, like BZY, have tunable catalytic properties by adjusting the dopant additions [101]. The ability to design nanocomposite catalyst microstructure by controlling the reducing conditions of powders with excess Ni phases will be examined.

1.4 Overview of Thesis Layout

This thesis is organized in the following chapters:

1. Chapter 1 presents general concepts that introduce the material. The motivation for this research is stated.
2. Chapter 2 provides an overview of existing literature detailing mechanisms of internal reduction and background of characterization techniques. Thermodynamic and kinetic predictions are applied to the NiO-10YSZ system.

3. Chapter 3 includes all experimental procedures including synthesis of pellets, reduction furnace assembly and calibrations, characterization parameters, and outlines the mathematical expressions to create a model for internal reduction.

4. Chapter 4 presents the paper titled “Microstructural Evolution During Internal Reduction of Polycrystalline Nickel-doped Yttria-stabilized Zirconia” submitted to Acta Materialia and supplemental findings.

5. Chapter 5 presents the paper titled “Tailored Metal-Ceramic Nanocomposites Prepared by Redox Cycling of Polycrystalline Ni-doped Yttria Stabilized Zirconia” submitted to Scripta Materialia and supplemental findings.

6. Chapter 6 presents “Excess barium nickel oxide in BaZr_{0.85-x}Ni_xY_{0.15}O_{3-δ} studied with SQUID magnetometry”.

7. Chapter 7 presents a general discussion to tie together the body of work presented in this thesis.

8. Chapter 8 provides with closing remarks.

9. Chapter 9 gives suggestions for future work.

10. Appendix A shows representative Mathematica calculations for determining gas mixtures to maintain constant oxygen partial pressure across various reduction conditions.

11. Appendix B summarizes the gas calibration factors for various gases used in this work.

12. Appendix C contains representative SQUID magnetometry sequences used in characterizing the reduced pellets.

13. Appendix D summaries the atom probe tomography specimens and run numbers associated with this research.
CHAPTER 2
BACKGROUND

This chapter is devoted to providing the fundamental background pertaining to reduction-oxidation reactions. A review of the Wagner model of oxidation and current models for internal reduction from literature are summarized. Emphasis is placed on defining thermodynamics and kinetics of the reduction-oxidation reaction in Ni-doped YSZ. Concepts of defect equilibrium and kinetics that govern mass transport are discussed, specifically for YSZ, and fundamental equations for calculating mass transport due to a chemical or an electrical potential gradient are outlined. A fundamental review of magnetic properties is presented since SQUID magnetometry is extensively used to quantify the internal reduction reaction in this work. The last sections provide a brief, fundamental overview of characterization techniques and used herein.

2.1 Reduction-Oxidation Reactions

The classic definitions for reduction-oxidation reactions are “oxidation is loss of electrons” and “reduction is gain of electrons”. Reduction-oxidation reactions can occur by the transfer of electrons, oxygen atoms, or hydrogen atoms that result in a change of total valency. The valency of the atomic species involved in an oxidation reaction increases, whereas the valency of an atomic species in a reduction reaction decreases. An informal term for the reduction-oxidation reaction used herein is redox reaction.

2.1.1 Conservation Rules

A review of the conservation rules required to maintain electroneutrality is presented before discussing the models. This set of rules governs defect chemistry, and requires that mass, charge, structure, and electronic states are conserved. The conservation of mass implies that atoms are neither created or destroyed in a system. The conservation of charge considers the crystal as a bulk, and requires that electroneutrality is maintained as defects are introduced. Defects are introduced as pairs having opposite charge in stoichiometric amounts to create a net neutral charge. The conservation of structure implies that individual lattice sites are neither created or destroyed. Further, the ratio of defects existing on cation or anion sites in the lattice cannot alter the overall stoichiometry of the oxide. The conservation of electronic states must be consistent with the electronic states of the constituents comprising the oxide. When considering the reactions involved in internal reduction and when writing them in Kroger-Vink notation these rules must be obeyed. This exposes a limitation to applying Kroger-Vink notation to internal reduction of NiO-doped 10YSZ; the nucleation of a new phase that does not exist on a lattice site occurs during internal reduction.
2.1.2 Model of Oxidation

The classic description of oxidation was described by Wagner [102]. In this widely accepted model, the oxidation rate is limited by the diffusion of ionic species through an oxide layer. The parabolic rate constant can be related to the partial ionic and electronic conductivities of the oxide layer, and depends on the chemical potential gradient induced by differences in oxygen activity between the metal and oxide layer. A diagram of Wagner’s oxidation model is shown Figure 2.1. In addition, the assumptions of Wagner’s oxidation theory are: 1) the oxide scale adheres perfectly to the metal, 2) diffusion of ions or electrons through the scale is rate limiting, 3) thermodynamic equilibrium is achieved at the metal-oxide and oxide-gas interfaces, 4) the oxide scale is stoichiometric, 5) local thermodynamic equilibrium exists in the oxide scale, 6) the oxide scale thickness is much greater than the distance of space charge effects, and 7) oxygen ions are not soluble in the metal.

![Diagram of Wagner's model of oxidation](image)

Figure 2.1: Illustration of Carl Wagner’s model of oxidation [103].

The driving force for the oxidation reaction to occur is the activity gradient between the metal-oxide and oxide-gas interfaces. The gradient drives the migration of cations and anions in the oxide scale to move in opposing directions. The migration of metal cations through the scale creates an electric field because electrons from the metal are required to compensate charge of the positive metal cations. The flux of metal cations with electrons and anions are balanced to preserve electroneutrality. The flux is described by:

\[ j_i = -\frac{\sigma_i}{Z_i^2 F^2} \left( \frac{\partial \mu_i}{\partial x} + Z_i F \frac{\partial \phi}{\partial x} \right) \]  

(2.1)

for species \( i \) with charge \( Z \), in a chemical potential gradient \( \frac{\partial \mu}{\partial x} \), and electrical potential gradient \( \frac{\partial \phi}{\partial x} \). Faraday’s constant is \( F \). The electroneutrality condition is maintained by the fast diffusion of electronic
carrier defects relative to the ionic species present in the oxide. Electroneutrality is given by:

\[ Z_c j_c + Z_e j_e = 0 \]  \hspace{1cm} (2.2)

where subscript \( c \) is for cations and \( e \) is for electrons. Since the electric potential gradient generated by transport of ionic and electronic is often unknown. The flux of cations can be solved for without the \( \frac{\partial \phi}{\partial x} \) term [103]:

\[ j_c = -\frac{\sigma_c \sigma_e}{Z_c^2 Z_e^2 F^2 (\sigma_c + \sigma_e)} \left[ \frac{\partial \mu_c}{\partial x} - \frac{Z_c}{Z_e} \frac{\partial \mu_e}{\partial x} \right] \]  \hspace{1cm} (2.3)

At the reaction front, the oxidation of metal, \( M \), with charge, \( Z_c \), can be described by:

\[ M = M^{Z_c} + Z_c e \]  \hspace{1cm} (2.4)

and at equilibrium the chemical potential is described by:

\[ \mu_M = \mu_c + Z_c \mu_e \]  \hspace{1cm} (2.5)

Since the cation and electrons are related by the valency, their chemical potentials are also dependent. This enables the flux of cations to be further simplified:

\[ j_c = -\frac{\sigma_c \sigma_e}{Z_c^2 Z_e^2 F^2 (\sigma_c + \sigma_e)} \frac{\partial \mu_c}{\partial x} \]  \hspace{1cm} (2.6)

The chemical potential of the cation, \( \mu_c \), changes changes with position in the oxide scale, thus, it is necessary to integrate [103]:

\[ j_c = -\frac{1}{Z_c^2 Z_e^2 F^2} \int_{\mu_c^M}^{\mu_c^a} \frac{\sigma_c \sigma_e}{(\sigma_c + \sigma_e)} d\mu_c \]  \hspace{1cm} (2.7)

The chemical potential at the metal-oxide interface is described by \( \mu_c^M \) and at the oxide-gas interface is described by \( \mu_c^a \). If the concentration of metal in the oxide scale is given by \( C_M \) then the flux can alternatively be written in terms of the growth velocity of the oxide scale, \( dx/dt \):

\[ j_c = C_c \frac{dx}{dt} \]  \hspace{1cm} (2.8)

The parabolic rate constant \( k \) describing the formation of the oxide scale is also written in terms of the growth velocity:

\[ k = \frac{dx}{dt} \]  \hspace{1cm} (2.9)

The velocity of the oxidation front can be solved to show the relationship that \( j_c/C_c \) is equal to \( k/x \). From the flux equation, one can now solve for the rate constant in terms of cations or anions (subscript \( a \)) depending on which species is more mobile [103]:

\[ k_c = -\frac{1}{Z_a^2 Z_e^2 F^2 C_a} \int_{\mu_a^M}^{\mu_a^a} \frac{\sigma_a \sigma_e}{(\sigma_a + \sigma_e)} d\mu_a \]  \hspace{1cm} (2.10)
\[ k_a = -\frac{1}{Z_a^2 F^2 C_a} \int_{\mu_a'}^{\mu_a''} \sigma_a d\mu_a \]  

(2.11)

When the transport number of electrons (or holes) is small compared with the transport numbers of cations or anions, the rate can be further simplified [103]:

\[ k_c = \frac{1}{Z_c^2 F^2 C_c} \int_{\mu_c'}^{\mu_c''} \sigma_c d\mu_c \]  

(2.12)

\[ k_a = \frac{1}{Z_a^2 F^2 C_a} \int_{\mu_a'}^{\mu_a''} \sigma_a d\mu_a \]  

(2.13)

Since the conductivity and diffusion coefficient can be related by the Nernst-Einstein equation:

\[ D_i = \frac{kT \sigma_i}{Z_i^2 F^2 C_i} \]  

(2.14)

it is possible to write the rates in terms of the diffusion coefficient for cations or anions in the oxide layer:

\[ k = \frac{1}{RT} \int_{\mu_c'}^{\mu_c''} D_c d\mu_c \]  

(2.15)

\[ k = \frac{1}{RT} \int_{\mu_a'}^{\mu_a''} D_a d\mu_a \]  

(2.16)

The diffusion coefficient is assumed to be a function of the chemical potential, but this simplification of the oxidation model does not take into account the driving force from an electrical potential gradient due to the accumulation or depletion of charged species.

### 2.1.3 Models of Internal Reduction

Internal reduction in solid state systems is a topic of research interest [89–92, 104, 105]. The reactant is introduced into a solid following the reaction of the gaseous species with the surface. The introduction of reactants at the surface creates a gradient in concentration which acts a driving force for diffusion. The reactant diffuses into the solid and leaves products behind the front. The resulting microstructure is a solid containing reduced products in the interior.

A fundamental manuscript for internal solid state reactions is by Schmalzried [89]. The theory of internal reduction is based on reverse oxidation kinetics. Consider an oxide solid solution (A,B)O. First, the surface of the oxide solid solution is exposed to a low oxygen partial pressure, \( P_{O_2} \). This creates a difference in oxygen activity of the gas compared with the oxygen activity of the oxide solid solution at the surface, \( \xi_S \). Due to the gradient of oxygen activity, the reaction front, \( \xi_F \), progresses into the oxide solid solution in attempt to achieve thermodynamic equilibrium with the gas. Reduced products, including point defects and metallic particles, are generated in the reacted zone, \( \Delta \xi \), as shown in (Figure 2.2). The reactants must be charge compensated by electronic defects diffusing into the oxide. Internal reduction can occur with conservation.
of the oxide matrix or destruction of the oxide matrix. Schmalzried provides a mathematical approach to calculate the rate of advancement of the reaction front, concluding the internal reduction front will progress at a parabolic rate given by:

$$\Delta \xi^2 = 2kt$$

where $t$ represents time. The reaction is limited by diffusion of the reactants/charge compensating defects across the thickness of the reaction front, $\Delta \xi$. Schmalzried also predicts there will be no coarsening of the metallic particles.

Ostyn and Carter [90] apply the Schmalzried model to an oxide solid solution $(A,B)O$, where the diffusivity of species $A$ and $B$ are given by $D_A$ and $D_B$ and the concentrations are $c_A$ and $c_B$, respectively, and the diffusivity of oxygen is $D_O$. The transport coefficient which is approximated by the product $c_i D_i$ which can be used to predict the rate limiting species. Here the model assumes $D_A, D_B \gg D_O$ and $c_A D_A \gg c_B D_B$, meaning species $B$ is rate limiting. Ostyn’s model for internal reduction is shown in Figure 2.3. The mechanism is not advanced from what was proposed by Schmalzried, however, the derivation of the rate constant is derived from characteristics of the oxide and reactant species. Ostyn’s derivation of $k$ is given by:

$$k \cong ZD_A(\xi') \frac{2}{x_B'}$$

where $Z$ is an enhancement factor given by $Z = n + 1$ where $n$ is the effective charge of the vacancies generated during internal reduction, $D_A(\xi')$ is the diffusion coefficient of the doped cation at the gas/solid
surface, $\xi'$, having the highest transport coefficient and $x'_{B}$ is the initial molar fraction of the cation with the lowest transport coefficient initially. The experimental results are reported for two systems (Ni,Fe)O and (Al,Fe)O. A reactant phase forms in the bulk of grains in the (Ni,Fe)O system but primarily along grain boundaries for (Al,Fe)O system. Ostyn concludes that the kinetic model for internal reduction applies best to the (Ni,Fe)O system, but not the (Al,Fe)O because the reaction occurs primarily along the grain boundaries. This conclusion supports the need for an advanced internal reduction model when describing polycrystalline systems. In fact, Backhaus-Ricoult et al. [104] also suggests that grain boundaries will provide a fast path for diffusion of reactant species in internal reduction.

Figure 2.3: Proposed mechanism of internal reduction in an oxide solid solution as described by Ostyn and Carter [90].

White et al. describe the kinetics for internal reduction occurring rapidly along the grain boundaries [73]. A major finding of this work is a parabolic reaction rate is expected even if the reaction occurs rapidly along grain boundaries. Electrons are highlighted as the rate limiting species for the internal reduction mechanism. The authors propose the following defect reaction at the reduction front:

$$\text{Ni}^{II}_{Zr} + O^{x}_{O} + V^{••}_{O} = \text{Ni}^{III}_{Zr} + V^{••}_{O} + O^{x}_{gb}$$  \hspace{1cm} (2.19)$$

where $\text{Ni}^{III}_{Zr}$ is only symbolic by necessity maintain charge neutrality, but effectively represents the neutral charged metallic Ni$^{0}$ particles that result from internal reduction of Ni$^{2+}$ ions. The reaction mechanism for internal reduction of polycrystalline NiO-doped 10YSZ proposed by White et al. is shown in (Figure 2.4). It is interesting to note that metallic Ni$^{0}$ particles are not observed in the grain interiors. Further this work does not elaborate on how the reaction kinetics and reduced microstructure change by varying temperature and oxygen partial pressure. This work will build upon the White et al. model through a systematic study.
examining how the microstructure and experimental parameters influence the overall internal reduction kinetics.

Figure 2.4: Proposed mechanism of internal reduction in polycrystalline NiO-doped 10YSZ as described by White et al. [73].

### 2.2 Thermodynamic Considerations for Reduction of NiO

An understanding of fundamental thermodynamics governing the oxidation and reduction are applied to predict the conditions for which Ni$^{2+}$ ions in 10YSZ will reduce to form metallic nickel. This step is important for selecting the experimental parameters. The thermodynamic driving force for the oxidation of a metal or the reduction of a metal oxide is quantified by the change in Gibbs free energy, $\Delta G$, and varies with temperature, $T$, according to:

$$\Delta G = \Delta H + T \Delta S$$

(2.20)

where $\Delta H$ is the change in enthalpy and $\Delta S$ is the change in entropy. The sign and magnitude of the change in Gibbs free energy are indications of the direction a reaction will proceed. When $\Delta G < 0$ the reaction favors the products and occurs spontaneously, when $\Delta G > 0$ the reaction favors the reactants and is non spontaneous, and when $\Delta G = 0$ the reaction favors neither the products or reactants and does not occur. A reaction will occur when it is thermodynamically unstable for the experimental conditions.

An Ellingham-Richardson diagram shows the equilibrium conditions for various metal redox reactions and is used to predict the equilibrium oxygen partial pressure at a given temperature. Consider the general reaction for the oxidation of nickel:

$$2\text{Ni} + \text{O}_2(g) = 2\text{NiO}$$

(2.21)
At equilibrium $\Delta G = 0$ and the reaction is neither oxidizing or reducing. The change in Gibbs free energy of formation of nickel oxide, $\Delta G_{f,NiO}$ is given by [106]:

$$\Delta G_{f,NiO} = -471200 + 172T \text{ Joules} \quad (2.22)$$

The affect of temperature on the Gibbs free energy of formation of nickel oxide is shown in Figure 2.5. The equilibrium oxygen partial pressure at $1000^\circ C$ for the $\Delta G_{f,NiO}$ is approximately $10^{-11}$ atm, and at $800^\circ C$ the equilibrium partial pressure is approximately $10^{-14}$ atm.

Since this focus of this work is reduction in hydrogen, it is necessary to write the reaction for the redox reduction of nickel in terms of $H_2$ in order to approximate the change in Gibbs free energy. The hydration reaction:

$$H_2(g) + \frac{1}{2}O_2(g) = H_2O(g) \quad (2.23)$$

is used to calculate the change in Gibbs free energy of formation of water, $\Delta G_{f,H_2O}$, given by [106]:

$$\Delta G_{f,H_2O} = -248500 + 55.85T \text{ Joules} \quad (2.24)$$

The change in Gibbs free energy of the reduction of nickel oxide is written by summing the reverse of the oxidation equation 2.21 and the hydration equation 2.23. The overall redox reaction in hydrogen is given by:

$$H_2(g) + NiO = Ni + H_2O(g) \quad (2.25)$$
where the overall change in Gibbs free energy, \( \Delta G_{\text{Red}} \), is calculated by:

\[
\Delta G_{\text{Red}} = -\frac{1}{2} \Delta G_{f,NiO} + \Delta G_{f,H_2O}
\]  

(2.26)

In order to determine the stability of \( \Delta G_{\text{Red}} \) the Gibbs free energy is expressed by the ratio of water partial pressure to hydrogen partial pressure:

\[
\Delta G_{\text{Red}} = -RT \ln \left( \frac{P_{H_2O}}{P_{H_2}} \right)
\]  

(2.27)

The ratio of \( P_{H_2O}/P_{H_2} \) is superimposed as isobars onto a plot of \( \Delta G_{\text{Red}} \) in similar fashion to the Ellingham-Richardson diagram for the oxidation, as shown in Figure 2.6. As the temperature decreases, the ratio of \( P_{H_2O}/P_{H_2} \) also decreases. This means in order for reduction to occur at lower temperatures, either the hydrogen content must increase with respect to the numerator or the water content must decrease with respect to the denominator. Figure 2.6 shows that the reduction reaction is sensitive to humidity and hydrogen content.

![Ellingham-Richardson diagram with \( P_{H_2O}/P_{H_2} \) isobars for the reduction reaction.](image)

A better way to visualize the influence of humidity on the reduction conditions is to plot percent hydrogen versus temperature, with isobars for various moisture contents, as shown in Figure 2.7. The isobars show where the reduction reaction is in equilibrium for a given percent hydrogen and at a given temperature. The relationship is an exponential decay. To the right of each isobar represents the percent hydrogen and temperatures suitable for reduction. To the left of each isobar the conditions are unsuitable for the reduction reaction. As the humidity increases the reaction equilibrium shifts to higher temperatures. As the percent
hydrogen decreases the reaction equilibrium shifts to lower temperatures. For the same hydrogen content, the oxygen partial pressure becomes more reducing as temperature decreases. The oxidation and reduction

zones guide the selected experimental conditions in this work.

The chemical potential of a species, $i$, can be expressed in relation to the concentration of a species in solution. The thermodynamic definition for chemical potential is:

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T,P,n_1,n_2,...}$$

A more familiar expression for chemical potential is:

$$\mu_i = \mu_i^0 + RT \ln a_i$$

Here $\mu_i^0$ is the standard state chemical potential, $R$ is the ideal gas constant, $T$ is temperature, and $a_i$ is the activity of species $i$ in solution. For pure species, $a_i = 1$. For gaseous species, activity is given by partial pressure, $P_i$. A similar set of equations can be written for the chemical potential of a defect, $d$, substituted for species $i$ in equation 2.28. The chemical potential for a defect is written [107].

$$\mu_d = \mu_d^* + RT \ln \frac{x_d}{1 - x_d}$$

Here $x_d$ is the site fraction given by $N_d/N$, where $N_d$ is the number of defect sites and $N$ is the total sites. Changes in defect concentration affects the oxygen activity of the oxide, acting as a driving force for mass transport.
The preferential nucleation site for metallic Ni\textsuperscript{0} is also driven by thermodynamics. The total free energy for nucleation is given by:

\[ \Delta G_{\text{tot}} = \Delta G_{\text{volume}} + \Delta G_{\text{interface}} \]  

(2.31)

where \( \Delta G_{\text{volume}} \) is the free energy associated with the creation of a second phase and \( \Delta G_{\text{interface}} \) is the free energy associated with the creation of a new surface. Equation 2.31 can be written in terms of a particle radius, \( r \):

\[ \Delta G_{\text{tot}} = \frac{4}{3} \pi r^3 \Delta G_V + 4 \pi r^2 \gamma \]  

(2.32)

where the free energy released per unit volume during the creation of a second phase is \( \Delta G_V \) and the interfacial energy per unit area is \( \gamma \). When plotted, the critical radius, \( r^* \), needed for a stable nucleus to form is given by the maximum in \( \Delta G_{\text{tot}} \), as shown Figure 2.8. The energy barrier associated with the formation of a stable nucleus having \( r^* \) is given by:

\[ \Delta G^* = \frac{16 \pi \gamma^3}{3 (\Delta G_V)^2} \]  

(2.33)

This equation provides the basis for calculating whether heterogeneous and homogeneous nucleation is more favorable. By taking a ratio [108]:

\[ \frac{\Delta G_{\text{het}}}{\Delta G_{\text{hom}}} = \frac{16 \pi \gamma^3}{3 (\Delta G_V)^2} \frac{2 f(\theta)}{16 \pi \gamma^3 \left(\frac{3 (\Delta G_V)^2}{3 (\Delta G_V)^2}\right)} = 2 f(\theta) \]  

(2.34)

where the geometry of the particle wetting on the surface is described by \( f(\theta) \):

\[ f(\theta) = \frac{2 - 3 \cos \theta + \cos^3 \theta}{4} \]  

(2.35)

and the contact angle, \( \theta \), can be experimentally measured and used to calculate the favorability factor for heterogeneous nucleation. A depiction of the contact angle is shown in Figure 2.9 for heterogeneous nucleation on a free surface and along a grain boundary. Quantification of the thermodynamic driving forces for nucleation at pores and grain boundaries versus homogeneous nucleation (in grain interiors) will provide greater insight into the internally reduced microstructure and distribution of metallic Ni\textsuperscript{0}.

### 2.3 Kinetic Considerations for Reduction of NiO

The kinetics describe how fast a reaction proceeds. Any reaction rate is limited by the slowest step or species involved in mass transport. In general, the kinetics can be surface or diffusion limited. Surface limited kinetics can be described by three steps: 1) adsorption, 2) dissociation, and 3) incorporation. Generally at low temperatures a reaction is surface limited. Diffusion limited kinetics involve mass transport through the bulk, and the rate is a limited by the diffusion of the slowest reactant. Generally at high temperatures a
Figure 2.8: Plot showing the competition between the energy needed to nucleate a volume of a new phase and the associated interfacial energy [108].

Figure 2.9: A depiction of the contact angle for heterogeneous nucleation (a) on a free surface and (b) on a grain boundary.

reaction is diffusion limited. Reactions are described as zero order, first order, or second order. The order of the reaction can gives clues about the rate limiting step. The trends of each reaction order versus time are shown in Figure 2.10. A zero order reaction will give a linear curve when plotted as concentration versus time. A first order reaction will give a linear curve when plotted as natural log concentration versus time. A second order reaction will give a linear curve when plotted as inverse concentration. These trends describe the effect of the reactant concentration on the initial rate.

Figure 2.10: Representative curves for (a) zero order reactions, (b) first order reactions, and (c) second order reactions.
Once metallic Ni\textsuperscript{0} particles have formed, their coarsening rate can be described as diffusion-limited or source/sink-limited. In the case that coarsening is limited by how fast the atoms in the lattice can diffuse to the metallic Ni\textsuperscript{0} particles, the particle size will increase according to [108]:

\[ <R(t)>^3 - <R(0)>^3 = K_D t \]  \hspace{1cm} (2.36)

where the mean particle size at time \( t \) is \(< R(t) >\) and the initial size is \(< R(0) >\), and \( K_D \) is a kinetic constant that depends upon diffusivity, surface energy, and solubility. In the other case where coarsening is limited by how quickly atoms can be added to the sink and subtracted from the source particles is given by [108]:

\[ <R(t)>^2 - <R(0)>^2 = K_S t \]  \hspace{1cm} (2.37)

where \( K_S \) is a kinetic constant that depends upon transport at the interface between the source and sink, surface energy, and solubility. The most likely mechanism for coarsening can be determined by plotting both equations as a function of time. The kinetics in this work will be quantified by measuring the magnetic response of the nickel dopant throughout various stages of the reduction reaction and applying these fundamental models.

\section*{2.4 Defect Equilibrium and Kinetics}

Defect concentrations in oxides are governed by thermodynamics and conservation rules. The kinetics describing the mass transport of defects is complex because the mass, charge, structure, and electronic states must be conserved. The mechanism and species involved in transport depend on the predominant defects, either Schottky or Frenkel. In the case of Schottky defects, ionic mobility is explained by vacancies. These vacancies can exist on cation or anion sites, resulting in mobility of both species. Alternatively, Frenkel defects result when a cation exists on an interstitial site and the anion lattice is assumed perfect. To maintain charge neutrality, cation vacancies are created, and therefore only cation mobility is influenced. In contrast, anti-Frenkel defects describe the opposite case where the cation lattice is assumed perfect and anion vacancies are created for charge neutrality. Only anion mobility is possible. It is widely accepted that anti-Frenkel defects are most common in the fluorite structure.

The equilibrium concentration of electronic defects can also vary with oxygen partial pressure changes and the general trends in concentration are described by the Brouwer diagram Figure 2.11. The Brouwer diagram can be used to calculate the majority and minority defect concentration at specific reduction conditions (oxygen partial pressure). This section calculates the concentrations of defects at the experimental conditions used in this work to determine the majority defects.
Figure 2.11: A general depiction of the Brouwer diagram, for which the majority carrier can be segmented by oxygen partial pressure: low (n-type defects dominate), medium (intrinsic defects dominate), and high (p-type defects dominate). [109].

An ionic material is classified by the majority carrier. When negative charge carriers are the majority defect involved in charge transfer, the material is classified as n-type. Electrons are donated to the lattice, causing the number of free electrons to outnumber holes. The n-type behavior results from either of two conditions, excess metal or deficit oxygen. Both conditions result in a net reduction of oxygen compared to the stoichiometric concentration. In metal excess, cations exist interstitially and an equivalent number of electrons exist in the conduction band. The metal excess is exhibited by ZnO:

\[
\text{ZnO} = \text{Zn}\,\left(\text{••}\right) + 2e^- + \frac{1}{2}\text{O}_2
\]  

(2.38)

In non-metal deficit, oxygen is evaporated from the structure:

\[
\text{O}_2^\times = \text{V}_O\,\left(\text{••}\right) + 2e^- + \frac{1}{2}\text{O}_2
\]  

(2.39)

The n-type transport is expected in low oxygen partial pressure conditions where reduction occurs. When positive charge carriers are the majority defect of the charge transfer, the material is classified as p-type. The majority defects which carry current are holes. This behavior results from metal deficit. The metal deficit case is exhibited by NiO:

\[
\frac{1}{2}\text{O}_2 = \text{O}^\times + 2h^- + \text{V}_{\text{Ni}}^\text{•}
\]  

(2.40)

The p-type transport is expected at high oxygen partial pressure conditions.
In order to determine the majority carrier for ZrO$_2$ at the experimental conditions used herein, the
Brouwer diagram was solved for low and medium oxygen partial pressure [110]. The governing equations
for high oxygen partial pressure are written but not solved. At low oxygen partial pressures, or reducing
conditions, O$_{2-}$ is pulled from the lattice. The governing defect reaction at low oxygen partial pressure is
given by:

$$\emptyset \rightarrow \text{Zr}^{\times} + \frac{1}{2} \text{O}_2(g) + \text{V}^{\bullet\bullet}_O + 2e'$$

which has a Gibbs free energy, $\Delta G_I$. The equilibrium constant, $k_I$ of the reaction is:

$$k_I = [V^{\bullet\bullet}_O][\text{Zr}^{\times}]P_{O_2}^2n^2$$

At medium oxygen partial pressures, in the intrinsic range, the oxide is stoichiometric. The governing
defect reaction at medium partial pressure is given by the dominant defect reaction for ZrO$_2$, which is the
anti-Frenkel defect:

$$\emptyset \rightarrow \text{V}^{\bullet\bullet}_O + \text{O}''_{i}$$

which has a Gibbs free energy, $\Delta G_{II}$. The equilibrium constant, $k_{II}$, of the reaction is:

$$k_{II} = [V^{\bullet\bullet}_O][O''_{i}]$$

Finally, at high oxygen partial pressures, in oxidizing conditions, extra O$_{2-}$ is stuffed into the lattice. The
governing defect reaction at high oxygen partial pressure is given by:

$$\emptyset + \frac{1}{2} \text{O}_2(g) \rightarrow \text{O}^{\times}_O + \text{V}''''_{Zr} + 4h^*$$

which has a Gibbs free energy, $\Delta G_{III}$. The equilibrium constant, $k_{III}$, of the reaction is:

$$k_{III} = \frac{[V''''_{Zr}]p^4}{P_{O_2}^2}$$

In all cases, the equilibrium constant can be written in terms of the Gibbs free energy:

$$k_{rxn} \cong \exp(-\Delta G_{rxn}/RT)$$

Alternatively, the Gibbs free energy can be defined by the terms of the standard entropy, $\Delta S^0$, and standard
enthalpy of formation, $\Delta H^0$:

$$k_{rxn} \cong k^0 + \exp\left(\frac{\Delta S^0}{k_B}\right) + \exp\left(-\frac{\Delta H^0}{RT}\right)$$

where $k^0$ is a constant that can be calculated for each reaction (I, II, and III shown above) by using equations
provided by Sasaki and Maier [110]. The terms needed to solve for the equilibrium constant at low oxygen
partial pressure are:

$$k^0 = N_C^2[P_{O_2}]$$
\[ \Delta S^0 = 5k_B \tag{2.50} \]
\[ \Delta H^0 = 5.5\text{eV} \tag{2.51} \]

where \( N_C \) is the average number of carriers. The terms at medium oxygen partial pressure are:

\[ k^0 = N_{O''} N_{\cdot\cdot\cdot O} \tag{2.52} \]
\[ \Delta S^0 = 5k_B \tag{2.53} \]
\[ \Delta H^0 = 3.0\text{eV} \tag{2.54} \]

where \( N_{O''} \) and \( N_{\cdot\cdot\cdot O} \) are the respective concentrations of defects. Since this work is focused on YSZ, the following equations were used to approximate the intrinsic oxygen vacancy concentration:

\[ k^0 = N_C^2 [Y'_Zr] \tag{2.55} \]
\[ \Delta S^0 = 5k_B \tag{2.56} \]
\[ \Delta H^0 = 5.5\text{eV} \tag{2.57} \]

where \( Y'_Zr \) is related to the concentration of the vacancies created by the addition of \( Y^{3+} \) on \( Zr^{4+} \) sites. The corresponding reactions for high oxygen partial pressure are not calculated because they are irrelevant for the reduction studies.

Additional equations must be defined for each reaction to conserve charge. The \( k_{rxn} \) is solved in terms of concentration of oxygen vacancies and electrons, needed to plot the Brouwer diagram for \( ZrO_2 \). In low oxygen partial pressure, the condition for electroneutrality is given by:

\[ n = 2[V_{O'}] \tag{2.58} \]

since \( V_{O'} \) and \( e' \) and dominant as the majority defects. Simplification of \( k_I \) gives:

\[ k_I = P_{O_2}^{\frac{1}{2}} n^2 [V^\bullet\bullet] = 4P_{O_2}^{\frac{1}{2}} [V^\bullet\bullet]^3 \tag{2.59} \]

and the solution for the concentration of oxygen vacancies becomes:

\[ [V^\bullet\bullet] = \left( \frac{k_A}{4} \right)^{\frac{1}{2}} \left( \frac{1}{P_{O_2}}^{\frac{1}{2}} \right) = \left( \frac{1}{4} k_A \right)^{\frac{1}{2}} (P_{O_2})^{-\frac{1}{6}} \tag{2.60} \]

The concentration of electrons can be easily solved using the condition for electroneutrality. It is shown that the concentration of electrons and oxygen vacancies both vary to the \(-1/6\) power in low oxygen partial pressure. In medium oxygen partial pressure, the condition for electroneutrality is given by:

\[ [V_{O'}] = [O''_i] \tag{2.61} \]
since \( O_1^{''} \) and \( V_{O}^{**} \) dominate as the majority defects. Simplification of \( k_{II} \) gives:

\[
k_{II} = [V_{O}^{**}][O_1^{''}] \tag{2.62}
\]

The concentration of oxygen vacancies, given by the total number of anti-Frenkel defects, is solved by:

\[
[V_{O}^{**}] = [O_1^{''}] = \sqrt{k_{II}} \tag{2.63}
\]

In this regime the concentration of oxygen vacancies does not vary with oxygen partial pressure. Again, to account for the vacancies created by the addition of \( Y^{3+} \) on \( Zr^{4+} \) sites, the condition for electroneutrality is given by:

\[
n = [Y_{Zr}'] \tag{2.64}
\]

The concentration of oxygen vacancies and electrons as minority carriers in medium oxygen partial pressure still depends upon oxygen partial pressure. To illustrate this, simplification of \( k_{III} \) gives:

\[
k_{III} = \frac{[Y_{Zr}'][2[V_{O}^{**}]]}{P_{O_2}^{\frac{1}{2}}} \tag{2.65}
\]

\[
[n] = [Y_{Zr}'] = \left( \frac{2k_{III}[Y_{Zr}']}[]{[V_{O}^{**}] P_{O_2}^{\frac{1}{2}}} \right) \tag{2.66}
\]

It is shown that the concentration of electrons varies to the \(-1/4\) power in medium oxygen partial pressure. The final calculated Brouwer diagram is shown in Figure 2.12. It includes the intrinsic oxygen vacancy concentration for \( ZrO_2 \) and \( 10YSZ \). A summary of \( C_X, C_S, \) and \( C_0 \) values for oxygen vacancies and electrons are reported in Table 2.1.

Table 2.1: The calculated values of the concentration of oxygen vacancies and electrons determined from the Brouwer diagram for various oxygen partial pressures.

<table>
<thead>
<tr>
<th>( P_{O_2} ) atm</th>
<th>( [V_{O}^{**}] ) cm(^{-3} )</th>
<th>( [e'] ) cm(^{-3} )</th>
<th>( [V_{O}^{**}] ) cm(^{-3} )</th>
<th>( [e'] ) cm(^{-3} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21 x 10(^{-11})</td>
<td>6.7 x 10(^{14})</td>
<td>1.3 x 10(^{15})</td>
<td>2.8 x 10(^{21})</td>
<td>2.1 x 10(^{11})</td>
</tr>
<tr>
<td>10(^{-15})</td>
<td>3.5 x 10(^{16})</td>
<td>7.0 x 10(^{16})</td>
<td>2.8 x 10(^{21})</td>
<td>7.8 x 10(^{13})</td>
</tr>
<tr>
<td>10(^{-19})</td>
<td>1.6 x 10(^{17})</td>
<td>3.3 x 10(^{17})</td>
<td>2.8 x 10(^{21})</td>
<td>7.8 x 10(^{14})</td>
</tr>
<tr>
<td>10(^{-19})</td>
<td>7.6 x 10(^{17})</td>
<td>7.9 x 10(^{18})</td>
<td>2.8 x 10(^{21})</td>
<td>7.8 x 10(^{15})</td>
</tr>
</tbody>
</table>

### 2.5 Mass Transport During Reduction of NiO-doped YSZ

Mass transport can occur due to a chemical potential gradient or an electrical potential gradient. From the conservation rules, the reaction mechanism of internal reduction includes the transport of ionic and
Figure 2.12: Brouwer diagram solved for YSZ showing how the defect concentration varies over oxygen partial pressure. In the selected conditions, the extrinsic defects introduced by the drop in oxygen partial pressure are less than the intrinsic oxygen vacancy concentration due to the dopant.
electronic defects. The respective flux densities are written:

$$j_i = -\frac{\sigma_i}{z_i^2F^2} (\nabla \mu_i - z_iF\nabla \phi) \quad (2.67)$$

Since the flux of $O^{2-}$, $j_{O^{2-}}$, is proportional to the coupled flux of $V_{O}^{**}$ and $2e'$, the ambipolar diffusion coefficient, $D^\delta$, must be calculated to quantify the diffusivity of $V_{O}^{**}$ and $2e'$ during reduction. In the absence of an external electric field, application of the electroneutrality condition leads to the following flux of oxygen vacancies: [107].

$$j_{V_{O}^{**}} = \frac{1}{2} j_{e'} = j_{O^{2-}} = j^\delta = -\frac{1}{4F^2} \frac{\sigma_{V_{O}^{**}}\sigma_{e'}}{\sigma_{V_{O}^{**}} + \sigma_{e'}} (\nabla \mu_{V_{O}^{**}} + 2\nabla \mu_{e'}) \quad (2.68)$$

The flux can be written as a diffusivity using the Nernst equation:

$$D = \frac{\sigma_iRT}{z_i^2F^2c_i} \quad (2.69)$$

$$D^\delta = \frac{RT\sigma_{O}^\delta}{4F^2c_{O}^\delta} = \frac{RT}{4F^2} \frac{\frac{1}{\sigma_{V_{O}^{**}}} + \frac{1}{\sigma_{e'}}}{\frac{1}{\sigma_{V_{O}^{**}}} + \frac{1}{\sigma_{e'}}} \quad (2.70)$$

Equation 2.70 is then rearranged in terms of diffusivity and concentration of $V_{O}^{**}$ and $e'$, as shown by [107]:

$$D^\delta = \frac{(D_{V_{O}^{**}}c_{V_{O}^{**}})(D_{e'}c_{e'})}{4(D_{V_{O}^{**}}c_{V_{O}^{**}}) + (D_{e'}c_{e'})} \left(\frac{1}{c_{V_{O}^{**}}} + \frac{4}{c_{e'}}\right) \quad (2.71)$$

Generally, the approximation that $D^\delta = D_{e'}$ can be used for YSZ in low oxygen partial pressure, except when redox active impurities are present [107]. Since Ni$^{2+}$ are reducible in low oxygen partial pressure, equation 2.71 will be used to calculate the ambipolar diffusion of $V_{O}^{**}$ and $e'$ during internal reduction.

In order for reduction or oxidation to occur, transport of ions and electronic defects must occur simultaneously. The traditional models for mass transport describe the mechanisms for motion of the ionic species, whereas the transport of electronic species is classified as polaron motion which requires brief introduction. The polaron was introduced by Landau as a quasi particle consisting of the electron and phonon cloud [111]. It is the cloud of phonons that attracts or repels the polaron to the other ionic species. The size of the polaron is defined relative to the lattice parameter. A small polaron occurs when the size of the phonon cloud is less than a lattice parameter. The motion of small polarons is similar to a hopping mechanism since the charge is generally localized to a specific site. A polaron is defined as large when the size of the phonon cloud exceeds the lattice parameter. Large polaron motion is similar to how electrons move through the conduction band in metals [112]. Electron motion in YSZ is proposed to occur by small polaron mechanism [113, 114]. The polarons motion is suggested to hop between the most electronegative species on the lattice [115].
2.5.1 Chemical Potential

Mass transport in a chemical potential is governed by Fick’s first law which describes the flux of a species $i$ due to a concentration gradient, $dc_i/dx$, as shown by:

$$J_i = -D_i \frac{dc_i}{dx} \quad (2.72)$$

The negative sign indicates that the flux occurs down the concentration gradient, toward the regions of lower concentration. The driving force for the diffusion is for the system to lower energy by reaching a new equilibrium state. The diffusion coefficient is expressed by:

$$D_i = D_0 \exp \left( -\frac{Q}{kT} \right) \quad (2.73)$$

where the diffusivity of the species is $D_i$ and the activation energy for the species to hop between sites is $Q$.

A summary of the diffusion coefficient and activation energies for species considered in the internal reduction of NiO-doped YSZ is presented in Table 2.2. At 1000°C the diffusivities rank:

$$D_{e'} > D_{h^\bullet} > D_{V_{O}^{\bullet\bullet}} > D_{Ni^{2+}} > D_{Y^{3+}} > D_{Zr^{4+}} \quad (2.74)$$

showing that electronic defects will diffuse more rapidly than vacancies and cationic species.

Table 2.2: A summary of bulk diffusion coefficient and activation energies of species in NiO-doped 10YSZ.

<table>
<thead>
<tr>
<th>Species</th>
<th>$D_0$ ($cm^2 s^{-1}$)</th>
<th>$Q$ (eV)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr$^{4+}$</td>
<td>0.062</td>
<td>4.6</td>
<td>[116]</td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>0.024</td>
<td>4.2</td>
<td>[117]</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>0.0067</td>
<td>3.8</td>
<td>[54]</td>
</tr>
<tr>
<td>$V_{O}^{\bullet\bullet}$</td>
<td>0.019</td>
<td>0.83</td>
<td>[37]</td>
</tr>
<tr>
<td>$e'$</td>
<td>0.54</td>
<td>0.55</td>
<td>[37]</td>
</tr>
<tr>
<td>$h^\bullet$</td>
<td>0.00016</td>
<td>0.1</td>
<td>[37]</td>
</tr>
</tbody>
</table>

To solve for the diffusivity, two mathematical diffusion models were used. In the first describing diffusion due to a concentration gradient in a semi-infinite media, the boundary conditions assume a plane source at the surface, where $x = 0$. The initial concentration is $C_o$ throughout the semi-infinite solid at $t = 0$ s, and the surface is maintained at constant $C_S$. The solution is written [118]:

$$\frac{C_X - C_0}{C_S - C_0} = 1 - erf \left( \frac{x}{2\sqrt{Dt}} \right) \quad (2.75)$$

where $C_X$ is the concentration at a depth equal to $x$ after some time $t$. In this case, $C_X$ is assumed to be the equilibrium concentration of reactant species involved in the redox reaction. The calculated depth is equal
to the depth of the front. This model is used to quantify the diffusion by a chemical potential gradient from any planar surface of the pellet (exterior surface, grain boundary, etc.). The second model for diffusion due to a concentration gradient describes a region bounded internally by a sphere having a radius \( r = a \). The region \( r > a \) has an initial concentration \( C_0 \) and the surface is maintained at constant \( C_S \). The solution is written \([118]\):

\[
\frac{C_X - C_0}{C_S - C_0} = \frac{a}{r} \text{erfc} \left( \frac{r - a}{2\sqrt{Dt}} \right)
\]

(2.76)

where \( C_X \) is the concentration at depth equal to \( x \) after some time \( t \). In this work, the radius \( r \) is assumed to be one half of the average spacing between metallic Ni\(^0\) particles and \( a \) gives the distance which has the equilibrium concentration \( C_X \). This model is used to quantify the diffusion by a chemical potential gradient that leads to growth of the metallic Ni\(^0\) particles.

### 2.5.2 Electrical Potential

In oxygen sensors, a gradient in oxygen partial pressure creates a voltage across the thickness of the oxide. Particularly in YSZ, where the intrinsic concentration of oxygen vacancies is high because of the addition of dopants, mass transport due to a concentration gradient resulting from a low oxygen partial pressure becomes less important until very reducing conditions are achieved. The voltage needed for mass transport by electrical potential to outweigh mass transport by a concentration gradient can be approximated, first considering the flux due to a linear gradient \([119]\):

\[
j_c = zFD \frac{dc}{dx} = zFD \frac{c_0}{L}
\]

(2.77)

where the bulk concentration of charge carriers is \( c_0 \) and the thickness of the specimen is \( L \). The flux due to an electrical gradient is given by:

\[
j_v = \sigma \frac{dV}{dx}
\]

(2.78)

where the voltage gradient is described by \( \frac{dV}{dx} \), assuming the gradient is linear. When the conductivity is written in terms of the bulk concentration, \( c_0 \), of charge carriers:

\[
\sigma = c_0(zF)^2 \frac{c_0}{L}
\]

(2.79)

then the flux due to the concentration gradient can be rewritten \([119]\):

\[
j_c = c_0(zF)^2 \frac{D V}{RT} \frac{1}{L}
\]

(2.80)

By setting \( j_c = j_v \), the minimum voltage needed to accomplish the same mass transport gradient as the maximum concentration gradient can be calculated by \([119]\):
\[ V = \frac{RT}{zF} \]  
(2.81)

At 1000°C for \( z = 2 \), a voltage drop of only 54.8 mV is needed to achieve an electrical potential that will exceed the chemical potential driving force for mass transport. This suggests that consideration of mass transport due to a chemical potential gradient will be important for describing mass transport in internal reduction.

Generally, the voltage resulting from a reaction is calculated by the Nernst equation shown by:

\[ E = E_0 - \frac{RT}{nF} \ln \frac{\prod a_{\text{products}}^{\nu_i}}{\prod a_{\text{reactants}}^{\nu_i}} \]  
(2.82)

Here \( \nu_i \) is the stoichiometric ratio of each species. In the case of an oxygen sensor, the voltage is calculated by:

\[ E = E_0 - \frac{RT}{nF} \ln \frac{P_{\text{II}}^I}{P_{\text{II}}^O} \]  
(2.83)

The value of \( E_0 \) can be calculated from the Gibbs free energy:

\[ \Delta G = -nFE_0 \]  
(2.84)

The magnitude of \( E_0 \) depends upon the thermodynamic potential of the change in Gibbs free energy. These equations can used to approximate the electrical potential that is created by specific reduction conditions. The electrical potential will be quantified for specific reduction conditions to explain the mass transport mechanisms during reduction.

### 2.6 Magnetic Properties

Magnetism results from electron orbital and electron spin motion. Orbital motion depends upon the size and shape of the path an electron orbits around a nucleus. The magnitude of orbital motion is the magnetic permeability, \( \mu \). Spin motion describe the rotation of an electron about an internal axis. The magnitude of spin motion is symbolized, \( \mu_B \), and named the Bohr magneton. Consider an atom, comprised of many electrons, each comprised of orbital and spin motion. The combination of orbital and spin motion produces a net magnetic moment that is unique for each atomic species. A lattice is composed of many, individual atoms which order to create the bulk magnetic properties of a substance.

The bulk magnetic properties that result from the magnetic ordering of atoms are described by diamagnetism, antiferromagnetism, paramagnetism, ferromagnetism, and in special cases, superparamagnetism. Other types of magnetism are possible, but beyond the scope of this work. Undoped 10YSZ has diamagnetic ordering, consisting of atoms with zero net magnetic moment. In an applied magnetic field, diamagnetic substances have a negative magnetic moment. Nickel oxide exhibits antiferromagnetic ordering, character-
ized by a small, positive net magnetic moment. The magnetic moment of antiferromagnetic materials is not influenced by an applied field; instead, those materials show a temperature dependence with a maximum magnetic moment occurring at the Néel temperature, $T_N$. A material exhibits antiferromagnetic behavior below $T_N$, displayed as an increase in magnetic moment as temperature increases, and paramagnetic behavior above $T_N$. An antiferromagnetic response is also observed in NiO-doped YSZ when all Ni$^{2+}$ is not in solution, but rather exists as NiO. An in-depth review of the remaining, relevant magnetic properties to this study and the material characteristics contributing to paramagnetism, ferromagnetism, and superparamagnetism is supported with magnetic theory.

2.6.1 Paramagnetism

A paramagnetic response is observed for Ni$^{2+}$ ions that are randomly substituted on the YSZ lattice and spaced sufficiently far apart to avoid interactions. Generally below about 2 molar percent, NiO-doped 10YSZ consists of Ni$^{2+}$ ions that have paramagnetic ordering. Atomic level mixing by by careful synthesis inhibits antiferromagnetic ordering of Ni$^{2+}$ ions in diamagnetic 10YSZ. In an applied field, the Ni$^{2+}$ ions partially align but complete alignment of the spins is prevented by thermal excitations. The net magnetism is positive. Without an applied magnetic field, the Ni$^{2+}$ ions have randomly oriented spins resulting in zero net magnetic moment. Paramagnetic behavior is modeled with the Curie-Weiss law:

$$\chi_m = C/(T - \theta)$$

where $\chi_m$ is mass susceptibility, $C$ is Curie constant, and $\theta$ is a constant having units of temperature and represents the x-axis intercept of inverse mass susceptibility, $1/\chi_m$, versus temperature, $T$.

2.6.2 Ferromagnetism

Metallic nickel, Ni$^0$, has ferromagnetic ordering. The magnetic moment exhibits a strong, positive net magnetic moment in an applied field that approaches a saturation magnetization, $M_S$. Above the Curie temperature, $T_C$, ferromagnetic materials show a paramagnetic dependence where $\theta$ equals the value of $T_C$. The $T_C$ for metallic Ni$^0$ is 631 K. Magnetic theory states that below $T_C$ ferromagnetic materials have spontaneous magnetization, even in the absence of an applied field, resulting in a complete alignment of the spins to produce the saturation magnetization, $M_S$. In reality, this is not always observed. At this point it is necessary to introduce magnetic domains to explain why metallic Ni$^0$ does not always exhibit spontaneous magnetization at room temperature.
2.6.2.1 Magnetic Domains

Similar to how individual atoms consist of electrons with no net magnetic moment, ferromagnetic materials can be divided into magnetic domains that cancel to produce a zero net magnetic moment. All of the spin states within a domain are aligned, but the domains are separated by domains walls. The domain walls do not necessary correlate with the microstructural features, such as grain boundaries. Using magnetic theory, the domain wall thickness, $\delta$, for metallic Ni can be calculated from [120]:

$$\delta = \sqrt{\frac{A}{K}}$$

(2.86)

where $A$ is the magnetic exchange stiffness which can be calculated and $K$ is the anisotropy constant. Physically the magnetic exchange stiffness is the force acting on a spin to keep it parallel, and is given by [121]:

$$A = \frac{nJ_{ex}S^2}{a}$$

(2.87)

where $n$ is the number of atoms per unit cell, $J_{ex}$ is the magnetic exchange force, $S$ is the spin and equals 1/2, and $a$ is the lattice parameter of metallic nickel. Physically the magnetic exchange force describes the tendency for spins to align with the majority of spins, given by [121]:

$$J_{ex} = \frac{3k_BT_C}{2zS(S + 1)}$$

(2.88)

where $z$ is the coordination number of atoms in the structure. The calculated thickness of a domain wall in metallic nickel is 16 nm at low temperature and 64 nm at room temperature. The formation of domain walls requires energy, so a particle having a diameter exceeding the domain thickness is not necessarily multidomain. By assuming a magnetostatic energy needed to stabilize the single domain particle equals the change in energy saved by reducing to a multidomain state, the critical radius $r_C$ for a single domain particle is given by [121]:

$$r_C = \frac{9(\rho K)^{1/2}}{\mu_0 M_S^2}$$

(2.89)

here $\rho_0$ is constant, and $M_S$ for metallic nickel is known. The results is $r_C = 6$ nm for metallic nickel. A second method to calculate the critical radius of a single domain particle is given by equation [121]:

$$r_C = \sqrt{\frac{9A}{\rho_0 M_S^2} \left[ \ln \left( \frac{2r_C}{a} \right) - 1 \right]}$$

(2.90)

This equation factors the cost of the magnetic exchange force density. The result is $r_C = 36$ nm for metallic nickel. It is interesting to note that the diameter for single domain particles lies between the thickness of the magnetic domain wall in nickel that is calculated at low and high temperatures.
2.6.3 Superparamagnetism

All superparamagnetic particles are single domain particles, but not all single domain particles are superparamagnetic. To illustrate the criteria for superparamagnetic behavior, consider a dispersion single domain metallic Ni\(^0\) particles existing in a 10YSZ matrix. Each particle has ferromagnetic ordering and an anisotropy energy, \(E\), represented by [121]:

\[
E = K \sin^2 \theta
\]  

(2.91)

where \(K\) is the anisotropy constant for metallic Ni\(^0\) and \(\theta\) is the angle between the saturation magnetization, \(M_S\), and the easy magnetic axis for metallic Ni\(^0\). Generally, \(M_S\) is independent of particle size until the surface area of the particle is much larger than the volume. The change in energy, \(\Delta E\), required to flip the particle is given by [121]:

\[
\Delta E = KV \left(1 - \frac{H_{ci} M_S}{2K}\right)^2 = 25k_B T
\]  

(2.92)

where \(H_{ci}\) is the intrinsic magnetic coercivity of the metallic Ni\(^0\) particle. The magnitude of coercivity is the field needed to force a particle into magnetic equilibrium. The particle size greatly influences \(H_{ci}\); Figure 2.13 shows the variation of coercivity as particle diameter, \(D\), increases. For larger, multidomain particles, the magnetic domains can cancel each other so the particle is in magnetic equilibrium and the coercivity is zero. A single-domain particle shows the maximum coercivity. Below a critical diameter, \(D_p\), the coercivity is zero again because thermal effects can achieve magnetic equilibrium. Particles that can spontaneously demagnetize after being magnetically saturated are called are superparamagnetic.

![Figure 2.13: The effect of particle size on the magnitude of coercivity, where MD is multidomain particles, SD is single domain particles, and SP is a superparamagnetic particles [120].](image)

Superparamagnetic particles also show a temperature dependence. Particles of the same volume, \(V\), have a characteristic blocking temperature, \(T_B\), given by [120]:

\[
T_B = \frac{2KVolume}{k_B}\]
Above $T_B$ the particles show superparamagnetic behavior and below $T_B$ the particles behave as stable, single-domain particles.

Magnetic theory is used to predict the size limitation for metallic Ni$^0$ particles that will exhibit superparamagnetic behavior. The critical radius required for a particle to show superparamagnetic stability of a particle for over 1 year is [121]:

$$r_{0}^{\text{year}} = \left( \frac{10k_B T}{K} \right)^{1/3}$$

The result is temperature dependent; $r_{0}^{\text{year}}$ at 5 K is 7 nm, $r_{0}^{\text{year}}$ at 100 K is 14 nm, and $r_{0}^{\text{year}}$ at 295 K is 21 nm. Since SQUID magnetometry measurement are collected below room temperature, the predicted particles sizes exhibiting superparamagnetic behavior are those less than approximately 14 nm in diameter.

### 2.7 Characterization Techniques

A brief introduction covering the general operating principles and vocabulary associated with characterization techniques is presented for techniques which the reader may be unfamiliar. When applicable, detection limitations and potential sources of error are discussed to assist the reader with interpretation of the experimental results.

#### 2.7.1 Focused Ion Beam (FIB) Milling

An alternative to conventional TEM specimen preparation technique is FIB milling. FIB is preferred over conventional TEM specimen preparation since this work examines nanoscale features of interest. The instrument includes a scanning electron microscope (SEM) and FIB source for imaging. In SEM imaging mode, secondary electrons (SE) are focused by a condenser lenses and accelerated at 5 kV towards the specimen. A beam deflector rasters across the surface of the specimen and the electrons to interact with the specimen [122]. The volume of interaction depends upon the accelerating voltage and the atomic number and density of the specimen. Inelastic scattering of the electrons in the specimen interaction volume causes emission of secondary electrons that are counted by the detector to produce a micrograph. Resolution in SEM is typically between 1 to 20 nm [122]. The SEM detector is located 52 degrees from the FIB detector in the specimen chamber. In FIB imaging mode, gallium (Ga$^+$) ions are accelerated at 30 kV toward the specimen. Resolution in FIB is around 5 nm. Both imaging modes and a nanomanipulator are needed to acquire a TEM liftout. Milling occurs when the Ga$^+$ impacts the surface of the specimen and sputters material. The amount of material sputtered by the Ga$^+$ depends upon the beam current. To prevent sputtering of areas of interest, platinum (Pt) is provided as a protective coating. High beam currents reduce milling time but cause
significant damage to the sample, including Ga\textsuperscript{+} ion implantation. Another artifact is curtaining, or areas that are milled thinner that adjacent material, due to porosity or uneven milling of the protective Pt layer. In addition, Ga\textsuperscript{+} ions readily alloy with copper, leading to sputtering and deposition of fine Cu-rich particles on TEM liftouts when low current cleaning cross-sections are not utilized and due to poor placement of the liftout on the Cu grid.

### 2.7.2 Transmission Electron Microscopy (TEM) Micrograph Analysis

An electron transparent specimen is required for TEM and this thickness varies depending upon the material. A Monte Carlo simulation model was used to model kinematic scattering resulting from a 200 kV accelerating voltage. For TEM analysis, a 10YSZ liftout should be less than 100 nm thick. Resolution for the TEM used in this work is approximately 0.2 nm [123]. The electron source used in this work is a lanthanum hexaboride (LaB\textsubscript{6}) filament. Briefly, electrons are accelerated at 200 kV from the LaB\textsubscript{6} source. The electron beam is focused down the optic axis by lenses (electromagnetic coils) and apertures are inserted to exclude incoherent electrons, those in a path that deviates from optic axis. The condenser lens is always inserted on the TEM used in this work, however, the aperture size is changeable. The objective aperture and selected area diffraction (SAD) aperture can be inserted/removed and the aperture sizes are changeable.

Some vocabulary is presented to aid interpretation of TEM micrographs within this work. An all-beams micrograph is taken with only the condenser lens inserted. The contrast is due to variations in specimen mass/thickness. Bright field and dark field micrographs are taken with the condenser and objective apertures inserted. The contrast is due to mass/thickness and diffraction. In bright field the absence of material, such as a pore, is brightest. The opposite is observed in dark field, for example, pores appear darkest. The brightest areas in dark field share the orientation direction selected with the objective aperture. The SAD lens is often inserted in diffraction mode to select a small region, such as an individual grain, from which to obtain a diffraction pattern.

### 2.7.3 Laser Atom Probe Tomography (APT) Analysis

Three dimensional, nanoscale reconstructions of a specimen are possible with APT [124]. First, very sharp tips of material are prepared with FIB, since the tips often contain nanoscale features of interest. The analysis is performed in a cryocooled chamber under ultra-high vacuum. An electric potential (voltage) is applied to a very sharp tip (< 100 nm) of specimen to create a high electric field at the tip radius. The high field effectively magnifies the charged species as they are projected away from the tip [125]. Charged species (atoms, ions, molecules, etc.) are field evaporated radially from the surface of the tip in a controlled manner by using laser pulses. The time of flight from the laser pulse to when the atoms contact the detector enables
the identification of the charged species by the mass-to-charge ratio [126]. The position the charged species contacts the detector can be used to identify the source location of the charged species in the specimen, and reconstructions are performed using IVAS software and manually identifying the peaks associated with the expelled, charge species. Since APT is a relatively new technique, particularly for analysis of oxides, it is important to optimize the analysis conditions to achieve the predicted stoichiometric ratios, as discussed later in the experimental procedure [127]. The benefit of APT to this work is atomic resolution and chemical quantification of nanoscale features.

2.7.4 Inductively Coupled Plasma (ICP) Analysis

ICP-AES (atomic emission spectroscopy) analysis is a quantification technique for determining the concentration of ionic species. The specimen of interest must be prepared into a solution prior to analysis, which is challenging when analyzing oxides known for superior anti-corrosion properties. Organic oxide precursors are often digested in hydrogen peroxide and oxides are dissociated directly in hydrofluoric acid or in a glass melt. The glass fusion can be dissolved in hydrochloric acid, when hydrofluoric acid is not desirable to use. An acid solution is desirable because it improves the solution stability and ensures that the analytes remain in solution. Analytes in an unstable solution can precipitate or attach to the container walls, and will not be accurately represented in the reported results [128]. An acidic solution is particularly of importance when concentrations of transition metal analytes are of interest because these are prone to hydrolysis and precipitation [129]. The ICP is generated by electromagnetic radiation and atomizes the solution. Light is passed through the atomized solution and enters the optic chamber of the spectrometer where the intensities of all wavelengths are measured simultaneously. The characteristic electromagnetic radiation of elements present in solution are counted to report the concentration of element present in solution. Record of the mass of solution and material digested or dissociated is critical to convert the reported concentration of the analyte measured in solution into the concentration of the analyte in the organic or oxide.

2.7.5 Principles of SQUID Magnetometry

A SQUID magnetometer measures the magnetic flux induced by the magnetization of a specimen. In general, magnetic flux, \( B \), is given by:

\[
B = \mu(M + H)
\]

(2.95)

where \( \mu \) is magnetic permeability and is constant, the magnetization \( M \) is characteristic of the specimen's unique magnetic properties, and the applied magnetic field \( H \) is input by the operator. The core of the SQUID is a device comprised of two Josephson junctions in parallel [120]. A Josephson junction is a magnetic flux meter that consists of three layers; the outer layers are made from a superconducting material.
and the inner layer is made from a non superconducting material. In the absence of an external magnetic influence, superconducting electrons tunnel through the non superconducting material and the magnitude of the current is equal in both Josephson junctions. The magnetization of a specimen in an applied magnetic field generates a voltage in the Josephson junction, resulting in a current. The current is subtracted from one Josephson junction and added to the other Josephson junction and the output is counted by the pick up coils within the SQUID. The sensitivity of the SQUID magnetometer is approximately $10^{-10}$ Am$^2$ [120]. The SQUID magnetometer used in this work is operable between 1.8 to 400 K, magnetic fields up to 7 T, and is capable of direct current (DC) or alternating current (AC) susceptibility measurements.

### 2.7.5.1 DC Susceptibility

Magnetic susceptibility that is measured as a response of DC magnetic field (static) is DC susceptibility. The DC susceptibility measurements essentially tell the equilibrium magnetization state of the specimen in the applied magnetic field. The pickup coils measure the magnetization of the specimen. The shape of the $M(H)$ and $M(T)$ curves output from DC susceptibility measurements can distinguish between the different types of magnetization.

### 2.7.5.2 AC Susceptibility

Magnetic susceptibility that is measured as a response of AC magnetic field (dynamic) is AC susceptibility. The AC drive field follows a sinusoidal wave and causes a time-dependent moment in the specimen. The wave properties are determined by the magnitude of the AC frequency input by the user. The pickup coils measure the time-dependent moment in the specimen. All AC susceptibility measurement data is output as two components, real $\chi'$ and imaginary $\chi''$. At low frequencies, the real $\chi'$ component is the slope of the $M(H)$ curve and shows the magnitude of the specimen magnetization. The imaginary $\chi''$ component is not represented by DC susceptibility and shows the phase losses between the specimen magnetization and the applied field.

Measurements of AC susceptibility are particularly useful for quantifying particle size. Recall equation 2.92, which gives the $\Delta E$ required to flip a magnetic particle. The objective of the AC field is to flip the magnetic particles. Particles that flip with the field are in phase while particles that demonstrate a lag are out of phase. Consider a very small and a very large particle. The smaller particle requires less thermal energy to reverse its magnetization and flip with the applied field. Maximum intensities in $\chi'$ for small particles occur at low temperatures. Increasing the particle size increases the temperature that provides sufficient thermal energy to flip large particles. Increasing the magnitude of the applied AC drive field increases the magnetic driving force for the particles to flip, making it easier for particles to stay in phase.
A DC field can be applied during AC susceptibility measurements. The DC field decreases the magnetic driving force for particles to flip in the opposite direction making it more difficult for a particle to stay in phase with the sinusoidal AC drive field. All particles also need time to flip with the applied field. Increasing the AC frequency effectively decreases the time between flips. Higher frequency measurements on a constant particle size need more thermal energy to enable the particle to flip with the AC drive field, so the maximum $\chi'$ shifts to higher temperature.
An overview of experimental methods is covered here beyond what is presented in the paper chapters. This chapter begins with the details of the synthesis of Ni-doped YSZ pellets. Capabilities of the reduction furnace assembled for this work are discussed, followed by the calibration procedures. Then the parameters for internal reduction and reduction-oxidation cycling are detailed. The remainder of the chapter is dedicated to the experimental parameters used in characterization of the reduced pellets, including mathematical expressions that provide the baseline for the geometric model to describe and predict internal reduction kinetics.

3.1 Synthesis

A high purity, chemical synthesis method was selected to prepare 0.5 molar percent NiO dopant in 10 molar percent Y$_2$O$_3$ in ZrO$_2$ (10YSZ) to encourage atomic level mixing of Ni$^{2+}$ ions [130]. Powders were prepared using high purity acetate precursors of Ni$^{2+}$, Y$^{3+}$, and Zr$^{4+}$ and an EDTA-citrate polymeric complexing method. Thermogravimetric analysis was used to determine stoichiometric amounts of the acetate precursors needed to prepare 0.5 molar percent NiO-doped 10YSZ. Calcination was performed in high purity (99.8 %) Al$_2$O$_3$ crucibles (CoorsTek, Golden, CO) heating at 5°C/min and soaking at 600°C for 10 h in air (Deltech, Inc., Denver, CO). Pellets of 4 mm thickness were formed from prepared powders in a 19 mm stainless steel die in a uniaxial press (Carver, Inc., Wabash, IN). The pellets were buried in 0.5 molar percent NiO-doped 10YSZ powder heated in high purity (99.8 %) Al$_2$O$_3$ (CoorsTek, Golden, CO) containers at 3°C/min to 1500°C for 4.5 h in air.

3.2 Reduction Furnace Assembly

This research required a dedicated, contaminant-free furnace so a custom reduction furnace was built for this work. This section highlights the features of the reduction furnace. A flow diagram is shown in Figure 3.1. The furnace assembly, including all components and communications, is completely installed onto a portable cart. The cart is equipped with a mass flow controller (MFC) for each gas type, calibrated for pure argon and 2 % hydrogen (argon balance), and a power supply to set gas flow from 0 to 110 sccm. There are ball valves located in the gas line between the tank regulator and MFC for each gas line to enable easy exchange of gas tanks. The gas line flows through heated bubblers to run humidified conditions, but the lines are interchangeable with a U-shaped gas line to run dry conditions. The bubblers are wrapped in heat
belt and insulated to control the dew point. Individual controllers for the bubbler heat belts are located on the front panel of the cart. Solenoid valves appear after the bubblers in each gas line to electronically open or close gas flow. The gas lines from the solenoid valve into the face plate are heated and insulated to prevent condensation when operating in humidified conditions. The humidity sensor also acts as a thermocouple and reports the temperature, dew point, and relative humidity of the inlet gas line. The faceplate on the reactor tube has three ports, one for inlet gas, the oxygen sensor, and thermocouple/exhaust. The oxygen sensor has an internal reference and S-type thermocouple, that is removable. The leads are attached with alligator clips to a multimeter for direct readout and recorded by the communication system. The additional load thermocouple in the reactor tube is K-type. All of the thermocouples, oxygen sensor, and humidity sensor are recorded by the communications system. The tubular furnace, furnace power supply, and controller are also located on the cart. A serial to USB converter box enables manipulation and record of setting and readout values displayed by the thermocouples and sensors. A laptop is attached to the assembly which offers a graphic user interface in LabView for the operator. The GUI enables control of the solenoid valves and mass flow controllers (including mass flow rate) on site or by remote access since the computer is accessible on the CSM network. The LabView software records all run data, including the actual and set point values of Ar and H₂ flow; the actual and set point values of bubbler temperature control; the inlet relative humidity, gas temperature, and dew point; the oxygen sensor voltage and converted oxygen partial pressure and temperature reading from the S-type inlet gas thermocouple; and the voltage and converted temperature reading from the K-type thermocouple located in the reactor. The reduction run data is recorded into a comma separated variable (.csv) file so the quality of the run and recorded parameters can be reviewed. A photo of the completed furnace assembly is shown in Figure 3.2. A complete build list for the assembly is provided in Figure 3.3.

3.3 Calibration of Oxygen Sensor

Two types of oxygen sensors were used in this work: 1) a Micropoas (Setnag, Marseille, France) high temperature internal reference oxygen sensor and 2) and standard zirconia oxygen sensor tube, shown in Figure 3.4. The advantage of the Micropoas oxygen sensor is the small size, approximately 1 cm, enables measurement of in-situ oxygen partial pressure during reduction runs up to 10⁻³⁵ atm. The Micropoas thermocouple and reference wires are protected by a ceramic sheath. Two thermocouple wires extend around the exterior of the sensor and one reference wire is enclosed in the interior of the sensor. A disadvantage is the Micropoas has a shorter lifetime than the standard zirconia oxygen sensor tube because the internal reference is susceptible to reduction.
Figure 3.1: Flow diagram of reduction build.

Figure 3.2: Dedicated furnace assembly for reduction runs.
<table>
<thead>
<tr>
<th>Item</th>
<th>Vendor</th>
<th>Model/Part Number</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tubular furnace</td>
<td>ATS</td>
<td>Series 3210</td>
<td>1200°C maximum, 3 in. ID x 12 in. OD x 16 in. long End cap/disk 1.5 in. thick bore 2 in. OD tube</td>
</tr>
<tr>
<td>Mass flow controllers and</td>
<td>MKS</td>
<td>CB147-1-10</td>
<td>Maximum flow rate, 110 sccm</td>
</tr>
<tr>
<td>accessories</td>
<td></td>
<td></td>
<td>Maximum flow rate, 110 sccm</td>
</tr>
<tr>
<td>Laptop</td>
<td>Dell</td>
<td>Inspiron 5320</td>
<td>Intel core i7-3612QM processor, 15.6 in. LED screen</td>
</tr>
<tr>
<td>Multimeter</td>
<td>Keithley</td>
<td>Model 2100/120</td>
<td>6-1/2 Digit USB digital multimeter, 120V</td>
</tr>
<tr>
<td>Oxygen sensor</td>
<td>Setrag</td>
<td>Micropos</td>
<td>15-pin Type D PR4000 for each MFC</td>
</tr>
<tr>
<td>Ceramic sheath for O2 sensor</td>
<td>Omega</td>
<td>FRX-02018-1B-18</td>
<td>Ceramic 4 hole round insulator</td>
</tr>
<tr>
<td>Humidity sensor and coil</td>
<td>Rotronic</td>
<td>HydroFlex 2 IM1</td>
<td>120mm x 15mm, stainless steel probe, 2m cable, 100 to +200°C</td>
</tr>
<tr>
<td>Bubblers</td>
<td>Rotohm</td>
<td>HygroClip 2 IM1</td>
<td>24 in. TC bobbins with 3 ea. 1/4 in. Swagelok connectors</td>
</tr>
<tr>
<td>Bubblers controller and</td>
<td>Omega</td>
<td>TMQSS-125U-6</td>
<td>Silicone rubber heater</td>
</tr>
<tr>
<td>accessories</td>
<td></td>
<td></td>
<td>Solid state relays</td>
</tr>
<tr>
<td>Tube fasteners</td>
<td>McMaster Carr</td>
<td>50111141</td>
<td>1/16 DIN controller</td>
</tr>
<tr>
<td>Insulation</td>
<td>McMaster Carr</td>
<td>99405K117</td>
<td>Subminiature with molded connector</td>
</tr>
<tr>
<td>Solder to USB</td>
<td>Omega</td>
<td>OMG-USB-SER-8</td>
<td>Worn-dyne hose and tube clamp</td>
</tr>
<tr>
<td>Solenoid valves</td>
<td>Swagelok</td>
<td>found extras in HH373</td>
<td>Melamine insulation with reinforced jacket</td>
</tr>
<tr>
<td>Tubular reactors</td>
<td>CoorsTek</td>
<td>66463</td>
<td>One-piece hook and loop valves</td>
</tr>
<tr>
<td>Flange and faceplate</td>
<td>MKS</td>
<td>100318006-L</td>
<td>Subminiature with molded connector</td>
</tr>
<tr>
<td>O-Rings</td>
<td>McMaster Carr</td>
<td>946H86</td>
<td>ASSY, toggle clamp</td>
</tr>
<tr>
<td>Data acquisition accessories</td>
<td>LabJack</td>
<td>SKU: U3-UV</td>
<td>Viton fluoroelastomer</td>
</tr>
<tr>
<td>Moveable cart</td>
<td>Outfitters</td>
<td>SKU: BBE-A2642</td>
<td>Seal, fitting, tubing</td>
</tr>
<tr>
<td>Fittings</td>
<td>Swagelok</td>
<td>SS-402-1 Ferrule</td>
<td>Seal, fitting, tubing</td>
</tr>
<tr>
<td>Metal tubing</td>
<td>Swagelok</td>
<td>SS-FLAT-A7A-24</td>
<td>Seal, fitting, tubing</td>
</tr>
<tr>
<td>K-type thermocouples</td>
<td>Omega</td>
<td>CAIN-18U-12</td>
<td>Seal, fitting, tubing</td>
</tr>
</tbody>
</table>

Figure 3.3: Itemized build list for reduction furnace.
The Micropoas internal reference oxygen sensor and S-type thermocouple were calibrated in synthetic air (21 % O₂/N₂ balance) by sweeping temperature between 600°C and 1000°C, the working range of the sensor. To determine the voltage, $E_0$, dependence on temperature in air a plot of DC voltage versus temperature is shown in Figure 3.5. The voltage dependence is given by:

$$E_0 = aT + b$$  \hspace{1cm} (3.1)

where $a$ is determined by the slope and $b$ is determined by the y-intercept. The measured voltage can be computed into oxygen partial using the Nernst equation in the form given by:

$$E = E_0 + \frac{RT}{4F} \ln \frac{P_{O_2}}{0.2095}$$  \hspace{1cm} (3.2)

In order to solve $P_{O_2}$ in atm, $E$ must be input in mV and $T$ must be input in degree K.

The external oxygen sensor was connected to the inlet gas line and placed in a furnace heated to 800°C. The external oxygen sensor was used to determine the the ratios of dry 1 % or 2 % H₂ gas and Ar to achieve desired oxygen partial pressures of $10^{-15}$ atm and $10^{-19}$ atm. The experimental flow rates of each gas type are shown in Table 3.1. The percent hydrogen needed to achieve equal oxygen partial pressures for 800°C, 900°C, and 1000°C can be extrapolated from Figure 3.6. A representative Mathematica spreadsheet used for the calculations is shown in Appendix A.

### 3.4 Calibration of Mass Flow Rate

In special cases, gases other than 2% H₂/Ar balance were used on the reduction furnace build. Since flow rate of the purchased mass flow controller (MFC) is calibrated by the manufacture for the specified gas/gas blends a correction must be applied to the gain value in the controller. A gas correction factor, $GFC$, calculation provide by MKS was used to set a gain for the new gas composition:

$$GFC = \frac{0.3106 (a_1 s_1 + a_2 s_2 + \ldots + a_n s_n)}{a_1 d_1 c_{p1} + a_2 d_2 c_{p2} + \ldots + a_n d_n c_{pn}}$$  \hspace{1cm} (3.3)
Figure 3.5: Micropoas internal reference oxygen sensor calibration data.

Figure 3.6: Plot showing oxygen partial pressure versus percent hydrogen for isotherms of 600°C, 800°C, and 1000°C.
Table 3.1: Experimental mixtures of Ar and H$_2$ used to calibration the external oxygen sensor.

<table>
<thead>
<tr>
<th>Tank</th>
<th>Inert Flow sccm</th>
<th>Reducing Flow sccm</th>
<th>Total Flow sccm</th>
<th>Percent Hydrogen %</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 % H$_2$</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>2.00</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>0.01</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>100</td>
<td>110</td>
<td>0.18</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>100</td>
<td>101</td>
<td>0.02</td>
</tr>
<tr>
<td>1 % H$_2$</td>
<td>100</td>
<td>0</td>
<td>100</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>50</td>
<td>100</td>
<td>0.05</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>100</td>
<td>110</td>
<td>0.09</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>100</td>
<td>101</td>
<td>0.01</td>
</tr>
</tbody>
</table>

For each gas type, the fractional flow is given by $a_n$, the molecular structure factor is given by $s_n$, the standard density is given by $d_n$, and the specific heat capacity is given by $c_{pn}$. A complete table of variables for each gas type and details showing the full calculations are given in Appendix B.

3.5 Reduction

Multiple series of reduction experiments were performed to study how changes to the thermodynamic and kinetic driving force for the internal reduction reaction changes the overall reaction kinetics and microstructure. All reduction experiments were performed in the dedicated reduction furnace assembly. The pellets were placed on a section of a high purity alumina reactor tube, selected because it supports the bottom corners of the pellet but has a gap for gas flow underneath the pellets. The alumina support was loaded into the reaction chamber using a measuring stick to consistently place the pellets at 33 cm from the tube opening and adjacent in proximity to the load thermocouple and oxygen sensor. Table 3.2 summarizes all of the experimental flow conditions for this work.

Beginning with experimental conditions to study the influence of temperature on the kinetic driving force, the oxygen partial pressure was controlled at $10^{-19}$ atm for 800°C, 900°C, and 1000°C at 0.5, 5, 10, and 25 h soak times. To achieve $10^{-19}$ atm at 1000°C a mixture of 2 sccm of dry 1 % H$_2$/N$_2$ balance and 110 sccm dry Ar (99.999 % purity) was flooded into the reactor chamber. To achieve $10^{-19}$ atm at 900°C, a mixture of 17 sccm of dry 2 % H$_2$/Ar balance and 100 sccm dry Ar (99.999 % purity) was flooded into the reaction chamber. To achieve $10^{-19}$ atm at 800°C, a mixture of 3 sccm of dry 1 % H$_2$/Ar balance and 100 sccm dry Ar (99.999 % purity) was flooded into the reaction chamber. All heating and cooling was done at 5°C/min using the equivalent flow rate of Ar (99.999 % purity) used in the reducing gas mixture. Appendix A summarizes
Table 3.2: Summary of experimental conditions for reduction.

<table>
<thead>
<tr>
<th>$T$ (°C)</th>
<th>$P_{O_2}$ atm</th>
<th>Humidity %</th>
<th>Inert Gas</th>
<th>Flow Rate sccm</th>
<th>Reducing Gas</th>
<th>Flow Rate sccm</th>
<th>Time h</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>100</td>
<td>1 % H$_2$/N$_2$ bal.</td>
<td>3</td>
<td>10</td>
</tr>
<tr>
<td>800</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>100</td>
<td>1 % H$_2$/N$_2$ bal.</td>
<td>3</td>
<td>25</td>
</tr>
<tr>
<td>900</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>100</td>
<td>2 % H$_2$/Ar bal.</td>
<td>17</td>
<td>0.5</td>
</tr>
<tr>
<td>900</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>100</td>
<td>2 % H$_2$/Ar bal.</td>
<td>17</td>
<td>5</td>
</tr>
<tr>
<td>900</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>100</td>
<td>2 % H$_2$/Ar bal.</td>
<td>17</td>
<td>10</td>
</tr>
<tr>
<td>900</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>100</td>
<td>2 % H$_2$/Ar bal.</td>
<td>17</td>
<td>25</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>66</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-19}$</td>
<td>0</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>75</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>0</td>
<td>Ar</td>
<td>110</td>
<td>1 % H$_2$/N$_2$ bal.</td>
<td>2</td>
<td>0.5</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>0</td>
<td>Ar</td>
<td>110</td>
<td>1 % H$_2$/N$_2$ bal.</td>
<td>2</td>
<td>5</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>0</td>
<td>Ar</td>
<td>110</td>
<td>1 % H$_2$/N$_2$ bal.</td>
<td>2</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>0</td>
<td>Ar</td>
<td>110</td>
<td>1 % H$_2$/N$_2$ bal.</td>
<td>2</td>
<td>25</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>10</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>0.5</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>10</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>5</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>10</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>10</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>10</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>1000</td>
<td>$10^{-15}$</td>
<td>10</td>
<td>Ar</td>
<td>0</td>
<td>2 % H$_2$/Ar bal.</td>
<td>100</td>
<td>50</td>
</tr>
</tbody>
</table>
the calculations used to maintain constant oxygen partial pressure.

Continuing with experimental conditions to study the influence of thermodynamic driving force on reaction kinetics, the oxygen partial pressure was controlled to $10^{-15}$ atm and $10^{-19}$ atm at 1000°C reduction for 0.5, 5, 10, and 25 h soak times. In addition, longer soak times of 66 and 75 h were conducted at 1000°C and $10^{-19}$ atm. To achieve $10^{-19}$ atm, 100 sccm of dry 2 % H$_2$/Ar balance was flooded into the reaction chamber at temperature. To achieve $10^{-15}$ atm, a mixture of 2 sccm of dry 1 % H$_2$/Ar balance and 110 sccm dry Ar (99.999 % purity) was flooded into the reaction chamber. In addition, humidified conditions were chosen such that the oxygen partial pressure was $10^{-15}$ atm at 1000°C when bubbling 100 sccm 2 % H$_2$/Ar balance through water to study the influence of humidity on surface reaction kinetics. All heating and cooling was done at 5°C/min in 100 sccm flowing Ar (99.999 % purity).

### 3.6 Reduction-Oxidation (Redox) Cycling

Two reduction-oxidation cycles of 0.5 molar percent NiO-doped 10YSZ pellets were performed by first reducing a series of pellets at 1000°C for 25 h in 100 sccm of dry 2 % H$_2$/Ar balance. Oxidation was performed at 1000°C in 100 sccm of dry 21 % O$_2$/Ar balance for 0.5, 5, 10, and 25 h to analyze the stages of oxidation. The redox cycle was completed a second time. Re-reduction of pellets was performed at 1000°C in 100 sccm of dry 2 % H$_2$/Ar balance for 0.5, 5, 10, and 25 h to analyze the stages of re-reduction. Re-oxidation was performed at 1000°C in 100 sccm of dry 21 % O$_2$/Ar balance 25 h. All heating and cooling was done at 5°C/min in 100 sccm flowing Ar (99.999 % purity). Additional pellets were oxidized at the same conditions for 0.5, 5, 10, and 25 h to analyze the stages of re-oxidation.

### 3.7 Characterization

The specimen preparation procedures for characterization and the specific operating parameters utilized for various characterization techniques are reported.

#### 3.7.1 Inductively Coupled Plasma (ICP) Analysis

Solutions for inductively coupled plasma-atomic emission spectroscopy (ICP-AES) were prepared. First, approximately 5 mg char was digested in 30 mL of 30% hydrogen peroxide. A pH ≤ 2 was achieved by adding drops of hydrochloric acid. Glass fusions were prepared using a 10 to 1 mass ratio of lithium tetraborate to powder specimen mixed in a small Pt-Au crucible. The mixture was heated at 5°C/min to 1000°C, soaked for 1 h, then removed at temperature and cooled in the crucible. The Pt-Au crucible was specifically selected for anti-wetting characteristics. The fusion bead was crushed and a small amount of glass powder was dissolved in hydrochloric acid. The solutions were submitted to the Department of Chemistry and Geochemistry at Colorado School of Mines for ICP-AES analysis.
3.7.2 Transmission Electron Microscopy (TEM) Analysis

Liftouts of 0.5 molar percent as-sintered and reduced NiO-doped 10YSZ were prepared using FIB milling (Helios Nanolab 600i; FEI, Hillsboro, OR). First, the pellets were cross-sectioned and cold-mounted in epoxy. The mounts were polished using 120, 240, 600, 800, and 1200 grit silica pads, followed with 0.5 and 0.03 micron suspended alumina. The mount was painted with colloidal graphite DAG around the pellet cross-sections and tracing a connection to the bottom of the mount. Then the epoxy mount was gold-sputter coated (Technics Hummer VI, Anatech Ltd., Union City, CA) and secured to the stage with copper tape. Regular cross-section milling geometry was selected to prepare a trench of 18 µm length by 15 µm width by 15 µm depth. The liftouts were flagged to a copper grid, and the thickness was reduced while viewing with electrons until the material appeared electron transparent.

3.7.3 Atom Probe Tomography (APT) Analysis

A 200 mesh slim bar copper grid was halved to support 8 tips (tips are spaced one post apart to prevent damage to neighboring tips during analysis). Cones of 0.5 molar percent as-sintered and reduced NiO-doped 10YSZ were milled using a FIB (Helios Nanolab 600i; FEI, Hillsboro, OR). Grain boundary triple points were identified in ion imaging and a protective layer of Pt was applied. Circular milling geometry was selected, starting with an outer diameter of 25 µm, inner diameter of 7 µm, and milling depth of 8 µm. The cone of material was liberated and Pt welded to a post using the nanomanipulator. Sharpening of the cones into tips was performed on the FIB using circular milling geometry, starting with an outer diameter of 8 µm and inner diameter of 3.5 µm. The inner diameter was decreased, repeating milling and diameter reduction down to 50 nm. The milling progress was witnessed in electron imaging. A 2 kV clean-up was performed until approximately 50 to 100 nm of material was removed (this depth of material is removed because it exhibits Ga⁺ ion damage). The tips were characterized in TEM using bright field and dark field to highlight grain boundaries, when present.

Before each series of tips were run, a flat test of the electrode was performed as a quality check. The flat geometry produced no field evaporation so the signal is produced by this test represents noise or contamination in the analysis chamber. The voltage at which a signal is observed represents the turn on voltage of the electrode, typically in the 7.5 to 9.0 kV range. In addition, a silicon standard tip was run to align the laser and specimen position. Since parameters for APT analysis of YSZ were not previously reported, the parameters were optimized to match oxygen stoichiometry using tips that did not exhibit grain boundaries. The first tips that were characterized were in as-reduced condition. A better optimization would use the as-sintered tips. The conditions were not changed for as-sintered tips run after as-reduced tips, as to compare the results. A typical good run can produce over 2 million ion counts. The best results were achieved
when Cryo A temperature equaled 35 K to 40 K, and Cryo B temperature equaled 40 K to 45 K. Lower temperature settings resulted in rapid loss of specimen by tip liberation. The best laser energy was 40 pJ. For all runs the evaporation rate was set to 0.5 % detection, the voltage was set to 500 V, pulse rate set to 500 kHz, and flight length set to 90 mm. The runs were set to stop at 7.0 to 9.0 kV, depending on the reported electrode voltage, to minimize turn on of the electrode.

### 3.7.4 SQUID Magnetometry

All measurements were performed at National Institute of Standards and Technology (NIST), Boulder, CO, on an MPMS-7 SQUID Magnetometer (Quantum Design, San Diego, CA).

#### 3.7.4.1 Direct Current (DC) Measurements

Extent of reduction was further examined with SQUID magnetometry to quantify the amount of metallic Ni\(^{0}\) in the reacted zone. A 50 to 100 mg section cut from the center of each reduced pellet was folded in the adhesive end of note pad and inserted into a standard drinking straw for measurement. DC susceptibility moment versus field curves were collected at 100 K to quantify the saturation magnetization. The diamagnetic response of 10YSZ was subtracted from the overall curve measured at 100 K to extract the pure ferromagnetic response. The value of the y-intercept of the corrected moment versus field curve gives the magnetic saturation of the metallic Ni\(^{0}\). An example sequence is shown in Appendix C.

#### 3.7.4.2 Alternating Current (AC) Measurements

The metallic Ni\(^{0}\) particle size was quantified with SQUID magnetometry. AC susceptibility curves were collected using an AC drive of 7 Hz, 100 \(\mu\)T AC drive amplitude, zero DC field, and scanning temperature from 1.8 K to 250 K. A 50 to 200 mg section cut from the center each reduced pellet was secured into a standard drinking straw for measurement. Output from AC susceptibility is reported as real, \(\chi'\), and imaginary, \(\chi''\), components versus temperature. An example sequence is shown in Appendix C.

### 3.8 Geometric Model of the Extent of Reaction

A model for internal reduction proposed by White et al. describing the formation of metallic Ni\(^{0}\) particles along a single grain boundary was extended to describe the SQUID data. The as-sintered geometry of the pellets are approximately 13 mm diameter by 4 mm thickness. By setting the diameter in excess of the thickness, the intention was to eliminate edge affects and cross-over of reacted zones moving inward from the top and bottom surfaces with reacted zones moving inward from the sides. At the center of the pellet, away from the edge, the extent of reaction is two-dimensional. Figure 3.7 shows an illustration of the two-dimensional cross-section showing the extent of reaction zone, \(\Delta \xi\). This model is dependent upon
microstructural features of the formed metallic Ni\textsuperscript{0} particles from the reducing treatment. In this simple

Figure 3.7: A two-dimensional illustration of the the extent of reaction zone for polycrystalline cross-sections, considering only the extent of reaction from one external surface.

geometric model, microscopic features include the grain size given by \( d \) and the spacing between particles given by \( \lambda \). Macroscopic features of specimen geometry are defined by width, \( w \), and length, \( L \). By knowing the specimen thickness, \( t \), this model is applied to predict the particle distribution in a volume of material. The mathematical expressions used to construct the geometric model for internal reduction are presented.

The extent of reaction, \( \Delta \xi \), is measurable for a given thermodynamic and kinetic potential. Basic geometry of a pellet cross-section (SQUID magnetometry specimen) can therefore be used to calculate the total area of reduction, \( A \), and total volume of reduction, \( V \), given by:

\[
A = 2 \Delta \xi w
\]

\[
V = 2 \Delta \xi wt
\]

A factor of 2 is included because the pellet cross section includes the extent of reaction from the top and bottom surfaces of the pellet. It is possible to calculate the number of grain boundaries, \( n \) present in the cross-section, as shown by equation 3.6. For simplicity, the model assumes the grain boundaries run parallel in a two-dimensional plane. This is reasonably assumption, since most brick layer models for grain boundary diffusion assume grain boundaries parallel to the diffusion motion are involved in the reaction [131–133]:

49
\[ n = \frac{w}{d} - 1 \]  \hspace{1cm} (3.6)

Then the number of particles existing along a single grain boundary, \( N_{1D} \), is given by:

\[ N_{1D} = \frac{\Delta \xi}{\lambda} \]  \hspace{1cm} (3.7)

Thus the number of particles existing in a two-dimensional plane, \( N_{2D} \), similar to the area depicted in Figure 3.7 is given by:

\[ N_{2D} = n N_{1D} = \left( \frac{w}{d} - 1 \right) \left( \frac{\Delta \xi}{\lambda} \right) \]  \hspace{1cm} (3.8)

Finally the number of particles existing in a volume of material, \( N_{3D} \), having a thickness, \( t \), is given by:

\[ N_{3D} = n N_{2D} \left( \frac{t}{\lambda} \right) = \left( \frac{w}{d} - 1 \right) \left( \frac{\Delta \xi t}{\lambda^2} \right) \]  \hspace{1cm} (3.9)

Here \( t/\lambda \) represents a grain boundary having a one-dimensional grain boundary that extends the thickness of the cross-section containing particles with particles spaced by \( \lambda \). To this point, the model assumes the particles are points but in fact the particles also have volume.

An independent method to calculate the number of particles is from SQUID magnetometry results. The number of particles measured by SQUID magnetometry is a function of the measured magnetization saturation, \( M_S \), and the microscopic particle radius, \( r_{Ni^0} \). From SQUID magnetometry, the mass of nickel can be calculated with:

\[ m_{Ni^0} = \frac{M_S}{\sigma_o} \]  \hspace{1cm} (3.10)

The \( M_S \) is a bulk measured value from the entire cross-sectional volume and the magnetization per unit mass, \( \sigma_o \), is a constant. For nickel, \( \sigma_o \) is approximately 57.5 emu g\(^{-1}\). The total volume of nickel can be calculated from the density, \( \rho \), as shown by:

\[ V_{Ni^0} = \frac{m_{Ni^0}}{\rho_{Ni^0}} \]  \hspace{1cm} (3.11)

The density of nickel, \( \rho_{Ni^0} \), is 8.912 g cm\(^{-3}\). To determine the number of nickel particles, \( N_{tot} \), the radius of the nickel particles, \( r_{Ni^0} \), must be known from microscopy or guesses can be input into the model to solve for:

\[ V_{tot} = \frac{4}{3} \pi r_{Ni^0}^3 \]  \hspace{1cm} (3.12)

Then the calculation for \( N_{tot} \) is a ratio of the measured and calculated values, given by:

\[ N_{tot} = \frac{V_{tot}}{V_{Ni^0}} \]  \hspace{1cm} (3.13)
Finally, it is possible to predict the extent of reaction, $\Delta \xi$, for a known specimen geometry that has been measured using SQUID by:

$$
\Delta \xi = \frac{N_{tot} \lambda^2}{\left( \frac{\omega}{\sigma} - 1 \right) t}
$$

This model provides a link for comparing the extent of reaction that is measured optically to the extent of reaction predicted by the SQUID magnetometry measurement of a pellet cross-section. The quality of the model is examined in the results.
CHAPTER 4
PAPER I:
MICROSTRUCTURAL EVOLUTION DURING INTERNAL REDUCTION OF POLYCRYSTALLINE NICKEL-DOPED YTTRIA-STABILIZED ZIRCONIA

This chapter presents the work carried out to investigate the microstructural evolution of polycrystalline Ni-doped 10YSZ pellets in reducing environments. This chapter is a paper entitled “Microstructural Evolution During Internal Reduction of Polycrystalline Nickel-doped Yttria-stabilized Zirconia” that was co-authored by James R. O’Brien and Ivar E. Reimanis was submitted to Acta Materialia.

4.1 Abstract

The nucleation and growth of metallic particles within metal-doped oxides in reducing conditions is relevant to the processing of materials for catalysis, fuel cells, and structural applications. Here, the precipitation of metallic nickel during the internal reduction of nickel-doped yttria stabilized zirconia is studied with electron microscopy and SQUID magnetometry. It is shown that the microstructure evolution proceeds in three distinct stages, each with its own kinetics description, dependent on the porosity and grain size. 0.5 molar percent NiO doped YSZ was synthesized, sintered, pressed into pellets, and then exposed to 1000°C in dry and wet 2% H$_2$ for various times. Metallic Ni$^0$ particles (> 100 nm) are first formed in pores connected to grain boundaries; subsequently, metallic Ni$^0$ particles (20 - 50 nm) precipitate at grain boundaries; and finally, superparamagnetic Ni$^0$ particles (<10 nm) form within the bulk YSZ grains. The transitions between stages depend upon concentration gradients and electrostatic potentials that act upon the relevant transporting species, namely oxygen vacancies, electrons, nickel ions and zirconium vacancies.

4.2 Introduction

The process of internal reduction, sometimes also referred to as partial reduction, is a convenient and potentially powerful way to make metal-ceramic composites for diverse applications [134–139]. In internal reduction, a mixed metal oxide solid solution is exposed to a reducing environment at elevated temperature such that the most noble of the metal cations reduces its oxidation state, leading to the precipitation of a second phase within the less noble metal oxide. When the oxygen partial pressure is low enough to form a metal, but not so low as to reduce the parent oxide, the resulting microstructure leads to a metal particulate reinforced ceramic with a microstructure that may exhibit enhanced structural, catalytic or other functional properties [140–144]. The process is distinctly different from direct reduction whereby an oxide converts to
a metal. Accordingly, the mass transport and kinetics describing the process are distinctly different from those of direct reduction.

The mechanism for internal reduction was first described by Schmalzried [145, 146]. Typically, it occurs by the growth of a reaction zone from the surface to the interior, described by parabolic kinetics, and rate-limited by the diffusion of cations, anions, or electronic charge carriers through the thickness of the reacted zone. The process has been well-described in homogeneous systems such as glass and in single crystal oxides [147–152]. However, complexities are introduced in the presence of microstructural features such as grain boundaries and porosity, as they introduce space charge layers and additional pathways for diffusion that may modify nucleation and growth conditions [153, 154]. In highly doped systems, like yttria-stabilized zirconia (YSZ), the intrinsic defect concentrations from the dopant may be several orders of magnitude higher than the extrinsic defect concentrations that are introduced by the externally applied chemical potential gradient [155]. Particularly when high concentrations of intrinsic defects exist, the mass transport of charged species is dominated by an electrical potential [119].

Nickel-YSZ composites have been extensively studied due to their potential use in catalyst systems as well as their use as anodes in solid oxide fuel cells (SOFCs) [156–161]. For SOFCs, NiO is typically mixed with YSZ, co-fired in air to partial density, and then exposed to a reducing atmosphere to directly convert NiO to metallic Ni (Ni\textsuperscript{0}). Invariably, some NiO dissolves in YSZ during the air firing step. Subsequently, Ni\textsuperscript{0} exsolves during the reduction step via a process of internal reduction. In studies with compositions below or near the solubility limit of NiO in YSZ (about 2 molar percent) it is possible to produce nanometer size dispersions of Ni\textsuperscript{0} in YSZ [93, 162, 163]. Depending on the starting YSZ microstructure and the specific reducing conditions, the possible size and distribution of Ni\textsuperscript{0} particles one can engineer is potentially enormous. The present study examines internal reduction in a polycrystalline NiO doped-YSZ containing a small amount (~5%) of porosity. 10 YSZ (10 molar percent Y\textsubscript{2}O\textsubscript{3} in ZrO\textsubscript{2}) was chosen over lower amounts of Y\textsubscript{2}O\textsubscript{3} to ensure stability of the cubic phase. 0.5 molar percent NiO was chosen because it is well below the solid solubility limit, yet high enough to facilitate detection by electron microscopy and magnetometry. It is shown that three distinct stages of internal reduction occur.

4.3 Experimental Procedure

Specimens in this study were prepared by sintering high purity powders that were synthesized by chemical methods described elsewhere [164]. All compositions were 0.5 mol % NiO in 10 mol % Y\textsubscript{2}O\textsubscript{3} stabilized ZrO\textsubscript{2} (10YSZ). Pellets 19 mm in diameter and 4 mm thick were formed in a stainless steel die with a uniaxial press (Carver, Inc., Wabash, IN, USA). The pellets were buried in 0.5 molar percent NiO-doped 10YSZ powders in high purity (99.8 %) alumina (CoorsTek, Golden, CO, USA) containers at 3°C min\textsuperscript{-1} to 1500°C for 4.5 h.
in air, conditions which result single phase YSZ with nickel completely in solid solution or as ions at internal interfaces, such as grain boundaries or pore surfaces. Magnetometry measurements reveal that no nickel exists as an ordered oxide; only disordered Ni\(^{2+}\) ions are present [165]. The density was measured to be 95.6% theoretical as measured by the Archimedes method. X-ray diffraction confirmed that the as-sintered material was single phase cubic zirconia [164]. The grain size was measured by the linear intercept method on SEM micrographs (Figure 4.1) to be 5.3 ± 0.5 \(\mu\)m. The pore size and spacing was quantified with image analysis: the average pore radius is 167 nm ± 81 nm, and the average spacing between pores, based on the density and pore size, is 1.5 \(\mu\)m. Previous research suggests that the pore surfaces are sites for Ni\(^{2+}\) ions [166].

![Figure 4.1: SEM micrograph showing the as-sintered polycrystalline microstructure of 0.5 molar % Ni-doped 10YSZ that contains average grains approximately 5 \(\mu\)m and approximately 5 % pre-existing porosity.](image)

Laser pulse atom probe tomography (APT) to characterize the Ni\(^{2+}\) ion distribution in as-sintered samples was performed prior to reduction treatments using 40 pJ laser energy and 40 K specimen base temperature ( Cameca, LEAP 4000X Si, Gennevilliers Cedex, France). APT specimens from the grain interiors and boundaries were prepared using focused ion beam (FIB) milling (FEI Helios Nanolab 600i, Hillsboro, OR). Data analysis was performed using CAMECA IVAS v.3.2.6. software.

Internal reduction experiments were performed on sintered pellets in a high purity (99.8%) alumina reactor tube (CoorsTek, Golden, CO) and tube furnace (ATS, Butler, PA). Gas flow (99.998% Ar or 2% H\(_2\)/Ar balance) was regulated with a solenoid valve and mass flow controller calibrated to the gas composition (MKS, Andover, MA). Conditions were chosen to produce a partial pressure of oxygen on the order of \(10^{-19}\) atm, a value calculated to be sufficiently low to lead to internal reduction [167]. The pellet was heated in 100 scm flowing Ar at 5°C min\(^{-1}\) to 1000°C. At 1000°C, the inlet gas was switched to 2 % H\(_2\). The
inlet gas enters in the back of the reactor tube, flowing over the pellet specimen, and is then exhausted through the face plate. A thermocouple and oxygen sensor is positioned near the pellet inside the reactor tube. The pellets were soaked in 100 sccm flowing 2% H\textsubscript{2} gas for various times (0.5, 5, 10, 25, 50, 66, and 75 h). The measured oxygen partial pressure inside the reactor tube was approximately 10\textsuperscript{-19} atm. Following the reduction hold time, the reactor tube was purged with 100 sccm flowing Ar until a temperature of 50\degree C was achieved.

Reduction experiments additional to those describe above were performed at a higher oxygen partial pressure and at lower temperatures. Table 4.1 summarizes the various conditions. While maintaining constant temperature of 1000\degree C, the oxygen partial pressure was increased to approximately 10\textsuperscript{-15} atm by two methods. In one, a dry condition was used by bleeding Ar gas into the reactor tube during the reduction treatment. For the other, a wet condition was employed by bubbling the 2% H\textsubscript{2} gas through water. Two additional experiments were performed at 800\degree C and 900\degree C while maintaining constant oxygen partial pressure of approximately 10\textsuperscript{-19} atm. Times were 0.5, 5, 10, and 25 h.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Reduction Temperature</th>
<th>Log10 $P_{H_2}$</th>
<th>Log10 $P_{H_2O}$</th>
<th>Reduction Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000\degree C, 10\textsuperscript{-19} atm</td>
<td>1000</td>
<td>-1.70</td>
<td>-3.49</td>
<td>0.5, 1, 5, 10, 25, 50, 66, &amp; 75</td>
</tr>
<tr>
<td>1000\degree C, 10\textsuperscript{-15} atm</td>
<td>1000</td>
<td>-3.87</td>
<td>-3.49</td>
<td>0.5, 5, 10, &amp; 25</td>
</tr>
<tr>
<td>1000\degree C, 10\textsuperscript{-15} atm (wet)</td>
<td>1000</td>
<td>-2.00</td>
<td>-1.33</td>
<td>0.5, 5, 10, 25, &amp; 50</td>
</tr>
<tr>
<td>900\degree C, 10\textsuperscript{-19} atm</td>
<td>900</td>
<td>-2.54</td>
<td>-3.49</td>
<td>0.5, 5, 10, &amp; 25</td>
</tr>
<tr>
<td>800\degree C, 10\textsuperscript{-19} atm</td>
<td>800</td>
<td>-3.54</td>
<td>-3.49</td>
<td>0.5, 5, 10, &amp; 25</td>
</tr>
</tbody>
</table>

Pellets were cross-sectioned with a diamond saw, mounted in cold-set epoxy, polished, and observed visually and with optical microscopy. The specimens underwent a change in color from tan to gray upon reduction. The change in color proceeded from the surface towards the center with increase in heat treatment time. The depth of this color change was measured directly on the cross sectioned specimen under a low power optical microscope. The mass of Ni\textsuperscript{0} formed in each of the reduced specimens was quantified with superconducting quantum interference device (SQUID) magnetometry (MPMS-7, Quantum Design Inc., San Diego, CA, USA). A small section approximately 50 mg to 100 mg was cut from the center of each reduced pellet to be used for magnetometry. The section was placed in folded paper and inserted into a standard drinking straw for measurement. Direct current (DC) susceptibility moment versus field curves were collected at 100 K to quantify the saturation magnetization. At 100 K, the magnetic moment consists of combined signals from the ferromagnetic response of metallic Ni\textsuperscript{0} particles and the diamagnetic response.
of 10YSZ. The diamagnetic response of 10YSZ was subtracted from the overall curve measured at 100 K to extract the ferromagnetic response which arises entirely from Ni\(^0\). The magnetic moment of metallic Ni\(^0\) is 57.50 emu g\(^{-1}\) [168].

The metallic Ni\(^0\) particle size was determined with alternating current (AC) SQUID magnetometry (MPMS-7, Quantum Design Inc., San Diego, CA, USA), as described below and in more detail in the Results section. AC susceptibility curves were collected using an AC drive of 7 Hz, 100 \(\mu\)T AC drive amplitude, zero DC field, and scanning temperature from 1.8 K to 250 K. A 50 mg to 200 mg section cut from the center each reduced pellet was secured into a standard drinking straw for measurement. Output from AC susceptibility is reported as real, \(\chi'\), and imaginary, \(\chi''\), components versus temperature. The shape and magnitude of the \(\chi'\) and \(\chi''\) versus temperature curves represent a combination of contributions from unreduced Ni\(^{2+}\) ions (paramagnetic), reduced metallic Ni\(^0\) single-domain particles (\(\leq 10\) nm, superparamagnetic), and reduced metallic Ni\(^0\) multi-domain particles (\(> 100\) nm, ferromagnetic). Paramagnetic behavior in \(\chi'\) follows a Curie-Weiss law, observed as exponential decay as temperature increases from 1.8 K. Superparamagnetic behavior is observed in \(\chi'\) as a peak at the blocking temperature, \(T_B\), which is dependent on metallic Ni\(^0\) particle size [169]. A gradual increase in \(\chi'\) from 100 K to 250 K is characteristic of ferromagnetic, multi-domain metallic Ni\(^0\). Deconvolution and modeling of each response contributing to the measured data is detailed in the results section.

Transmission electron microscopy (TEM) images were collected with a 200 kV accelerating voltage TEM (Phillips (FEI) CM200, Hillsboro, OR) on specimens prepared by FIB.

### 4.4 Results

Representative APT reconstructions of specimens taken from the grain interior and boundary regions are shown in Figure 4.2 and Figure 4.3, respectively. A random distribution of Ni\(^{2+}\) ions is observed in the grain interior after 1.3 million counts. At the grain boundary, the reconstruction side view appears to show increased Ni\(^{2+}\) counts; however, a top view reconstruction shows no Ni\(^{2+}\) segregation along the grain boundary after 1.5 million counts. The reconstruction top view shows higher Ni\(^{2+}\) counts in one grain interior compared to the other, attributed to the difference in orientation between the two grains which can influence the field evaporation rate. The concave curvature of the grain interior producing higher counts causes the appearance of increased Ni\(^{2+}\) counts in the side view along the grain boundary due to volume overlap. A larger specimen volume causes the density of counts to increase.

The progression of a reaction front is optically visible as shown in Figure 4.4 for a pellet that was exposed to \(10^{-15}\) atm at 1000\(^\circ\)C for various times. The thickness of the reacted zone, easily measured because of the difference in color between the as-sintered condition (tan) and the reacted zone (gray), is summarized
Figure 4.2: TEM micrograph showing pre-analysis representative APT specimen prepared from grain interior region of as-sintered pellet and reconstructions showing only Ni\textsuperscript{2+} species in characterized volume of 1.3 million atomic counts. A side and top view of reconstructions for only Ni\textsuperscript{2+} species shows a random distribution in the grain interior.

Figure 4.3: TEM micrograph showing pre-analysis representative APT specimen prepared from grain boundary region of as-sintered pellet and reconstructions showing only Ni\textsuperscript{2+} species in characterized volume of 3.5 million atomic counts. A side view of the reconstruction might appear to show higher counts at the grain boundary; however, a top view reconstruction shows no segregation along the grain boundary. The concave curvature of the grain interior with higher counts and the conical shape of the specimen produces a larger volume at greater depths and increased Ni\textsuperscript{2+} count density.
for four of the specimens in Figure 4.5. Error bars represent a 95% confidence interval calculated from 20 measurements of the reaction zone thickness. The longest time for each of the four data sets in Figure 4.5 represents the time it took for the entire specimen to turn gray. It is clear that lower $P_{O_2}$ and higher temperature lead to a higher rate of reaction (higher slopes in Figure 4.5). Furthermore, the reaction rate is slightly decreased in wet $H_2$ conditions. TEM of specimens from the data sets shown in Figure 4.5 revealed that $Ni^0$ particles approximately 100 - 200 nm formed within the pre-existing pores in the YSZ (Figure 4.6). Extensive TEM of these same specimens showed that in only a few cases, very fine $Ni^0$ particles were formed at grain boundaries away from pores, the same as those observed for longer reduction times, presented below. It was therefore concluded that the gray color of the reaction zone described above is due to the formation $Ni^0$ particles in pre-existing YSZ pores. Inspection of the data reveals that they generally are parabolic in time, up to a certain time. As described in more detail in the Discussion, the precipitation of $Ni^0$ within YSZ grain boundary pores is the first of three stages of reduction. Based on the parabolic growth rate observed (Figure 4.5), the kinetics are assumed to be diffusion limited.

Figure 4.4: Optical micrographs of cross-sectioned 1000°C, $P_{O_2} \sim 10^{-15}$ atm (wet) reduced pellets. The reaction front moves inward from the exterior surfaces and results in a color change in the cross-section (tan to gray) as metallic $Ni^0$ particles form. The extent of reduction is shown for various soak times: (b) 0.5 h, (c) 5 h, (d) 10 h, (e) 25 h, and (f) 50 h when the reaction front has swept the entire cross-sectional thickness.
Figure 4.5: Plot of the square extent of reaction versus time for the various experimental conditions: 1000°C, Dry $P_{O_2} \sim 10^{-19}$ atm, 900°C, Dry $P_{O_2} \sim 10^{-19}$ atm, 1000°C, Dry $P_{O_2} \sim 10^{-15}$ atm, and 1000°C, Wet $P_{O_2} \sim 10^{-15}$ atm. The thickness of the reaction layer squared varies linearly as a function of reduction time, indicating that the reaction is diffusion limited (parabolic kinetics). As expected, the highest rate (steepest slope) occurs in the 1000°C $10^{-19}$ atm reduced pellet. The error bars represent a 95% confidence interval.

Magnetic moment versus field curves for the pellet reduced at 1000°C $P_{O_2} \sim 10^{-19}$ atm at various times (Figure 4.7) show that the saturation magnetization, $M_s$, (the plateau of the curves) increases with increasing reduction time. The precision of the SQUID magnetometry measurement is represented by the size of the data points. Since $M_s$ is directly related to the mass of metallic Ni$^0$, and because the initial amount of Ni$^{2+}$ present (0.5 mol %) is known, the percent of reduction, defined as the percent conversion of Ni$^{2+}$ to metallic Ni$^0$, may be determined. $M_s$ was determined for all the pellets and used to calculate the percent of reduction which is observed to depend strongly on the temperature and environment (Figure 4.8). Generally, the percent of reduction is linear with time except for very long times.

Figure 4.6: TEM micrographs of reduced specimen after 5 h at 1000°C in 2% H$_2$ showing faceted metallic Ni$^0$ particle in pre-existing pore that is representative of stage 1 reduction.
Figure 4.7: Magnetization versus field curves taken at 100 K showing the magnetic saturation for reductions at various times in 1000°C, Dry $P_{O_2} \sim 10^{-19}$ atm. The magnitude of magnetic saturation correlates to the mass of metallic Ni$^0$ due to reduction. As more Ni$^0$ particles form with longer soak times the magnetic saturation increases. The precision of the SQUID magnetometry measurement is represented by the size of the data points.

TEM of specimens reduced at times between 10 and 50 h in pellets reduced at 1000°C $P_{O_2} \sim 10^{-19}$ atm revealed that Ni$^0$ particles formed at YSZ grain boundaries (Figure 4.9(a)), a second stage of internal reduction. Strain contrast was associated with every particle observed. These grain boundary precipitates were abundant throughout the specimens. Longer reduction times led to larger Ni$^0$ particle sizes for particles situated at the grain boundaries. The Ni$^0$ particles at the pre-existing pores did not coarsen with time. TEM within YSZ grains revealed the presence of fine Ni$^0$ particles (Figure 4.9(b)), but only for longer reduction times compared with times required for grain boundary particles to form. The formation of Ni$^0$ particles within the YSZ grains represents a third stage of internal reduction as described in the Discussion. No strain contours were observed with these Ni$^0$ particles, and each one had associated with it a pore of about the same size as the particle. A precipitation-free zone extending about 200 nm from the grain boundary was observed adjacent to most grain boundaries.

The real and imaginary part of the AC susceptibility for pellets reduced at 1000°C $P_{O_2} \sim 10^{-19}$ atm for various times reveals information about the distribution of nickel (Figure 4.10). The precision of the SQUID magnetometry measurement is represented by the size of the data points. For the 5 h reduction time, the data follow a Curie-Weiss law, indicating the presence of a large number of disordered Ni$^{2+}$ ions. Furthermore, these data show a gradual increase in AC susceptibility with temperature beyond about 100 K, consistent with the presence of ferromagnetic Ni$^0$ in the pre-existing pores (compare to Figure 4.6). In contrast, the 10 h reduced pellet shows the onset of a peak around 11 K, a classic signature of superparamagnetic metallic
Figure 4.8: Plot showing the percent of reduced metallic Ni\(^0\) versus soak time calculated from the saturation of mass magnetization for various reduction treatments. The pellets reduced at 1000°C, \(P_{O_2} \sim 10^{-19}\) atm show deviation from a linear trend as soak times increase indicating there is a change in reduction kinetics. A linear trend is observed for the other experimental conditions which did not show microstructural features associated with stage 3 reduction at these soak times. The precision of the SQUID magnetometry measurement is represented by the size of the data points.

Figure 4.9: TEM micrographs of reduced specimen after 25 h at 1000°C, \(P_{O_2} \sim 10^{-19}\) atm showing (a) YSZ grain boundary with coarsened metallic Ni\(^0\) particles and increased strain contrast representative of late stage 2 reduction and (b) interior of YSZ grain with superparamagnetic Ni\(^0\) particles in voids representative of stage 3 reduction.
Ni<sup>0</sup>. Ni<sup>0</sup> particles may exhibit superparamagnetic behavior when the particle size is below about 20 nm [169]. These AC susceptibility results are consistent with the observation of very fine Ni<sup>0</sup> particles in TEM (Figure 4.9(a)). The longer reduction times in Figure 4.10 show an increase in AC susceptibility and a shift of the peak to higher temperatures, revealing that the superparamagnetic particles coarsen with increased reduction time. The radius of metallic Ni<sup>0</sup> particles can be calculated from the blocking temperature, T<sub>B</sub>, which is the temperature at which the peak in AC susceptibility occurs in Figure 4.10 [168]:

\[
T_B = \frac{KV}{25k_B}
\]

where V is the volume of a spherical particle, related directly to the particle radius, k<sub>B</sub> is Boltzmann constant and K is the anisotropy constant for nickel [170]. A summary of the measured diameters of metallic Ni<sup>0</sup> particles for reduction times up to 50 h is tabulated in Table 4.2. Superparamagnetic particles were only observed in specimens reduced at 1000°C, P<sub>O2</sub> ∼ 10<sup>−19</sup> atm for > 10 h but < 75 h (due to coarsening). At lower oxygen partial pressure (P<sub>O2</sub> ∼ 10<sup>−15</sup> atm) Ni<sup>0</sup> precipitation within bulk YSZ was not observed, even up to 50 h.

Table 4.2: A summary of the observed blocking temperatures with calculated particle diameter shows coarsening of superparamagnetic metallic Ni<sup>0</sup> particles.

<table>
<thead>
<tr>
<th>Reduction Time (h)</th>
<th>Blocking Temperature (K)</th>
<th>Particle Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>11</td>
<td>4</td>
</tr>
<tr>
<td>25</td>
<td>38</td>
<td>7</td>
</tr>
<tr>
<td>50</td>
<td>92</td>
<td>9</td>
</tr>
</tbody>
</table>

Table 4.3: A summary of the parabolic rate of stage 1 reduction, comparing the measured rate to the corrected rate that accounts for the extra distance that oxygen vacancies diffuse along porosity.

<table>
<thead>
<tr>
<th>Reduction Condition</th>
<th>k (uncorrected)</th>
<th>k (corrected)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000°C, 10&lt;sup&gt;−19&lt;/sup&gt; atm</td>
<td>4.10 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>1.18 × 10&lt;sup&gt;−8&lt;/sup&gt;</td>
</tr>
<tr>
<td>1000°C, 10&lt;sup&gt;−15&lt;/sup&gt; atm</td>
<td>5.62 × 10&lt;sup&gt;−8&lt;/sup&gt;</td>
<td>1.62 × 10&lt;sup&gt;−9&lt;/sup&gt;</td>
</tr>
<tr>
<td>1000°C, 10&lt;sup&gt;−15&lt;/sup&gt; atm (wet)</td>
<td>8.82 × 10&lt;sup&gt;−8&lt;/sup&gt;</td>
<td>2.55 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
</tr>
<tr>
<td>900°C, 10&lt;sup&gt;−19&lt;/sup&gt; atm</td>
<td>1.90 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
<td>2.55 × 10&lt;sup&gt;−7&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

4.5 Discussion

The observations presented above show that grain boundaries and porosity significantly influence the progression of internal reduction, and dictate the resultant metal-ceramic composite microstructure. A
Figure 4.10: Real $\chi'$ and imaginary $\chi''$ components of the AC susceptibility for 5, 10, 25, and 50 h soak times. The $\chi'$ for the 5 h soak shows a combination of Ni$^{2+}$ and large metallic Ni$^{0}$ particles (gradual increase after 100 K). The maximum in $\chi'$ is indicative of Ni$^{0}$ particle size, where lower temperatures correspond with superparamagnetic Ni$^{0}$ particles. The peak at 11 K in the 10 h soak shifts to higher temperatures as soak time increases, indicative of metallic Ni$^{0}$ particle growth. Note that the scale of the Y-axis is 10 times larger in the 25 and 50 h soak times than the 5 and 10 h soak times. The precision of the SQUID magnetometry measurement is represented by the size of the data points.
careful inspection of the data reveals that internal reduction in polycrystalline NiO-doped YSZ occurs in three distinct stages, depicted in Figure 4.11. In the first, metallic nickel (Ni\(^0\)) forms in pre-existing pores attached to fast diffusion pathways (grain boundaries). In this stage, the color of the specimen changes from tan to gray. Though a visible reaction front proceeds through the entirety of the pellet thickness, not all the Ni\(^{2+}\) ions are exsolved in this stage. In the second stage, Ni\(^0\) forms at YSZ grain boundaries. In the last stage, Ni\(^0\) forms within the YSZ grains. The stages exhibit distinctly different kinetics, with different thermodynamic driving forces, and are thus discussed separately.

4.5.1 Stage 1

It has been previously established that diffusing species for internal reduction in YSZ are oxygen vacancies, electrons, and Ni\(^{2+}\) ions [93]. While the transference number of oxygen vacancies in bulk YSZ is much greater than that of electrons [171], the opposite is true at the grain boundaries where space charge effects dominate [172–177]. In particular, the rate-limiting species along grain boundaries are expected to be oxygen vacancies. During stage 1 (Figure 4.9(a)), it is proposed that oxygen vacancies and electrons diffuse along grain boundaries to pre-existing pores where they react with Ni\(^{2+}\) ions which have segregated at the pore surfaces in the as-processed material [166]. Ni\(^{2+}\) ions at the pore surfaces are transported by surface diffusion to the intersection of the grain boundary and the pore where reduction occurs. Because surface diffusion is expected to be relatively high compared to grain boundary or bulk diffusion, and the distances Ni\(^{2+}\) diffuses are small (on the order of the pore size), it must be that the overall reaction rate is limited by the diffusion of oxygen vacancies along the grain boundaries, consistent with previous results reported for Ni-YSZ [93]. It is noted that the size of the Ni\(^0\) particles formed (100 - 200 nm) is consistent with monolayer coverage of the pre-existing pore by Ni\(^{2+}\) ions prior to the reduction exposure \(^1\).

The observation that Ni\(^0\) particles form in pre-existing pores (Figure 4.6) prior to the formation of Ni\(^0\) at grain boundaries implies either that the grain boundaries in the as-sintered material do not contain Ni\(^{2+}\) ions prior to reduction, or that nucleation and growth of Ni\(^0\) at the grain boundary has a significant activation barrier, or both. The presence of strain contours around grain boundary saturated Ni\(^0\) particles indicates that there is likely an elastic strain energy component to the activation energy for nucleation. Furthermore, atom probe tomography results show that Ni\(^{2+}\) ions are indeed not segregated at the grain boundaries compared with the bulk (Figure 4.2 and Figure 4.3), meaning that Ni\(^{2+}\) ions must diffuse to the boundaries to form Ni\(^0\) particles. Therefore, the diffusion of Ni\(^{2+}\) ions to the grain boundaries (part of stage 2 described next) must be slower than the diffusion of oxygen vacancies and electrons to the pre-existing

\(^1\)The Ni\(^{2+}\) monolayer coverage of a pore with diameter equal to 334 nm means that there will be 107 Ni\(^{2+}\) ions available to react to form Ni\(^0\). Considering the density of Ni is 8.93 g/cm\(^3\), the Ni\(^0\) particle size would be 63 nm, consistent with the observed size.
pores that contain abundant Ni\textsuperscript{2+} ions.

Data in Figure 4.5 allow a determination of the kinetics of the rate limiting species, oxygen vacancy diffusion, along YSZ grain boundaries. It should be noted that if the specimen did not contain pre-existing pores, the slopes of the curves Figure 4.5 would represent precisely the reaction rate constants for oxygen vacancy diffusion. For parabolic kinetics, the reaction rate constant, k, may be described by $\Delta \xi = kt^{1/2}$, where $\Delta \xi$ is the (measured) reaction front thickness and t is time [135, 146]. However, the pre-existing pores serve as a sink and one must account for the extra time needed to fill this sink. During this extra time, oxygen vacancies continue to diffuse along the grain boundary to the growing Ni\textsuperscript{0} particle at the pre-existing pores. The extra time is equal to the time it takes for an oxygen vacancy-electron pair to diffuse to the pore times the number of nickel atoms present. The latter is determined by the size of the particle (100 - 200 nm), the density of nickel (8.93 g/cm\textsuperscript{3}) and the atomic mass of nickel. Table 4.3 shows the reaction rate constant predicted with and without this consideration (uncorrected and corrected). It is clear that a model which does not account for the extra Ni\textsuperscript{2+} in the pores would underestimate the grain boundary diffusion of reactant species and overestimate the distance the reactant species travel. The corrected rate constant is in agreement with the reported diffusivity values of oxygen vacancies [178–180].

The completion of stage 1 may be determined by calculating the total mass of Ni\textsuperscript{0} particles in the pre-existing pores. The size and number of pores dictate the time. In the present specimens, monolayer Ni\textsuperscript{2+} coverage of the porosity means that stage 1 is complete once about 13% of the Ni\textsuperscript{2+} ions are reduced. This number is consistent with SQUID magnetometry (Figure 4.8) where it is observed that for the specimen with the fastest kinetics (1000°C, $P_{O_2} \sim 10^{-19}$ atm; open circles), about 15% of the Ni\textsuperscript{2+} is reduced to ferromagnetic Ni\textsuperscript{0} after 10 h.

4.5.2 Stage 2

The onset of stage 2 reduction begins when Ni\textsuperscript{2+} ions diffuse to the grain boundaries, and once any nucleation barrier is overcome. An estimate of the barrier for nucleation at the grain boundary compared with that in the bulk may be determined by calculating the ratio of the free energy of formation at the grain boundary to homogeneous free energy of formation. This ratio may be represented by the dihedral angle of the particle at the boundary [108]. An average dihedral angle of 120° was measured from high-resolution STEM micrographs of three Ni\textsuperscript{0} particles, implying that the free energy of grain boundary nucleation requires one-third less energy than homogeneous nucleation, consistent with the observation that stage 2 occurs prior to stage 3.

The formation of Ni\textsuperscript{0} particles at the boundary requires diffusion of the Ni\textsuperscript{2+} ions through the YSZ lattice to the boundary. Due to the negative space charge potential in YSZ [153], the grain boundaries are
Figure 4.11: Schematic of the stages of reduction in polycrystalline Ni-doped 10YSZ at 1000°C. Electronic defects are introduced at the surface. In stage 1 (a) oxygen vacancies and electrons diffuse along the grain boundaries as charge neutral species and react with Ni$^{2+}$ in pre-existing pores. In stage 2 (b) Ni$^{2+}$ on Zr$^{4+}$ sites diffuse to the grain boundaries where it reacts with electrons to form metallic Ni$^{0}$ and drives a counter flux of zirconium and oxygen vacancies into the grain interiors. In stage 3 (c) superparamagnetic Ni$^{0}$ forms due to the increased concentration of vacancies in the grain interiors that lower the nucleation energy by creating a free surface (void) and coarsen with longer times. The shaded region around the grain boundary indicates the space charge layer.
presumably saturated with electrons that are available to react with Ni\(^{2+}\) ions that diffuse through the bulk YSZ. The Ni\(^{0}\) grain boundary precipitates coarsen with time to form single domain Ni\(^{0}\) particles, ultimately achieving sizes between 20 and 50 nm.

In the context of confirming that Ni\(^{2+}\) is the rate-limiting species in stage 2, it is worthwhile considering the possible transport mechanism. It is generally agreed that Ni\(^{2+}\) ions in solid solution substitute for Zr\(^{4+}\) ions on the YSZ lattice [181, 182]. The following equation describes this defect reaction (Kroger-Vink notation).

\[
\text{NiO} \underset{\text{YSZ}}{\rightarrow} \text{Ni}''_\text{Zr} + V''_\text{O} + O''_\text{O} \quad (4.2)
\]

Under reducing conditions, the formation of Ni\(^{0}\) must lead to the creation of vacant Zr\(^{4+}\) sites. Previous studies have shown that vacant Zr\(^{4+}\) sites form defect clusters with oxygen vacancies and that cation diffusion in YSZ occurs by the migration of these defect clusters [183–186]. The formation of such defect clusters during the formation of Ni\(^{0}\) particles at the grain boundary during reduction may be described by:

\[
\text{Ni}''_\text{Zr} + O''_\text{O} + 2e'_\text{gb} + V''_\text{O} \leftrightarrow \text{Ni}^0_\text{gb} + (V'''_\text{Zr} + V''_\text{O})'' 
\]

where \((V'''_\text{Zr} + V''_\text{O})''\) denotes the defect cluster and the subscript gb indicates the presence of the species at the grain boundary. Thus, every Ni\(^{2+}\) ion that is reduced to form Ni\(^{0}\) leads to a defect cluster whose presence contributes to the further diffusion of Ni\(^{2+}\) ions to the grain boundary. The linear trend between % reduced (which equates with volume) and time (Figure 4.8) implies zero-order rate kinetics which commonly result with heterogeneous reactions where very few species are in proximity to participate in the reaction but a source exists to supply more reactant species. [187]

4.5.3 Stage 3

In stage 3, Ni\(^{2+}\) in the grain interior reacts to form superparamagnetic Ni\(^{0}\) particles (Figure 4.9) like those previously reported in NiO-YSZ [188]. Kondo, et al [188] discussed possible reasons that a void was produced with each Ni\(^{0}\) particle. It is proposed here that the voids associated with the formation of superparamagnetic Ni\(^{0}\) particles must be the result of the following reaction describing stage 3 reduction:

\[
(V'''_\text{Zr} + V''_\text{O})' + \text{Ni}''_\text{Zr} + 2e' + V''_\text{O} \leftrightarrow \text{Ni}^0 + V'''_\text{Zr} + V''_\text{O} + 2V''_\text{O} 
\]

The creation of vacant Zr\(^{4+}\) sites enhances the substitutional diffusion of Ni\(^{2+}\) to the Ni\(^{0}\) particle. The loss of a compound unit of ZrO\(_2\) explains the void formation upon formation of metallic nickel particles. Even though stages 2 and 3 are both rate-limited by the diffusion of Ni\(^{2+}\) ions through the YSZ lattice, the detailed mechanisms are different (Figure 4.11). Stage 3 is effectively activated only when there exists a critical concentration of vacancy clusters that serve as nucleation sites for Ni\(^{0}\). A clue describing the stage 3
reaction mechanism is a precipitate free zone (PFZ) that is observed adjacent to the grain boundaries. It was first hypothesized that the PFZ observed is correlated to a depletion of Ni\(^{2+}\). However, the thickness of the PFZ exceeds the calculated diffusion distance for Ni\(^{2+}\) predicted by Fick’s laws. An alternative hypothesis is that the PFZ is correlated to the absence of oxygen vacancies needed for nucleation sites. To explain this, one can calculate the electrostatic effect superimposed on the mass transport of V\(_{O}^{\bullet\bullet}\) due to the space charge layer, \(\lambda^*\), from [189]:

\[
\lambda^* = \lambda \sqrt{\frac{4e}{k_B T} \Delta \varphi}
\]

(4.5)

where the Debye length is \(\lambda\) (40 nm) and the electrochemical potential induced by the chemical potential gradient in oxygen activity is \(\Delta \varphi\) (340 mV). Details of this calculation are presented elsewhere [167]. The calculated \(\lambda^*\) is around 140 nm, approximately equal to the thickness of the PFZ. It is therefore likely that the formation of the PFZ is related to the space charge layer, and in particular, the absence of oxygen vacancies. The role of oxygen vacancies in YSZ is similar to Guinier-Preston precipitation hardening in metals [190–192], where the vacancies serve as heterogeneous nucleation sites because they effectively reduce the misfit strain energy imposed on the lattice. Additionally, the increased vacancy concentration enhances the kinetics of solute transport in the grain interiors, leading to coarsening of Ni\(^0\) particles.

4.5.4 Conclusions

The present work provides new insight into the mechanism of internal reduction of polycrystalline nickel doped YSZ. How the reactant species diffuse through the polycrystal and the preferential nucleation sites for metallic Ni\(^0\) particles strongly depends upon microstructural features, such as pre-existing porosity and grain boundaries. Both surfaces and grain boundaries lower the free energy for nucleation of metallic Ni\(^0\). Grain boundaries promote accelerated mass transport due to space charge effects.

The reduction reaction occurs in three distinct stages and the result is a distribution of metallic Ni\(^0\) particles sizes in the reduced microstructure. Ni\(^{2+}\) ions exists as a monolayer in pre-existing porosity, and therefore the size of metallic Ni\(^0\) depends upon the size of the pore. The exsolution of Ni\(^{2+}\) requires time for diffusion of the ions to nucleation sites, first forming along grain boundaries. Once a critical vacancy concentration has been reached in the grain interior due to the reduction reaction, voids form due to the formation of vacancy defect clusters. These defect clusters create voids that provide nucleation sites for very fine metallic Ni\(^0\) particles. The sensitivity of the reduction reaction to microstructural features provides a foundation for microstructural design by controlling porosity and grain size.

The influence of the electrical potential on mass transport is quantified to explain the precipitation free zone that is observed in the internal reduction microstructure. The reactant species are introduced by the
gradient in oxygen partial pressure, and mass transport along the grain boundaries is preferred due to the space charge effect. The calculated space charge layer thickness is in good agreement with the experimental results of the PFZ thickness. In the PFZ there is an absence of defect clusters. Without defect clusters the nucleation energy for metallic Ni\(^0\) is too high.

### 4.5.5 Acknowledgments

This research is funded by the National Science Foundation, Division of Materials Research, Ceramics Program, under Grant Number 1003030. Special thanks are extended to the Magnetics Group at NIST Boulder, CO, USA, for access to a SQUID magnetometer. A. Morrissey thanks Prof. Brian Gorman and Dr. Dave Diercks for atom probe tomography training; and Dr. Michael Sanders and Prof. Ryan O’Hayre for insightful discussions.

### 4.6 Supplemental Evidence

Additional experimental results that are pertinent to the discussion of the internal reduction mechanisms are included in this section. The subsections include results of control experiments, highlights of the bulk and grain boundary compositional analysis quantified by APT, optical microscopy showing the extent of reaction for all conditions, and further discussion of reduction kinetics.

#### 4.6.1 Optical Microscopy of Reduced 10YSZ

To test the hypothesis that the darkening of Ni-doped 10YSZ pellets is primarily due to the formation of metallic Ni\(^0\) particles, an undoped 10YSZ pellet was reduced for 66 h. After reduction the exterior of the pellet remained white, however, the cross-section of the reduced pellet was colored light gray. Optical microscopy comparing the unreduced pellet with the 66 h reduced pellet is shown in Figure 4.12. The light gray colored interior of the reduced 10YSZ pellet is attributed to the increased concentration of electronic defects. The fact that the exterior of the pellet is white after 66 h reduction indicates that the pellet exterior may have oxidized during cooling due to the humidified Ar gas. The decreased kinetics due to the temperature drop prevented complete oxidation of the pellet interior. Although some darkening of the Ni-doped 10YSZ must be explained by the introduction of electronic defects, the formation of metallic Ni\(^0\) particles is the major contribution to the blackening of the pellets upon reduction.

#### 4.6.2 TEM of Unreduced Ni-doped 10YSZ

To establish a baseline for evaluating TEM micrographs, as-sintered Ni-doped YSZ pellets were analyzed. Representative TEM micrographs highlighting microstructural features of the unreduced Ni-doped 10YSZ is provided in Figure 4.13. Extensive TEM was performed and did not show any particles in pre-existing
pores or along the grain boundaries. The bulk of the grains also contained no voids or secondary phases, as observed after internal reduction.

4.6.3 APT Compositional Analysis of Unreduced Ni-doped 10YSZ Specimens

To map the distribution of Ni$^{2+}$ ions in relation to grain boundaries before the reduction treatments, APT runs collected from tips prepared from an as-sintered Ni-doped 10YSZ specimen. The runs which produced the best count statistics are summarized in Table 4.4. The data presents representative runs showing grain interior and grain boundary results. The atomic percent of oxygen in the as-sintered specimens is higher
than the nominal value because the same run conditions were used that were optimized to analyze reduced specimens. Generally, the atomic percent of zirconium is approximately equal to the nominal value and the atomic percent of yttrium is always lower than the nominal value. This does not necessarily mean that the yttrium content is low, instead, the optimum conditions for oxygen are likely different from those for yttrium. The atomic percent of nickel for the grain interior and grain boundary regions is comparable. APT deconstructed bulk compositional results are reported here for $\text{Zr}^{4+}, \text{Y}^{3+}, \text{Ni}^{2+}$ and $\text{O}^{2-}$ as-sintered specimens.

Table 4.4: Summary of atom probe tomography runs for grain interior and grain boundary.

<table>
<thead>
<tr>
<th>Run</th>
<th>Counts</th>
<th>Single %</th>
<th>Multiple %</th>
<th>Partial %</th>
<th>Zr at. %</th>
<th>Y at. %</th>
<th>Ni at. %</th>
<th>O at. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Interior</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2742</td>
<td>1,317,204</td>
<td>68.2</td>
<td>30.9</td>
<td>0.8</td>
<td>26.09</td>
<td>3.89</td>
<td>0.26</td>
<td>69.56</td>
</tr>
<tr>
<td>2745</td>
<td>3,190,687</td>
<td>68.8</td>
<td>30.5</td>
<td>0.7</td>
<td>27.27</td>
<td>5.33</td>
<td>0.15</td>
<td>67.24</td>
</tr>
<tr>
<td>Grain Boundary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2744</td>
<td>3,464,178</td>
<td>65.9</td>
<td>33.2</td>
<td>0.9</td>
<td>26.98</td>
<td>5.02</td>
<td>0.27</td>
<td>67.79</td>
</tr>
<tr>
<td>2746</td>
<td>2,408,968</td>
<td>68.5</td>
<td>30.9</td>
<td>0.6</td>
<td>27.73</td>
<td>4.78</td>
<td>0.23</td>
<td>67.25</td>
</tr>
</tbody>
</table>

Nominal atomic %

|       | 27.15 | 6.03  | 0.15  | 66.67 |

TEM images of pre-run analysis of run 2742 is shown in Figure 4.14. Damage to the grid precluded post-run TEM analysis. At low magnification, a partial arc of a pre-existing pore can be seen away from the tip, further down the APT tip shank. Figure 4.15 shows the top down view of run 2742 reconstruction that generally shows an even distribution of atomic species in the grain interior.

TEM images of pre-run analysis of run 2745 is shown in Figure 4.16. Damage to the grid precluded post-run TEM analysis. Figure 4.17 shows the top down view of run 2745 reconstruction that generally shows an even distribution of atomic species in the grain interior.

TEM images of pre-run analysis of run 2744 is shown in Figure 4.18. Damage to the grid precluded post-run TEM analysis. A grain boundary is observed that run parallel to the shank angle of the APT tip. Figure 4.19 shows a side view of run 2744 reconstruction showing some streaking of zirconium and nickel in one region that appears consistent with the grain boundary angle. Occasional streaks of elevated zirconium and nickel were generally observed in the unreported runs, and were not always correlated with grain boundary regions. It is suggested that the streaking could be indicative of a surface artifact from
Figure 4.14: TEM micrographs showing Run 2742 pre-run APT run analysis.

Figure 4.15: Run 2742 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.
Figure 4.16: TEM micrographs showing Run 2745 pre-run APT run analysis.

Figure 4.17: Run 2745 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.
milling. Sharp edges will have a high field in the applied bias and preferentially expel atoms.

TEM images of pre-run analysis of run 2746 is shown in Figure 4.20. Damage to the grid preclude post-run TEM analysis. Figure 4.21 shows a side down view of run 2746 reconstruction showing the atomic species are generally evenly distributed in the tip volume analyzed. The overall conclusion is the as-sintered specimen shows no nickel segregation along the grain boundaries.

### 4.6.4 APT Compositional Analysis of Reduced Ni-doped 10YSZ Specimens

APT runs collected form tips prepared from the 1000°C, 10^{-10} atm wet reduced 50 h specimen having the best count statistics are summarized in Table 4.5. This specimen only reached stage 2 reduction. The data includes representative runs showing the bulk composition of grain interior and grain boundary regions. The atomic percent of oxygen in the reduced specimens is very close to the nominal value because the run conditions were optimized on reduced specimens. Generally, the atomic percent of zirconium is higher than the nominal value and the atomic percent of yttrium is lower than the nominal value. The yttrium content is consistently low, even in the as-sintered tips. The zirconium content is higher compared with the as-sintered values, which could indicate there is a decreased oxygen content in the reduced specimens. In the grain
Figure 4.19: Run 2744 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.20: TEM micrographs showing Run 2746 pre-run APT run analysis.
interior, the atomic percent of nickel is still comparable to values obtained for the as-sintered tips. At the grain boundary only one good tip was prepared, and the compositional analysis indicates nickel depletion. Since the grain boundary contains particles of metallic Ni\(^0\) that are spaced appropriately 50 nm apart, it is expected that any nickel at the grain boundary has diffused to coarsen the metallic Ni\(^0\) particles and the result is depleted regions adjacent to the particles.

Table 4.5: Summary of atom probe tomography runs for grain interior and grain boundary of reduced specimens.

<table>
<thead>
<tr>
<th>Run</th>
<th>Counts</th>
<th>Single %</th>
<th>Multiple %</th>
<th>Partial %</th>
<th>Zr at.%</th>
<th>Y at.%</th>
<th>Ni at.%</th>
<th>O at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain Interior</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2747</td>
<td>2,900,341</td>
<td>69.9</td>
<td>28.3</td>
<td>0.8</td>
<td>28.05</td>
<td>5.36</td>
<td>0.35</td>
<td>66.23</td>
</tr>
<tr>
<td>2748</td>
<td>2,107,607</td>
<td>66.2</td>
<td>33.1</td>
<td>0.7</td>
<td>27.26</td>
<td>5.37</td>
<td>0.19</td>
<td>67.17</td>
</tr>
<tr>
<td>Grain Boundary</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2417</td>
<td>2,821,294</td>
<td>67.7</td>
<td>31.7</td>
<td>0.6</td>
<td>28.54</td>
<td>5.08</td>
<td>0.095</td>
<td>66.29</td>
</tr>
</tbody>
</table>

Nominal atomic %

27.15  6.03  0.15  66.67

TEM images of pre- and post-run analysis of run 2747 is shown in Figure 4.22. Figure 4.23 shows a top down view of run 2747 reconstruction showing some streaking of zirconium and nickel that was not
associated with any observation features in TEM. The streaking was also observed in as-sintered specimens and is believed to be the result of a milling artifact creating sharp lines on the tip surface.

![TEM micrographs showing Run 2747 pre- and post-run APT run analysis.](image)

Figure 4.22: TEM micrographs showing Run 2747 pre- and post-run APT run analysis.

TEM images of pre- and post-run analysis of run 2748 is shown in Figure 4.24. It is noteworthy to highlight a milling artifact on the surface of the APT, seen as a groove at the sharpest point in the tip radius. The milling artifact is seen in the top down view of run 2748 reconstruction, shown in Figure 4.25. All elements show linear streaking across the tip that can be correlated to the groove along the tip radius. This result confirms the sensitivity of APT to milling artifacts.

TEM images of pre-run analysis of run 2417 is shown in Figure 4.26, where a grain boundary can be observed that runs almost axially down the tip. Damage to the tip during TEM analysis precluded post-run analysis of this APT specimen. Figure 4.27 shows a side view of run 2417 reconstruction, showing an increased oxygen content associated with the grain boundary. Based upon space charge model for YSZ the region adjacent to the grain is expected to show a negative potential, or depletion of oxygen vacancies. It is possible that the orientation of the grain boundary has resulted in enhanced counts of oxygen at the grain boundary, or the grain boundary core has very different properties from the space charge layer.
Figure 4.23: Run 2747 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.24: TEM micrographs showing Run 2748 pre- and post-run APT run analysis.
Figure 4.25: Run 2748 APT reconstruction showing a deconstructed elemental map of Zr, Y, Ni and O species.

Figure 4.26: TEM micrographs showing Run 2417 pre-run APT run analysis.
4.6.5 Optical Microscopy of Reduced Ni-Doped Specimens

This section contains optical images for each set of reduction reaction cross-sections that supplement the kinetic data presented in the paper. Figure 4.28 show the cross-sections for 1000°C 10⁻¹⁵ atm (wet) reduced specimens. Figure 4.29 shows the cross-sections for 1000°C 10⁻¹⁵ atm (dry). Both have approximately the same oxygen partial pressure and show similar reaction kinetics.

Lower temperature reduction treatments were performed keeping oxygen partial pressure constant around 10⁻¹⁹ atm. Figure 4.30 shows the reaction front for the 1000°C reduction treatment. Figure 4.31 shows the reaction front for the 900°C reduction treatment. Figure 4.32 shows reaction front for the 800°C reduction treatment. The extent of reaction is less with decreasing reduction soak temperature. The more reducing conditions (10⁻¹⁹ atm) result in a darker extent of reaction than the previously shown results for less reducing conditions (10⁻¹⁵ atm). The reaction front at 800°C proceeded very irregularly, and shows that the reaction proceeds quickly along pre-existing cracks in the sintered pellet, but generally exhibits limited mass transport through the bulk.

4.6.6 Cross-sectioning Reduced Pellets for SQUID Magnetometry

To evaluate the effect of the reduced edges on the percent reduction, a sequence of five cross-sections were taken from an individual pellet as shown in Figure 4.33. The pellet was reduced at 1000°C for 50 h, and the reduction front spanned the entire thickness of the pellet. The cross-sections were taken in approximately 1 mm increments, from the edge moving in radially to the center. The calculated percent reduction from the
Figure 4.28: Optical micrographs of cross-sectioned 1000°C $10^{-15}$ atm (wet) reduced pellets showing the extent of the reduction reaction front from the top and bottom surfaces after (b) 0.5 h, (c) 5 h, (d) 10 h, (e) 25 h, and (f) 50 h.
Figure 4.29: Optical micrographs of cross-sectioned 1000°C 10^{-15} atm (dry) reduced pellets showing the extent of the reduction reaction front from the top and bottom surfaces after (b) 0.5 h, (c) 5 h, (d) 10 h, and (e) 25 h.
Figure 4.30: Optical micrographs of cross-sectioned 1000°C $10^{-19}$ atm reduced pellets showing the extent of the reduction reaction front from the top and bottom surfaces after (b) 0.5 h, (c) 5 h, (d) 10 h, (e) 25 h, and (f) 50 h.
Figure 4.31: Optical micrographs of cross-sectioned 900°C 10^{19} atm reduced pellets showing the extent of the reduction reaction front from the top and bottom surfaces after (b) 0.5 h, (c) 5 h, (d) 10 h, and (e) 25 h.

Figure 4.32: Optical micrographs of cross-sectioned 800°C 10^{19} atm reduced pellets showing the extent of the reduction reaction front from the top and bottom surfaces after (b) 10 h and (c) 25 h.
SQUID magnetometry results is plotted against the cross-sectional position in Figure 4.34. The edge has approximately 2 percent higher reduction of Ni$^{2+}$ than sections taken from the center of the pellet. The edge of the pellet includes the extent of reduction from three sides of the pellets, whereas the center of the pellet includes the extent of reduction from only the top and bottom surfaces, perhaps with some symmetrical overlap of the fronts. The edge effect is shown to span the entire radius of the pellet for long reduction times. To avoid edge effects in reported data, consistent cross-sections should be used whenever possible and pellets having a larger radius are recommended for future studies.

Figure 4.33: Schematic overlay on pellet photos showing the location of cross-sections 1 through 5 used to evaluate the edge effects on the reduction measurement.

Figure 4.34: Percent reduction versus radial position of cross-section showing the edges have a higher percent reduction than middle sections.
4.6.7 Thermodynamic and Kinetic Driving Forces in the Stages of Reduction

The internal reduction reaction in polycrystalline Ni-doped 10YSZ proceeds in three stages. The tendency in early stages is for nucleation of Ni\(^0\) particles on heterogeneous surfaces (pre-existing pores or grain boundaries). The average dihedral angle was determined from high resolution STEM of Ni\(^0\) particles decorating the grain boundary, as shown in Figure 4.35, with an average angle of 117 degrees. The thermodynamic driving force for heterogeneous nucleation at grain boundaries is approximated using equation 2.80, giving a result of 0.29. This means that the \(\Delta G^*_{het}\) is reduced by approximately a factor of 3 compared with the \(\Delta G^*_{hom}\) which provides a driving force for Ni\(^0\) nucleation at grain boundaries before internally in the grains. The calculation was repeated for Ni\(^0\) particles in pores that formed in early reduction times. Some of the particles that formed in pre-existing pores are highly faceted while others are hemispherical in shape, as shown in Figure 4.36, giving an average angle of 92.9 degrees. This means that the \(\Delta G^*_{het}\) is reduced by a factor of 2 compared with the \(\Delta G^*_{hom}\).

![Figure 4.35: High resolution STEM showing a Ni\(^0\) particle at a grain boundary in reduced Ni-doped 10YSZ.](image)

In stage 3, the homogeneous formation of superparamagnetic Ni\(^0\) particles existing in voids are shown to coarsen over increasing soak time in reducing conditions. Since the particle size is quantified by SQUID magnetometry, the number of Ni\(^0\) particles can be calculated from the volume of the particle. Then the volume of YSZ that must be reduced to yield the same quantify of Ni\(^2+\) particles can be calculated, such that the radius can be compared to the diffusion distance calculated from equation 2.76. These results are
compared in Table 4.6. To further quantify the kinetics as diffusion or source/sink limited, the particle sizes were plotted as squared and cubed values of the particle radius versus time, shown in Figure 4.37. The data is best fit with a squared relationship of radius size versus time indicating that the growth is source/sink limited coarsening. This results suggests the reaction is limited by the rate which Ni$^{2+}$ atoms can be removed from solution with YSZ and/or attached to the sink particles. The creation of metallic Ni$^0$ must coincide with the creation of a vacant zirconium site.

Table 4.6: The diffusion distance due to a concentration gradient is compared to the radius of a sphere of YSZ needed to produce an equivalent amount of nickel ions to explain coarsening of superparamagnetic Ni$^0$ particles.

<table>
<thead>
<tr>
<th>Reduction Time (h)</th>
<th>Radius of YSZ Sphere Needed (nm)</th>
<th>Diffusion Distance of Nickel (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>20.3</td>
<td>24.6</td>
</tr>
<tr>
<td>75</td>
<td>30.9</td>
<td>28.0</td>
</tr>
</tbody>
</table>

4.6.8 Space Charge Layer Calculations

This section provides details of the calculation to approximate electrical potential driving force of mass transport during the internal reduction reaction. The space charge effect from the grain boundary core is given by:

$$
\lambda^* = \lambda \sqrt{\frac{4e}{k_B T} \Delta \phi(0)}
$$

(4.6)

where the Debye length is $\lambda$, the charge of an electron is $e$, and the change in electrical potential at the surface ($x = 0$) is given by $\Delta \phi(0)$. The Debye length is given by:
Figure 4.37: Kinetics modeling the growth of superparamagnetic Ni\(^0\) particles show that the data is best fit with a squared function.

\[
\lambda = \sqrt{\frac{\varepsilon \varepsilon_0 RT}{2z^2 F^2 c_\infty}}
\]

where the dielectric constant of YSZ is \(\varepsilon\), the concentration of charged species is \(c_\infty\), the temperature is \(T\), and the rest of the variables are constants. For this calculation, \(\varepsilon\) for YSZ is known to be 55-60 \([193]\) and \(c_\infty\) was assumed to be the equilibrium concentration of oxygen vacancies introduced by the reducing gas (reference Figure 2.12). The electrical potential is calculated using equation 2.83 and equation 2.84. First, the value of \(E_0\) can be calculated through equation 2.84 for the equilibrium \(\Delta G_{\text{rxn}}\) for the reduction reaction which equals -50285 J mol\(^{-1}\). The result is 0.261 V. Then \(\Delta \phi\) can be solved using equation 2.83, where \(P_{H_2O}\) is approximately \(10^{-3.49}\) atm and \(P_{H_2}\) is approximately \(10^{-1.7}\) atm. The result for \(\Delta \phi\) is 0.334 V. The Debye length measures the distance for which the effects of an electrostatic potential will persist to influence a charge species in solution, equal to 39.6 nm. The space charge layer during the reduction reaction of Ni-doped 10YSZ was calculated to be 138 nm. The space charge layer is a plausible explanation for the particle free zone observed after stage 3 reduction.
CHAPTER 5

PAPER II:
TAILORED METAL-CERAMIC NANOCOMPOSITES PREPARED BY REDOX CYCLING OF
POLYCRYSTALLINE NI-DOPED YTTRIA STABILIZED ZIRCONIA

This chapter presents the work carried out to investigate the reversibility of redox cycling of Ni-doped 10YSZ pellets. This chapter is a paper entitled “Tailored Metal-Ceramic Nanocomposites Prepared by Redox Cycling of Polycrystalline Ni-doped Yttria Stabilized Zirconia” that was co-authored by James R. O’Brien and Ivar E. Reimanis and was submitted to Script Materialia.

5.1 Abstract

We demonstrate it possible to tailor unique metal-ceramic nanocomposites through redox cycling of Y_2O_3-stabilized ZrO_2 containing 0.5 molar percent NiO (below the solubility limit). Upon the first reduction, Ni^{2+} ions precipitate as metallic Ni^0 at pores, grain boundaries, or within the grain interiors with specific size ranges (∼ 5 nm/ ∼ 30 nm/ ∼ 200 nm) for each. Upon oxidation, Ni^{2+} ions form, but their distribution is not the same as the original microstructure. In particular, NiO forms, and subsequent reduction leads to a distribution of metallic Ni different from that in the first reduction. One can ratchet the dissolution/precipitation behavior to form particular nanoscale arrangements.

5.2 Body Text

Nanocomposite oxides containing dispersed metallic or metal-oxide nanoparticles offer improved structural and/or energy-related properties compared with monolithic oxides [194]. The high interfacial area may lead to space charge layers that enhance the mass transport of charged species [195, 196] and may be designed for use in electroceramic devices and sensors [197–200]. It is generally challenging to engineer stable metal-ceramic nanocomposites due to thermodynamic and kinetic instabilities at the nanoscale [198].

Internal reduction has previously been considered as a method to make nanoscale Ni-YSZ composites [188]. Ni^{2+} ions dissolved in the YSZ lattice may be exsolved in a reducing atmosphere to form metallic Ni^0. The YSZ microstructure plays an important role in the size and distribution of Ni^0. In particular, microstructural features such as grain boundaries and porosity may be sites for fast transport pathways and may be preferential sites for Ni^{2+} ions and/or metallic Ni^0 [93, 162, 201]. Space charge effects also would be expected to play a role [153, 193].

The reduction-oxidation behavior of nickel-doped YSZ has been widely studied in context of solid oxide fuel cell (SOFC) anodes [160, 202–206]. Typically, Ni contents up to about 40 molar % are used, leading
to an interconnected Ni-porous-YSZ microstructure with a high density of triple point boundary reaction sites [157, 207, 208]. The direct reduction and direct oxidation are of interest not only in SOFC anode fabrication, but in operation. In the present work, a composition of 0.5 molar percent NiO dopant is chosen since it is well below the solubility limit [156, 165], thereby facilitating a study to examine the exsolution and dissolution of Ni$^{2+}$ ions in YSZ. Previous studies on the redox behavior of Ni-YSZ have not been performed for levels below the solubility limit.

The specimens were prepared by high purity chemical synthesis described elsewhere [166]. The redox cycles were conducted in a dedicated furnace [167]. It was shown that all nickel exists as randomly distributed Ni$^{2+}$ ions and that no NiO is present [167]. Reduction was performed at 1000°C for 25 h flowing in H$_2$ gas (2% H$_2$/Ar balance). Oxidation was performed at 1000°C for 25 h in flowing synthetic air (21% O$_2$/Ar balance). A temperature of 1000°C was selected because it is below the temperature where grain growth occurs [209]. All heating and cooling was performed in flowing Ar gas. After the first reduction step metallic Ni$^0$ forms in a manner that is highly dependent on the YSZ microstructure. A distribution of Ni$^0$ size is observed: $\sim$200 nm within pores, $\sim$20 nm along grain boundaries, and $\sim$5 nm within voids created during the reaction in the grain interior. For the present study, two redox cycles were performed, and the steps of the cycles are herein referred to as reduction 1, oxidation 1, reduction 2, and oxidation 2. In order to characterize the oxidation kinetics, additional times of 0.5, 5, and 10 h were performed for specimens in the oxidation 1 step.

Optical characterization of cross-sectioned and polished pellets was conducted with a low power optical microscope. The extent of the reaction front was quantified by averaging 20 measurements of the depth from the top and bottom surfaces of the pellets. The reaction rate constant and kinetic information were extracted by plotting the squared extent of reaction versus time.

Electron microscopy characterization was performed on specimens prepared by focused ion beam (FIB) milling (FEI, Helios Nanolab 600i) with transition electron microscopy (TEM, Phillips (FEI), CM200) at 200 kV accelerating voltage to show general features of reduction 1 and oxidation 2 microstructures.

AC susceptibility measurements were collected from $\sim$100 to 200 mg of material removed from the pellet with super-conducting quantum interference device (SQUID) magnetometry (Quantum Design, MPMS-7) set to an AC drive field of 7 Hz, AC drive amplitude of 100 $\mu$T, and zero DC field while scanning temperature from 1.8 to 250 K. The sample of pellet was carefully sectioned so that it represents the entire pellet cross-section. DC susceptibility measurements were also collected by sweeping the field from 1 T to -5 mT at 100 K to obtain a value of magnetic saturation which was used to calculate the percent of reduction using a well-established technique [165].
Optical images of the pellets shown in Figure 5.1 depict the color change and extent of reaction. The as-sintered pellet is tan. Reduction 1 turns the entire pellet thickness black. In oxidation 1, the extent of the oxidation front is partial, resulting in a tan coloration, but leaves a black reduced core. The tan coloration of the oxidation 1 pellet is a lighter tint than the as-sintered pellet. Reduction 2 returns the entire pellet thickness to black. In oxidation 2, the extent of the oxidation front is partial, resulting in a green coloration, but leaves a black reduced core. The color changes (tan, black, and green) are the result of changing states of nickel [210]. Tan is due to the substitution of Ni\(^{2+}\) on Zr\(^{4+}\) sites, black is due to Ni\(^{0}\) particles, and green is due to NiO. The green color after the second redox cycle indicates there is likely substantial NiO in the pellet after oxidation 2; this is confirmed with magnetometry, as described below.

Figure 5.1: Optical images showing cross-sections of as-sintered, reduction 1, oxidation 1, reduction 2, and oxidation 2 pellets. Oxidation 1 and 2 pellets contain a reduced core.

The squared extent of reaction versus time follows a linear trend (R\(^2\)=1.00). Thus, the oxidation reaction follows a parabolic rate law indicating a diffusion limited reaction. It may be described as [211]:

\[
\frac{dx}{dt} = \frac{k'}{x}
\]  

(5.1)

where the rate constant \(k'\) is proportional to the rate limiting species of the reaction, \(t\) is time, and \(x\) is the thickness of the reaction front. The slope of the squared extent of reaction versus time gives a rate of \(7.8 \times 10^{-8}\) cm\(^2\) s\(^{-1}\). The parabolic rate constant, \(k'\), may be expressed in relationship to the diffusion coefficient of oxygen, \(D_X\) by [211]:

\[
k' = \frac{1}{RT} \int_{\mu'_X}^{\mu''_X} D_X \, d\mu_X
\]  

(5.2)

where the chemical potential of the reducing or oxidizing gas is given by \(\mu''_X\) and the chemical potential of the oxide is given by \(\mu'_X\), R is the molar gas constant, and T is the temperature. The chemical potential of the oxide depends on the defect concentration of oxygen vacancies, which depends upon the oxygen partial pressure, \(P_{O_2}\):

\[
d\mu_X = \frac{1}{2} RT \, d \ln P_{O_2}
\]  

(5.3)

and the expression for \(k'\) is simplified to [211]:

91
\[ k' = \frac{1}{2} \int_{P_{O_2}'}^{P_{O_2}''} D_X \ d \ln P_{O_2} \]  

Assuming the products of the oxidation reaction form at an oxygen partial pressure above the equilibrium of the reduction reaction \((P_{O_2} = 4.5 \times 10^{-11})\), and taking \(D_X\) for oxygen vacancies to be \(9.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}\) [212], \(k'\) is calculated to be \(2.1 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}\). If the reduced pellets have fully equilibrated to the oxygen partial pressure of the reducing gas \((P_{O_2} = 1 \times 10^{-19})\), \(k'\) is calculated to be \(3.9 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}\). These calculated rate constant values are in good agreement with the experimentally measured \(k'\) in this work \((7.8 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1})\). The oxidation reaction is therefore rate limited by the outward diffusion of oxygen vacancies and electrons as the pellet equilibrates oxygen activity to match that of air.

Magnetic DC susceptibility measurements were used to quantify the percentage of metallic \(\text{Ni}^0\). A summary of the calculated percent \(\text{Ni}^0\) in pellet cross-sections from each redox step is presented in Table 5.1. The percent \(\text{Ni}^0\) gives the total \(\text{Ni}^{2+}\) ions that have been reduced after the reduction step, or the total unoxidized \(\text{Ni}^0\) particles existing in reduced core after the oxidation step. To confirm the DC susceptibility is from the reduced core, a volume of only the oxidation 2 shell was measured by polishing away the reduced core. Results indicate that only \(\sim 0.2\%\) of \(\text{Ni}^0\) remains in the shell. Further, the unoxidized \(\text{Ni}^0\) particles in the core show no remnant magnetization in DC susceptibility measurements (all curves pass through the origin) meaning that the metallic \(\text{Ni}^0\) remains entirely in the superparamagnetic state (\(\sim 5\) nm particle size) in the reduced core.

<table>
<thead>
<tr>
<th>Total (\text{Ni}^0) %</th>
<th>Reduction 1</th>
<th>Oxidation 1</th>
<th>Reduction 2</th>
<th>Oxidation 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction 1</td>
<td>43</td>
<td>4</td>
<td>66</td>
<td>24</td>
</tr>
</tbody>
</table>

Magnetic AC susceptibility measurements were used to quantify the size of the metallic \(\text{Ni}^0\) particles. The AC susceptibility curves shown in Figure 5.2(a) are consistent with TEM results for reduction 1, revealing a peak in \(\chi'\) at \(\sim 50\) K. The superparamagnetic \(\text{Ni}^0\) particles that exist in the grain interiors (Figure 5.3(c)) dominate the magnetic signal and produce this peak. The peak remains at \(\sim 50\) K after oxidation confirming that the size of the superparagmagnetic \(\text{Ni}^0\) particles remains unchanged. The AC susceptibility for oxidation 1 shown in Figure 5.2(b) also reveals that \(\chi'\) increases as temperature approaches 0 K, consistent with paramagnetic behavior of unordered \(\text{Ni}^{2+}\) ions. The weak paramagnetic signal is observed because the superparamagnetic signal results from only \(\sim 4\%\) of \(\text{Ni}^0\). For the second redox cycle, the AC susceptibility curve shown in Figure 5.2(c) shows a shift in \(\chi'\) to \(\sim 175\) K, consistent with the growth of superparamagnetic \(\text{Ni}^0\) particles. Superparamagnetic \(\text{Ni}^0\) particles grow with longer reduction times [201]. The AC suscepti-
bility for oxidation 2 shown in Figure 5.2(d) reveals a shift in $\chi'$ back to $\sim 50$ K which is consistent with superparamagnetic Ni$^0$ particle size in the first redox cycle.

Figure 5.2: Plots of AC susceptibility showing the real $\chi'$ and imaginary $\chi''$ components for (a) reduction 1, (b) oxidation 1, (c) reduction 2, and (d) oxidation 2. The temperature for which the peak in $\chi'$ occurs corresponds to particle size. The growth of Ni$^0$ particles from reduction 1 to 2 is observed by the peak shift to higher temperature. The peak in oxidation 1 and 2 is equivalent to reduction 1, and indicates the size of superparamagnetic Ni$^0$ particles in the reduced core volume is stable after redox cycling.

Thorough TEM of the oxidation zones in oxidation 1 and oxidation 2 pellets reveal no particles of either metallic Ni$^0$ or NiO in the pores or along the grain boundaries. For reference, Figure 5.3(a) shows a Ni$^0$ particle at the grain boundary and associated strain contrast in the reduced microstructure. In Figure 5.3(b), the Ni$^0$ particles and strain contours observed along the grain boundaries have dissipated. In Figure 5.3(c), the reduced microstructure shows the appearance of superparamagnetic Ni$^0$ that has formed in voids due to reduction. The oxidized microstructure in Figure 5.3(d) shows that the voids appear filled. It is likely that NiO forms in the void area surrounding the Ni$^0$ particles, leading to a core/shell structure.
Figure 5.3: TEM micrographs showing (a) a metallic Ni\(^0\) particle at a grain boundary and associated strain contrast, (b) absence of metallic Ni\(^0\) and strain contrast at the grain boundary after oxidation 1, (c) as-reduced microstructure with metallic Ni\(^0\) particles that have nucleated in voids in a grain interior during internal reduction, and (d) oxidation 2 microstructure having voids filled with NiO in the grain interior after the second redox cycle.

A schematic in Figure 5.4 summarizes the representative microstructures for the various redox cycles. As-sintered microstructural features include pores and grain boundaries with a homogeneous Ni\(^{2+}\) distribution. Reduction 1 displays a distribution of Ni\(^0\) with sizes depending on location: \(~200\) nm in pores, \(~30\) nm along grain boundaries, and \(~5\) nm is grain interiors. Oxidation 1 converts the Ni\(^0\) in grain interiors to NiO, while Ni\(^0\) in pores and grain boundaries dissolves in YSZ as part of the oxidation front. This is supported by the 20\% decrease in Ni\(^0\) measured in reduction 1 compared with oxidation 1. Although the reduced core volume accounts for \(~50\%) of the cross-sectional volume, the black color is only due to 4\% Ni\(^0\). This suggests that all the Ni\(^0\) in pores and grain boundaries in the reduced core has dissolved as Ni\(^{2+}\) or converted to NiO. Reduction 2 results in a distribution of Ni\(^0\) particle sizes similar to reduction 1, with the exception that Ni\(^0\) particles in the grain interiors grow. Oxidation 2 follows the trend of oxidation 1, and also results in 20\% decrease in Ni\(^0\) measured in reduction 2 compared with oxidation 2. This also suggests that all the Ni\(^0\) in pores and grain boundaries in the reduced core has dissolved as Ni\(^{2+}\) or converted to NiO. Although the reduced core volume accounts for \(~75\%) of the cross-sectional volume, the black color is due only to 24\% Ni\(^0\).

In the context of evaluating the reversibility of the redox cycled microstructure, the initial internal reduction results in exsolution of Ni\(^{2+}\) from the YSZ. The subsequent expected dissolution of Ni\(^{2+}\) back into the YSZ upon treatment in the oxidizing conditions does not occur at 1000°C. Since the formation of superparamagnetic Ni\(^0\) is associated with a void, believed to result from the loss of a stoichiometric unit of \(\text{ZrO}_2\) \cite{201}. The mechanism for Ni\(^{2+}\) lattice transport is no longer active because the vacant zirconium sites, \(\text{V}''''\text{Zr}\), are expended to create the void. The AC susceptibility data shows refinement of the microstructure by
Figure 5.4: A summary of the microstructure features is illustrated for each pellet. As-sintered pellets contain pores and grain boundaries with even Ni$^{2+}$ distribution. Reduction 1 has a distribution of Ni$^{0}$ form with sizes depending on location: $\sim$200 nm in pores, $\sim$30 nm along grain boundaries, and $\sim$5 nm in grain interiors. Oxidation 1 converts the Ni$^{0}$ in grain interiors to NiO, while Ni$^{0}$ in pores and grain boundaries dissolve in the oxidation front. This is not the case for the reduced core, where $\sim$5 nm Ni$^{0}$ remain and all the Ni$^{0}$ in pores and grain boundaries has converted to NiO. Reduction 2 results in a distribution of Ni$^{0}$ particle sizes similar to reduction 1, with exception that Ni$^{0}$ particles in the grain interiors grow. Oxidation 2 follows the trend of oxidation 1.

partial oxidation that results in a narrow distribution of superparamagnetic Ni$^{0}$ particles after the second redox cycle.

Complete oxidation results in full conversion of the superparamagnetic Ni$^{0}$ particles to NiO nanoparticles in the YSZ grain interiors. Higher temperature and longer oxidation soak times are needed to promote entropic dissolution of the Ni$^{2+}$ [166]. These results demonstrate that it is possible to create unique metal-oxide and oxide-oxide nanocomposite structures via selective redox cycling.

5.3 Acknowledgments

We would like to thank the National Science Foundation, Division of Materials Research, Ceramics Program, Grant Number 1003030 for funding this work. Special thanks are extended to the Magenetics Group at NIST Boulder, CO, for access to a SQUID magnetometer.

5.4 Supplemental Evidence

The supplemental evidence presents additional experimental results that are pertinent redox cycling of Ni-doped 10YSZ and were not included in the publication. These results include optical microscopy of various redox soak times. Images and cross-sections of all the redox cycled pellets are shown in Figure 5.5 and Figure 5.6, where the progression of the oxidation front is shown after the first cycle (Figure 5.6(a)) and second cycle (Figure 5.6(b)). The extent of oxidation 2 appears to be less than the extent of the oxidation 1 reaction. Further, the oxidation 2 reaction resulted in the pellet turning green. The slower reaction could be explained by the increased amount of metallic Ni$^{0}$ that results from the reduction 2 leading to a higher
conversion of NiO particles in the bulk of the grains causing an overall slower reaction.

Figure 5.5: Optical micrographs showing an as-sintered pellet and the top view of redox cycled pellets.

![Image]

Figure 5.6: Optical micrographs showing the extent of the reaction front for redox cycled pellets after (a) one cycle and (2) cycles.

![Image]

It is interesting to note that the extent of the oxidation front of the second redox cycle is less than that of the first redox cycle. To further investigate the kinetics of the redox reaction, the extent of oxidation reaction in cross-sections taken at 0.5, 5, 10, and 25 h, as shown in Figure 5.7, for oxidation 1. As discussed in the publication, the kinetics of the oxidation 1 front were shown to be in agreement with the diffusivity of O\textsuperscript{2-} ions. The extent of reduction reaction in cross-sections taken at 0.5, 5, 10, and 25 h for reduction 2 is shown in Figure 5.8. The reason for the reduced areas remaining in the center of the 0.5 h pellet compared with the non-reduced center of the 5 h pellet is unknown, but might be due to the crack creating a fast path for diffusing species in the 0.5 h pellet. In Figure 5.9, kinetics of the reduction 2 front are plotted in comparison to the kinetics of the reduction 1 front showing that the reduction rate is approximately constant after two
Figure 5.7: Optical micrographs showing the extent of the oxidation front for redox cycled pellets (oxidation 1) after (a) 0.5 h, (b) 5 h, (c) 10 h, and (d) 25 h.

Figure 5.8: Optical micrographs showing the extent of the reduction front for redox cycled pellets (reduction 2) after (a) 0.5 h, (b) 5 h, (c) 10 h, and (d) 25 h.
redox cycles. The mechanism for reduction 2 will be different because NiO oxide particles exist in the bulk that are directly reduced, but the kinetics of the reaction rely on the reaction species getting to the NiO particles by bulk diffusion that should remain unchanged through redox cycling.

Figure 5.9: Plot showing the squared extent of reaction squares versus time for the reduction 1 and reduction 2 reaction fronts.
CHAPTER 6
EXCESS BARIUM NICKEL OXIDES IN BaZr\textsubscript{0.85-X}Ni\textsubscript{X}Y\textsubscript{0.15}O\textsubscript{3-δ} STUDIED WITH SQUID
MAGNETOMETRY

This chapter presents the work carried out to investigate the solubility of nickel dopant in BZY15. Yttria-doped barium zirconates have excellent protonic/ionic/electronic conductivity suitable for a variety of electrochemical applications, except high sintering temperatures result in loss of stoichiometry. The sintering temperature is often lowered by the addition of transition metal dopants but excess amounts result in second phases that are detrimental to conductivity. The formation of second phases is studied by preparing stoichiometric compositions of nickel-doped (x = 0 to 0.08) BaZr\textsubscript{0.85-X}Ni\textsubscript{X}Y\textsubscript{0.15}O\textsubscript{3-δ} crystalline powders by a high-purity citrate-polymeric method from all acetate precursors. Paramagnetic susceptibility measurements at 5 K provide a simple way to quantify the oxidation states of Ni\textsuperscript{2+/3+} ions in powders. Calcination at 900°C produces a BZY core that is not barium deficient. When Ni-dopant is added a BaNiO\textsubscript{2.1} surface-matched shell covers the BZY powders. Increasing Ni-dopant or decreasing surface area by particle growth results in BaNiO\textsubscript{2.5} nodules that form on the core/shell powders. The excess surface nodules are selectively reduced to produce nano-Ni metal particles having narrow size distribution that are fully bonded to the core/shell powders. It is expected that these materials having unique core/shell particle structures are capable of superb catalytic reactivity. The results show that nanoscale microstructural design is possible when SQUID magnetometry is used to optimize the Ni-dopant concentration.

6.1 Introduction

Barium zirconates have been highly debated for over one hundred years [213]. Yttria-doped barium zirconate (Y\textsubscript{2}O\textsubscript{3}-doped BaZrO\textsubscript{3} or BZY) is a widely studied ceramic proton/oxide/electronic hole conductor due to high conductivity at reduced operating temperatures compared with conventional solid oxide fuel cell (SOFC) electrolytes [39, 40]. The versatility of the majority carrier species is attributed to the chemical stability of BZY under reducing, oxidizing, or carbon dioxide atmospheres. The broad range of environmental conditions and excellent coking resistance of BZY is ideal for electrochemical and catalysis applications [41–43]. A major drawback to using BZY is that high sintering temperatures are usually required to achieve full density [44], resulting in volatilization of barium and a loss in stoichiometry. Transition metal oxides are often added to BZY to improve sintering [45–47]. Specifically, the addition of NiO is shown to lower the sintering temperature, increase density, and increase electronic conductivity [49, 86].
The mechanism by which transition metal dopants aid sintering is not understood. Some research suggests that low melting point phases form and aid densification at lower temperatures by liquid phase sintering [87, 163]. Since the Ni$^{2+}$ solid solution limit in BZY is not known, it is difficult to predict the conditions under which excess Ni phases form. Ricote and Bonanos show with lattice parameter measurements that the solubility of Ni$^{2+}$ in BZY is less than 1.0 molar percent [49]. However, Ni$^{2+}$ ions are expected to segregate to surfaces and therefore, the tendency to form other phases would depend on the BZY particle size [166]. Specifically, low calcination temperatures yield fine powders having high surface area that may accommodate large amounts of Ni$^{2+}$ without the formation of second phases.

Nickel-doped oxides, such as Ni-BZY, are of interest as catalysts [99, 100]. Raney nickel is commonly used in catalyst production for many industrial scale chemical reactions [214]. It consists of very fine Ni particles and has potential to be extremely pyrophoric. A primary challenge is adhering Raney nickel to oxide support surfaces while preventing coarsening. When Ni$^{2+}$ ions are segregated at surfaces, reduction to metallic nickel can be facilitated compared with Ni$^{2+}$ ions that exist in solid solution or within a second phase, like Y$_2$BaNiO$_5$, that is difficult to reduce [215]. Mixed ionic and protonic conducting oxides, like BZY, allow tuning of catalytic properties by varying dopant levels [101] and permeation selectivity by preparing a core shell type design [216]. For these reasons it is desirable to define excess Ni dopant and understand what excess Ni phases form to determine if selective reduction can be used to prepare catalysts.

A sensitive technique to characterize low concentrations of nickel dopant in oxides is SQUID magnetometry [57]. The value of this technique is the ability to quantify the excess Ni phases because unique magnetic susceptibilities are reported for nickel ions [57], nickel oxide [217, 218], barium nickel oxides [219–222], and yttirum barium nickelates [86, 87, 223, 224]. BaNiO$_x$ phases were first prepared in the 1950s [219, 220] and are more stable for stoichiometric synthesis in slightly reducing conditions [225] which is expected in this work due to the decomposition of acetates precursors.

High purity Ni doped BZY15 powders and pellets were chemically synthesized and characterized by measuring magnetization versus temperature curves. By plotting the mass magnetization versus Ni concentration for powders and pellets at a constant temperature, the excess Ni$^{2+}$ ions in powders can be determined and modeled as function of powder size. The contribution of magnetic moment per Ni$^{2+}$ ions in powders and pellets was calculated using magnetic theory to describe the impurity phases in the pellets. A comparative analysis of powders and pellets allows quantification of the solubility of Ni$^{2+}$ in BZY to show that excess Ni$^{2+}$ leads to the formation of BaNiO$_x$. This work further demonstrates that selective reduction of the second phases enables synthesis of nanocomposite powders.
6.2 Experimental

**Synthesis.** Various compositions of nickel doped \((x = 0, 0.005, 0.01, 0.02, 0.04, \text{and} 0.08)\) BZY15 \((\text{BaZr}_{0.85-x}\text{Ni}_x\text{Y}_{0.15}\text{O}_{3.4})\) was synthesized using a high purity, chemical precursor route that encouraged atomic level mixing of acetate precursors [166]. Briefly, stoichiometric ratios of cation solutions were heated while stirring, then mixed with EDTA acid and citric acid anhydrous. The chelating agents were dissolved in ammonium hydroxide. Heating and stirring continued until the solution condensed into a gel and dried into char.

Powders were produced by calcining the char in air at 900°C, 950°C, and 1000°C (3°C/min) for 10 h. Nanocomposite powders were prepared from 4.0 molar% powders calcined at 900°C for 10 h, by reduction in 2% H\(_2\) at 600°C for 30 minutes and 900°C for 5 h. Cylindrical pellets 11 mm in diameter by 1 mm thickness were made by uniaxially pressing powders calcined at 900°C for 10 h. The pellets were buried in an equivalent composition powders and sintered in air (2°C/min, 5 h hold 800°C) at 1600°C for 24 h. The successful sintering of lower Ni content samples requires a 4 h hold at 800°C on warming.

**X-Ray Diffraction and Rietveld Refinement.** Fresh powders were characterized with XRD using a CuK\(_\alpha\) radiation source (X’Pert Pro; PANalytical Inc., Westborough, MA). Patterns were collected using a scan speed of 0.3 degrees s\(^{-1}\) over a 2\(\theta\) range of 10 to 140 degrees. Rietveld refinement was performed using GSAS software (Revision 1251) [226, 227]. A silicon standard (NIST SRM 640d) was refined to qualify the refinement procedure. This software does not output error of the calculations so error bars are not included in the data presented.

**SQUID Magnetometry.** The results for measured powders are designated as “fresh” or “aged”. “Fresh” describes powders that were characterized within two weeks of calcination. “Aged” describes powders that were characterized after several months of sitting in ambient conditions. Characterization of fresh versus aged powders is used as further confirmation of phase identification when excess phases are determined present and should hydrate in ambient environment. A summary of the calcination and characterization dates of fresh versus aged powders is presented in Table 6.1. Powder samples weighing 50 to 100 mg are encased in gelatin capsule and put into clear plastic straw attached to the end of a DC transport rod. Fresh 900°C and 950°C calcined powders were measured with an MPMS-7 SQUID magnetometer (Quantum Design, Inc.) as moment versus temperature M(T) at 0.01 T DC field and stable temperature scans from 1.8 to 25 K. The 900°C powders were aged by keeping them in the exact same gelatin capsules for 3 months. The 950°C powders were aged by keeping them in the exact same gelatin capsules for 6 months. The aged powders were remeasured with the MPMS-7 as moment versus field M(H) from 1 T to zero at 5 K.
Table 6.1: Summary of characterized powders categorized by calcination and characterization date to define fresh versus aged designation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Calcination Date</th>
<th>Characterization Date</th>
</tr>
</thead>
<tbody>
<tr>
<td>900°C Powders</td>
<td>03/11/2014</td>
<td>03/25/2014 06/12/2014</td>
</tr>
<tr>
<td>950°C Powders</td>
<td>08/29/2013</td>
<td>09/02/2013 12/16/2013</td>
</tr>
</tbody>
</table>

For SQUID analysis of pellets, approximately 100 mg of a rectangular-shaped pellet sample was wedged in the middle of straw, eliminating asymmetric background signal contributions that can distort the raw scan response function. The pellets were measured with the MPMS-7 as M(T) curves at 0.01 T DC field and stable temperature scans from 1.8 to 25 K. Independent confirmation measurements were performed on separate pieces from same 1.0 molar % Ni and 2.0 molar % Ni sintered pellets. This data was collected on a MPMS-3-AC magnetometer (Quantum Design, Inc.). The magnetic susceptibility for M(T) was calculated using the data point measured at 5 K, whereas, the slope of the M(H) curves produces the value for magnetic susceptibility.

For SQUID analysis of the reduced powder nanocomposites, M(H) curves were collected at 100 K with stable field scan from 1 T to -1 T back to 1 T for complete magnetization loop with the MPMS-7. The programmed sequence then measured AC susceptibility of the nanocomposite powders using an AC drive frequency of 7 Hz, 100 $\mu$T AC drive amplitude, zero DC field, and stable temperature scans from 1.8 to 250 K. Data from AC susceptibility measurements is plotted as a real component, $\chi'$, and imaginary component, $\chi''$, versus temperature in units of emu/Oe/gram-Ni metal. The amount of Ni metal in each sample was determined from the saturation moment at 0.5 T and 100 K, after correcting for the linear background contribution and by using the conversion factor 57 emu/g-Ni. At low frequencies, the real $\chi'$ component is the slope of the M(H) curve and shows the magnitude of the specimen magnetization. The imaginary $\chi''$ component is not represented by DC susceptibility and shows the phase losses between the specimen magnetization and the oscillating field.

**Microscopy.** Reduced powders were suspended in acetone, and transferred to a holey carbon copper mesh grid for analysis. Transmission electron microscopy (TEM) micrographs were collected (CM-200; FEI Inc., Hillsboro, OR) at 200 kV accelerating voltage.
6.3 Results

The XRD patterns shown in Figure 6.1 for powders calcined at 900°C match cubic BZY (reference pattern ICDD 04-016-4803, \(a = 4.2178 \text{ Å}\)) [228], and are free from extraneous peaks. In contrast, the XRD patterns for all powders calcined at 950°C and 1000°C (Figure 6.2 and Figure 6.3) display peaks at \(2\theta\) equal to \(~23\) and \(~34\) degrees that match BaCO\(_3\) (reference pattern ICDD 01-071-2394, \(a = 5.3126 \text{ Å}, \ b = 8.8958 \text{ Å}, \) and \(c = 6.4284 \text{ Å}\)) [229]. The same relative intensity for the BaCO\(_3\) peak appears and is independent of Ni content.

![Figure 6.1: Powder X-ray diffraction patterns for various nickel content in BZY15 powders calcined at 900°C for 10 h shows no impurity peaks and matches cubic phase BZY.](image)

The M(T) curves for aged powders are shown in Figure 6.4 as inverse mass susceptibility versus temperature. The value for correction of the diamagnetic response of un-doped BZY was experimentally measured to be \(-6 \times 10^{-6} \text{ m}^3 \text{ kg}^{-1}\). The Curie-Weiss fit was applied to calculate the spins per Ni giving 2.83 Bohr magnetons as predicted by magnetic theory for unordered Ni\(^{2+}\) containing 2 spins per Ni ion [168]. This value has been verified experimentally for a perovskite system [144]. A slight curvature with increasing temperature is observed only in the 2.0 molar % Ni sample and may be a measurement artifact from mounting material or impurity phase during synthesis. Alternatively, it may be intrinsic for an ordered second phase. Any of these explanations produce temperature independent paramagnetic signal. In contrast, the M(H) 5 K data point for the fresh powders was used to calculated the spins per Ni. A summary of spins per Ni in BaNiO\(_x\) phases are shown in Table 6.2. The fresh powders yield 1.83 Bohr magnetons per Ni ion matching
Figure 6.2: Powder X-ray diffraction patterns for various nickel content in BZY15 powders calcined at 950°C for 10 h shows impurity peaks at $2\theta$ equals ~23 and ~34 degrees for all powders.

Figure 6.3: Powder X-ray diffraction patterns for various nickel content in BZY15 powders calcined at 1000°C for 10 h shows impurity peaks at $2\theta$ equals ~23 and ~34 degrees for all powders.
the BaNiO$_{2.1}$ formula up to 2.0 molar % Ni. The decreased value of spins per Ni is due to the combination of Ni$^{2+}$/3+ oxidation states.

Figure 6.4: M(T) curves for powders calcined at 900°C for 10 h shows all Ni dopant levels follow the same linear slope.

Table 6.2: The measured spins per Ni ion at low temperature for various BaNiO$_x$ type phases. The reference is spins per Ni for fresh powders only.

<table>
<thead>
<tr>
<th>Reference</th>
<th>Spin Per Ni BaNiO$_{2.1}$</th>
<th>Spin Per Ni BaNiO$_{2.5}$</th>
<th>Spin Per Ni BaNiO$_{2.0}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fresh</td>
<td>1.83</td>
<td>0.97</td>
<td>0</td>
</tr>
<tr>
<td>Aged</td>
<td>2.0</td>
<td>2.0</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 6.5 shows the mass magnetization at 5 K versus the target molar % Ni content for fresh/aged powders and sintered pellets. It is apparent the paramagnetic susceptibility increases linearly to 4.0 molar percent Ni in the fresh powders, with the slope equal to 2 free spins per Ni ion. The aged powders show decreased magnetic susceptibility above 2.0 molar %. By extrapolation, the value for 8.0 molar % Ni aged powder gives 5.5 molar % Ni in Ni$^{2+}$ high spin state, leaving the difference of 2.5 molar % Ni. As discussed later, the difference of 2.5 molar % Ni is assigned to a known non-magnetic phase (BaNiO$_{2.0}$ formula). The as-sintered powders slowly hydrate in air driven by redox reaction converting all Ni$^{3+}$ (1 free spin) into Ni$^{2+}$ (2 free spins), while the non-magnetic phase (BaNiO$_{2.0}$) remains unchanged.
By knowing the spins per Ni for various BaNiO\textsubscript{x} phases and using Figure 6.5, it is possible to solve the phase fractions using a series of equations. A summary of phase fractions for fresh powders are listed in Table 6.3 for 900°C and 950°C calcined powders. The 4.0 molar % Ni fresh powder has a second phase that corresponds to Ni\textsuperscript{3+} oxidation state and the BaNiO\textsubscript{2.5} formula. The 8.0 molar % Ni fresh powder is a mixture containing 3 phases. By assuming that the 2.0 molar % Ni exist as BaNiO\textsubscript{2.1}, the remaining magnetic contribution must be 3.5 mol % Ni as BaNiO\textsubscript{2.5}; therefore, the remaining 2.5 molar % Ni as must exist as nonmagnetic BaNiO\textsubscript{2.0}. The 950°C calcined powders were prepared and measured one year earlier. The 4.0 molar % Ni fresh/aged powders at 950°C calcination temperatures reproduce the same values as the 900°C powders and show that phases present do not significantly change over the duration of six months. The 8.0 molar % Ni data from 950°C calcined powder contains lower BaNiO\textsubscript{2.5} fraction than the 4.0 molar % Ni fresh/aged powders; the reason for this is offered in the Discussion.

Preparing pellets from the 900°C calcined powder and sintering at 1600°C produced dramatically different results; the fresh powders contain only BaNiO\textsubscript{2.1} phase and the pellets contain only the BaNiO\textsubscript{2.5} phase. The M(T) curves for the sintered pellets are shown in Figure 6.6. The higher 4.0 and 8.0 molar % Ni content pellets had clear signs of liquid phase sintering, resulting in loss of material and very low paramagnetic values in Figure 6.5. For this reason the amount of Ni per gram sample is unknown, preventing analysis for other possible phases. The mass magnetization of sintered pellets up to 2.0 molar % Ni follow a linear trend and
Table 6.3: The spins per Ni ion measured at 5 K for various Ni dopant levels in fresh/aged powders and sintered pellets. The aged powders are in close agreement to theoretical predicted value of 2.83 Bohr magnetons for high spin Ni$^{2+}$. All powders were measured at NIST.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Spins per Ni</th>
<th>Percent of Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>BaNiO$_{2.1}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BaNiO$_{2.5}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>BaNiO$_{2.0}$</td>
</tr>
<tr>
<td>Powders 900°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 m/o Ni</td>
<td>Fresh</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>1.99</td>
</tr>
<tr>
<td>1.0 m/o Ni</td>
<td>Fresh</td>
<td>1.60</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>2.06</td>
</tr>
<tr>
<td>2.0 m/o Ni</td>
<td>Fresh</td>
<td>1.71</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>1.96</td>
</tr>
<tr>
<td>4.0 m/o Ni</td>
<td>Fresh</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>1.99</td>
</tr>
<tr>
<td>8.0 m/o Ni</td>
<td>Fresh</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>1.36</td>
</tr>
<tr>
<td>Powders 950°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.0 m/o Ni</td>
<td>Fresh</td>
<td>1.30</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>2.01</td>
</tr>
<tr>
<td>8.0 m/o Ni</td>
<td>Fresh</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>Aged</td>
<td>1.25</td>
</tr>
<tr>
<td>Sintered Pellets</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 m/o Ni</td>
<td>NIST</td>
<td>1.08</td>
</tr>
<tr>
<td>1.0 m/o Ni</td>
<td>NIST</td>
<td>0.99</td>
</tr>
<tr>
<td>1.0 m/o Ni</td>
<td>UCSD</td>
<td>1.00</td>
</tr>
<tr>
<td>2.0 m/o Ni</td>
<td>UCSD</td>
<td>1.00</td>
</tr>
</tbody>
</table>
show 1 free spin per Ni ion. This indicates that the sintered pellets contain only Ni$^{3+}$ oxidation state, either as BaNiO$_{2.5}$ phase or Ni$^{3+}$ ions substituted into BZY lattice. The scaled results for DC susceptibility at 5 K from 3 different SQUID instruments all match the same value $1.43 \times 10^{-3}$ emu/Oe/gram-Ni within ± 2% absolute accuracy. This is exactly half the value $2.86 \times 10^{-3}$ emu/Oe/gram-Ni obtained for the aged powder samples with Ni$^{2+}$ d$^8$ high spin state. These results verify that volatilization of nickel is not significant when calcining at 900°C.

Figure 6.6: M(T) curves for pellets sintered at 1600°C for 24 h show very different slopes, particularly for higher Ni dopant concentrations. The data presented for 4.0 molar % Ni and 8.0 molar % Ni cannot be used to quantify excess phases because the pellets melted during sintering.

The crystallite size and lattice parameter results determined by Rietveld refinement are summarized in Table 6.4 for powders calcined at 900°C. The smaller crystallite sizes for Ni doped samples indicates a slower rate of crystal growth that could be expected from the BaNiO$_{2.1}$ phase existing as surface monolayer impeding mass transport. Further increases in Ni result in exsolution of BaNiO$_{2.5}$ phase at the surfaces and should start to enhance growth, as observed by the increased crystallite size with increasing Ni. The lattice parameter of the undoped sample matches literature values reported for BZY15 that is not Ba deficient. All the Ni doped samples have a larger lattice parameter. There is a proportionally sharp increase in lattice parameter with the addition of 0.5 molar % Ni, but as additional Ni is added the lattice parameter remains constant through 4.0 molar % Ni, until a slight increase at 8.0 molar % Ni. The influence due to only a small amount of molar % Ni addition provides more evidence against random Ni ion substitution into BZY lattice for powders calcined at 900°C. The lattice parameter increase at 8.0 molar % Ni expected to be even larger.
given increasing Y/Zr ratio expands bulk lattice, but instead is countered by the matching surface BaNiO$_{2.1}$ monolayer.

Table 6.4: Crystallite size determined by Rietveld refinement using GSAS and results listed are for 900°C-10 hour calcined powders.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Crystallite Size</th>
<th>Lattice parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td>(Å)</td>
</tr>
<tr>
<td>Undoped BZY15</td>
<td>54</td>
<td>4.1238</td>
</tr>
<tr>
<td>0.5 m/o Ni-BZY15</td>
<td>35</td>
<td>4.2098</td>
</tr>
<tr>
<td>1.0 m/o Ni-BZY15</td>
<td>31</td>
<td>4.2082</td>
</tr>
<tr>
<td>2.0 m/o Ni-BZY15</td>
<td>43</td>
<td>4.2087</td>
</tr>
<tr>
<td>4.0 m/o Ni-BZY15</td>
<td>40</td>
<td>4.2081</td>
</tr>
<tr>
<td>8.0 m/o Ni-BZY15</td>
<td>41</td>
<td>4.2103</td>
</tr>
</tbody>
</table>

The 4.0 molar percent Ni doped powders were selectively reduced. Figure 6.7 and Figure 6.8 show TEM micrographs for 4.0 molar % Ni powders reduced in dry hydrogen at 600°C for 30 minutes or 900°C for 5 hours, respectively. There are unique interference fringes that are consistent with excess BaNiO$_{2.5}$ phase surface layer on unreduced 4.0 molar % Ni doped BZY powders shown in Figure 6.9, and the layer diminishes as the extent of reduction increases. The complete M(H) loop run at T=100 K is shown in Figure 6.10. The extent of reduction is 3 % complete at 600°C after 30 minutes and 51 % complete at 900°C after 5 hours. The M(H) loops also show clear differences; the 600°C reduction is a typical super-paramagnetic response while hysteresis is observed in 900°C reduced sample. In Figure 6.7, note the small < 10 nm Ni metal particles randomly distributed and bonded on the surface of the BZY particles visible in the micrograph. In contrast, the 900°C reduced sample does not have either the fringes from excess BaNiO$_{2.5}$ phase nor the < 10 nm Ni metal sizes. Instead, the Ni metal has coarsened to approximately 30-40 nm size particles (Figure 6.8), approximately the size of BZY particles, and the BZY particles are very pristine (Figure 6.9(c)). The corresponding AC susceptibility data for 600°C reduced powders is shown in Figure 6.11 and is consistent with superparamagnetic nickel particles. The maximum of $\chi'$ occurs at the blocking temperature, $T_B$, and is used to calculate the size of metallic Ni$^0$ particle [168]:

$$r_{Ni} = \sqrt[3]{\frac{75 T_B k_B}{4\pi K}}$$  \hspace{1cm} (6.1)

where $k_B$ is the Boltzmann constant, and $K$ is the magnetic anisotropy constant for nickel metal (4.5 x 10$^3$ J/m$^3$)[121]. From the blocking temperature equation, the average particle size is calculated to be 9 nm. The corresponding AC susceptibility data for 900°C reduced powders is also shown in Figure 6.12 and
is consistent with larger ferromagnetic nickel particles. If the metallic Ni particles are single domain, the blocking temperature exceeds 250 K, suggesting the average metallic Ni particle size is greater than 32 nm by applying the same equation. The AC data below 100 K confirms no SP nano-Ni metal particles < 15 nm that would be detectable at a parts per million level. Finally, the AC data below 10 K clearly has a Curie-Weiss paramagnetic signal expected for Ni$^{2+}$ ions and fits roughly half the total Ni content. It is assumed to represent the BaNiO$_{2.1}$ mono-layer that does not reduce to Ni metal. To assist the reader with interpretation of AC susceptibility results, generally $\chi' > 0.1 \text{ emu/Oe/g-Ni metal}$ and $\chi''$ near 10% of peak $\chi'$ signal indicates the metallic particles are within single domain size range. In comparison, multi-domain particles will have $\chi' < 0.05 \text{ emu/Oe/g-Ni metal}$ and small (zero) $\chi''$ values.

Figure 6.7: TEM micrograph showing partially sintered 4.0 molar % Ni-doped BZY15 nano powders reduced at 600°C for 30 minutes having < 10 nm superparamagnetic metallic Ni particles on the surface (circled).

Figure 6.8: TEM micrograph showing partially sintered 4.0 molar % Ni-doped BZY15 nano powders reduced at 900°C for 5 h having > 30 nm ferromagnetic metallic Ni particles on the surface (circled).
Figure 6.9: TEM micrograph showing 4.0 molar % Ni-doped BZY15 (a) as-calcined, (b) after reduction at 600°C for 30 minutes, and (c) after reduction at 900°C for 5 h. The BaNiO$_x$ layer and nodules that are visible in as-calcined powders decreases after reduction at 600°C for 30 minutes, and is completely reduced at 900°C after 5 h leaving pristine crystalline surfaces.

Figure 6.10: Magnetization versus field at T = 100 K for 4.0 molar % Ni powders reduced at 600°C, 30 min or 900°C, 5 hours. The units are emu/g-sample and note the right hand scale (600°C sample) is 1/10th the left hand scale (900°C sample).

The M(H) curve at 100 K for the 600°C reduced powders verifies that all Ni metal particles are < 10 nm, having zero remnant magnetization. By applying a linear Curie-Weiss fit to AC data from 50 to 250 K the average Ni metal size is determined to be 7 nm. The M(H) curve at 100 K for the 900°C reduced sample shows larger remanent magnetization and higher coercive field than bulk Ni metal properties that is consistent with single domain particle size.

6.4 Discussion

Excess BaCO$_3$ is commonly observed in many types of nano-powder synthesis [230], and is believed to be related to large exothermic enthalpy of formation with ideal BaZrO$_3$ perovskite structure [231]. In the ideal
Figure 6.11: AC susceptibility versus temperature curves for 900°C, 5 h reduced 4.0 molar % Ni powders.

Figure 6.12: AC susceptibility versus temperature curves for 600°C, 30 min reduced 4.0 molar % Ni powders.
perovskite structure, Ba fully occupies the A-site of the lattice and Zr fully occupies the B-site. Additions of Y and Ni substitute onto B-sites (Zr) and are accompanied by the formation of oxygen vacancies to account for the difference in charge. The atomic radius of Y is greater than Zr which can cause significant lattice distortions. There is an energy balance between the endothermic incorporation of the larger Y ion on the B-site of lattice and lattice destabilization due to vacancy clustering that can lead to Y to occupy the A-site, leading to the expulsion of Ba from the lattice. Both processes can be managed successfully with the optimal conditions and thermodynamic control. The 900°C calcination temperature is high enough to overcome the activation energy for controlled nucleation of crystalline nano-particles and maintain uniform distribution of Y.

A mechanism is proposed for 900°C, 10h calcined powders in order to explain the results. At lower temperatures, BaNiO$_{2.0}$ phase forms under reducing atmosphere as the char is burning off and is followed by the nucleation of BZY crystalline phase. The 900°C calcination temperature is a key processing parameter needed to produce an ideal structure of uniform Y distribution on B-site and that is not Ba deficient. The final step is the formation of lattice matched surface monolayer BaNiO$_{2.1}$ phase on pristine BZY crystallites. As the BZY crystallites grow during calcination, the drop in total surface area will force excess BaNiO$_{2.1}$ phase to precipitate, forming BaNiO$_{2.5}$ phase nodules bonded to surfaces or between grains. A schematic of this mechanism is shown in Figure 6.13.

The BaNiO$_{2.5}$ phase measured in the fresh powders has entirely Ni$^{3+}$ that has 1 paramagnetic electron per Ni. The aged powders reflect the redox/hydration reaction converting all Ni$^{3+}$ into high spin Ni$^{2+}$ state. A mechanism for the hydration reaction is proposed to show the reduction of Ni$^{3+}$ to Ni$^{2+}$ in BaNiO$_{2.5}$:

$$4H^+ + 4\text{BaNi}^{3+}O_{2.5} + 4e' \rightarrow 4\text{BaNi}^{2+}O_{2.5}H$$

(6.2)

The oxidation reaction is then written:

$$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4e' + 4\text{H}^+$$

(6.3)

The water is introduced by humidity in the environment or absorbed by the gelatin capsule, and then is absorbed onto the surfaces of the powders. The combined redox reaction is then written:

$$2\text{H}_2\text{O} + 4\text{BaNi}^{3+}O_{2.5} \xrightarrow{\text{3 months}} 4\text{BaNi}^{2+}O_{2.5}H + \text{O}_2$$

(6.4)

This hydration reaction results in no change in the diamagnetic BaNiO$_{2.0}$ phase. Instead of BaNiO$_{2.0}$, NiO and BaY$_2$NiO$_5$ are potential sources of low paramagnetic signal and would not hydrate in air; however, the magnetic moment of a Ni$^{2+}$ ion NiO is approximately 0.5 Bohr magnetons [232] and the magnetic moment of a Ni$^{2+}$ ion in Y$_2$BaNiO$_5$ is estimated to be around 0.66 to 1.5 Bohr magnetons. This range of values for Y$_2$BaNiO$_5$ is based upon experimentally measured values for other rare earth nickelates [233, 234]. The
Figure 6.13: Schematic describing the mechanism of excess BaNiO$_x$ phase formation during decomposition of char precursor.
magnetic data presented in this work strongly supports the proposed mechanism of excess BaNiO$_x$ phases.

A model by Straumal et al. is applied in order to validate that the paramagnetic response of Ni$^{2+/3+}$ ions up to 2.0 molar % Ni doped powders exists as a monolayer on the surface [235, 236]. The results are plotted in Figure 6.14 showing the maximum excess BaNiO$_x$ phase that can be initially accommodated on the surface is equal to approximately 5.3 molar % Ni. This value is in good agreement with the interpolated value of 5.5 molar % excess Ni in the 8.0 molar % Ni powder. The true solid solution limit for Ni dopant in BZY is likely dependent on Ba deficiency. The available surface area of 40 nm BZY powders allows 2.0 molar % Ni as lattice matching surface monolayer BaNiO$_{2.1}$ phase. Thus, 4.0 molar % Ni powders are an equal mixture of 50 % BaNiO$_{2.1}$ and 50% BaNiO$_{2.5}$ phases, which is experimentally measured in this work. The initial surface area of the BZY crystallites is a determining factor limiting the total amount BaNiO$_{2.1}$ and BaNiO$_{2.5}$. In the 950°C calcination of 8.0 molar % Ni powder, the interpolated concentration of dopant is 4.7 molar % excess Ni, which is less than the interpolated value for the 900°C calcination. The reduction in excess Ni for the higher calcination temperature must reflect that the initial BZY crystals grew to a larger size and resulted in less surface area for BaNiO$_{2.1}$ phase. This is reasonable given the excess BaCO$_3$ phase observed in the 950°C calcined powders indicates faster kinetics during particle growth and is consistent with higher calcination temperatures.

![Figure 6.14](image-url)

Figure 6.14: A model was applied to determine the molar % Ni that can be accommodated as a monolayer based upon particle size.

The sintering behavior of the 4.0 molar % Ni powder indicates the excess BaNiO$_x$ phase rapidly melts on heating to 1600°C giving the pellet a melted appearance upon cooling. The lower 2.0 molar % Ni requires a
hold at 800°C to convert the hydrated nodules back to BaNiO$_{2.1}$ oxide state. Without this hold, the pellet crumbles into a powder in ambient conditions within days after sintering. Still this work demonstrates it is possible to get low molar % Ni content pellets sintered at 1600°C without loss of Ba or excess barium nickel oxide phases that will hydrate and mechanically degrade.

Future work is needed to confirm BaNiO$_{2.0}$ in the 8.0 molar % samples. The unusual feature casting doubt is that BaNiO$_{2.0}$ phase is not expected to remain stable in oxidizing conditions at 900°C calcination [234]. If future work proves that BaNiO$_{2.0}$ is present, the reason could be that the low temperature, acetate precursor synthesis method imparts exceptional stability. This preparation of BaNiO$_{2.0}$ would provide good sintering aid, rather than just adding excess NiO or BaY$_2$NiO$_5$. Re-oxidation of the 900°C reduced powder should produce non-magnetic NiO phase and enable measurement of paramagnetic BaNiO$_{2.1}$ phase that was not reduced. The reduction of 1.0 molar % Ni powder at 600°C and 900°C can be used to test the extent of Ni metal formed. Finally, synthesis of 5.0 molar % Ni calcined at 900°C for 5 hours and reduced at 600°C for various times is predicted to give smaller BZY particles having 1 to 2 % BaNiO$_{2.5}$ nodules that can be reduced to < 5 nm Ni metal on surface BaNiO$_{2.1}$ monolayer. The initial decrease in lattice parameter as Ni dopant increases could be the substitution of the smaller Ni$^{2+}$ ion on Zr$^{4+}$ sites in the BZY lattice, as predicted by Vegard’s law [237]; however, the constant lattice parameter for higher molar % Ni is more consistent with a surface layer model. To verify the proposed mechanism, in situ XRD on heating the char could identify if pure BaNiO$_{2.0}$ phase formation is complete before BZY starts to crystallize.

6.5 Conclusions

This work demonstrates that SQUID magnetometry is a powerful technique for studying excess Ni$^{2+/3+}$ containing phases in powders and pellets. Calcination for 10 hours in air at 900°C represents the optimum parameters for producing a perovskite core structure that is not barium deficient. The powders contain high spin magnetic phases, either BaNiO$_{2.1}$ or BaNiO$_{2.5}$, based upon the quantitative paramagnetic results measured in fresh powders. A nonmagnetic component in 8.0 molar % Ni powders is consistent with low spin BaNiO$_{2.0}$. The fraction of each phase varies as a function of Ni content and depends upon hydration, observed as changes in magnetic susceptibility of aged powders. Paramagnetic susceptibility at 5 K provides a simple way to quantify the oxidation states of Ni$^{2+/3+}$ ions. A measured value of 1.43 x 10$^{-3}$ emu/Oe/g-Ni for sintered pellets indicates all Ni$^{3+}$ oxidation state (BaNiO$_{2.5}$ phase). In fresh powders, a lattice matching surface monolayer BaNiO$_{2.1}$ covers the pristine BZY particles. As these particles grow during calcination, a drop in total surface area forces BaNiO$_{2.5}$ phase to precipitate as nodules and at grain boundaries. The reduction of BaNiO$_{2.5}$ is studied with the 4.0 molar % sample. TEM and low frequency SQUID based AC susceptibility prove that super-paramagnetic nano-Ni metal is bonded to the surface and has narrowed size
distribution. The partial reduction in 30 minutes at 600°C produces nanocomposite BZY15 core (40 nm) surrounded by a BaNiO$_{2.1}$ shell (monolayer) with ~7 nm metallic Ni$^0$ particles. It is expected that nanopowders having this unique core/shell structure are capable of superb catalytic reactivity. Since surface excess BaNiO$_{2.5}$ phase reduces rapidly in hydrogen, Ni-doped BZY powders containing excess BaNiO$_x$ dopant make excellent catalytic nanocomposite precursors. The results show that nanoscale catalytic design is possible when SQUID magnetometry is used to optimize the Ni-dopant concentration.

6.6 Supplemental Findings

The supplemental findings include additional results that support the story presented above, including ICP-AES of chars and physisorption of 4.0 molar % Ni powders reduced at 600°C for 30 minutes.

6.6.1 ICP-AES Results

The results for char and powder ICP analysis is presented in Table 6.5. The char results demonstrate the target concentrations of Ni are approximately equal to the measured concentrations, with exception of 8.0 molar % Ni, and confirm the synthesis is well-controlled. The char decomposition mass loss was assumed to be approximately 86% in order to calculate the molar % Ni dopant. ICP results for powders calcined at 900°C would provide greater confidence that no Ni is lost in calcination but difficulty preparing fusions precluded analysis.

Table 6.5: Summary of the calculated molar % of Ni dopant in BZY char.

<table>
<thead>
<tr>
<th>Target Ni Dopant</th>
<th>Measured molar % Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>BZY Control</td>
<td>0.00</td>
</tr>
<tr>
<td>0.5 molar %</td>
<td>0.54</td>
</tr>
<tr>
<td>1.0 molar %</td>
<td>1.14</td>
</tr>
<tr>
<td>2.0 molar %</td>
<td>2.14</td>
</tr>
<tr>
<td>4.0 molar %</td>
<td>4.31</td>
</tr>
<tr>
<td>8.0 molar %</td>
<td>9.07</td>
</tr>
</tbody>
</table>

6.6.2 Physisorption Results

The results of nitrogen physisorption measured by the Department of Chemistry at Colorado School of Mines are summarized in Table 6.6. The 4.0 molar % Ni doped BZY powders reduced at 600°C for 30 minutes were measured without making any effort to optimize the results.
Table 6.6: Summary of nitrogen physisorption measurements taken on the 4.0 molar % Ni doped BZY powders reduced at 600°C for 30 minutes.

<table>
<thead>
<tr>
<th></th>
<th>Average of 2 runs</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>BET Surface Area (m$^2$ g$^{-1}$)</td>
<td>25.6183</td>
<td>0.7065</td>
</tr>
<tr>
<td>BJH Adsorption Pore Volume (cm$^3$ g$^{-1}$)</td>
<td>0.1257</td>
<td>0.0092</td>
</tr>
</tbody>
</table>
CHAPTER 7
GENERAL DISCUSSION

This work highlights how an improved understanding of the microstructure can be used in conjunction with processing techniques in order to design nanocomposite materials. Specific discussion of the evolution of metallic Ni\textsuperscript{0} in internally reduced YSZ, the stability and reversibility of the internally reduced microstructure under redox cycling, and the selective reduction in core/shell/surface BZY powders has already been presented in the papers prepared from this work. The purpose of this chapter is to present a general discussion of the significant results obtained from this work and summarize the insights for designing unique microstructures from partial reduction of doped oxides.

7.1 Reduction of Ni-doped YSZ

Unlike many of the ceramic systems previously studied, YSZ is unique because it is an oxygen ion conductor. The existing models for reduction are based upon assumptions that the oxygen ion mobility is very limited and ignore the effects of microstructural features. Also known from previous internal reduction studies, metallic Ni\textsuperscript{0} forms in pre-existing pores and along the grain boundaries, even in the absence of superparamagnetic Ni\textsuperscript{0} particles in the grain interior. APT analysis of pellets containing 0.5 molar percent NiO dopant in 10YSZ was used to confirm there is no Ni\textsuperscript{2+} segregation along the grain boundary in the as-sintered condition. The significance of this result is that Ni\textsuperscript{2+} must diffuse to the grain boundary in order to explain the formation of metallic Ni\textsuperscript{0} particles at this location after reduction; therefore, a systematic study was conducted to describe the stages of the internal reduction in a polycrystalline pellet. Pellets were treated at various reduction temperatures, oxygen partial pressures, and times to quantify the kinetics of reduction and how the microstructural features of a polycrystalline pellet with porosity influence the reduction mechanism.

The internal reduction of polycrystalline Ni-doped YSZ occurs in three stages, each having a unique mechanism and kinetic description. In reducing conditions, oxygen vacancies and electrons diffuse into the pellet due to an electrical potential gradient. The mass transport of elections is reported to occur rapidly along the space charge layer at the grain boundaries. In stage 1, Ni\textsuperscript{2+} ions that decorate pre-existing porosity as a monolayer react with the electrons to form metallic Ni\textsuperscript{0} particles. Large metallic Ni\textsuperscript{0} particles are formed in this reduction reaction step. The introduction of electrons and vacancies creates a electrical potential between the grain boundaries and the grain interior. In stage 2, Ni\textsuperscript{2+} on Zr\textsuperscript{4+} sites adjacent to the grain boundary reacts with electrons and creates vacant zirconium sites. The nucleation at a grain boundary
is favorable over homogeneous nucleation in the grain interior. The vacant zirconium sites also provide a chemical gradient for Ni\(^{2+}\) diffusion to the grain boundaries. It is proposed that the increasing concentration of vacant zirconium sites and oxygen vacancies in the bulk as the oxide approaches equilibrium with the reducing gas create nucleation sites for metallic Ni\(^0\) formation in the grain interior. This results in the formation of superparamagnetic Ni\(^0\) particles that form in a voids scattered throughout the grain interior in stage 3. Further work using STEM mapping and APT is necessary to investigate the nucleation event for the superparamagnetic Ni\(^0\) particles.

The results of the evolution of metallic Ni\(^0\) particles during the reduction of polycrystalline YSZ ultimately show that careful control of microstructure will influence the reduced microstructure. The possibilities to tailor unique microstructures are endless. The stage 1 reaction can be minimized by achieving higher density pellets, or maximized by the addition of pore-formers. The stage 2 reaction kinetics can be increased with cationic species having higher diffusivity than Ni\(^{2+}\). Not only is selective reduction possible to create metal-oxide nanocomposites, but oxidation of the internally reduced microstructure produces highly dispersed, nano-NiO particles in the grain interiors. The redox cycling of internally reduced polycrystalline Ni-doped YSZ reveals that the voids which act as nucleation sites for superparamagnetic Ni\(^0\) particles are stable at the redox conditions used in this work. The metallic Ni\(^0\) oxidizes but does not dissolve back into the 10YSZ lattice. Further redox cycling alternates between a metal-oxide and oxide-oxide nanocomposite, enabling further microstructural manipulation and design.

### 7.2 Reduction of Ni-doped BZY

The internal reduction studies can be applied to new ceramic systems. Protonic conducting materials offer unique mass transport behavior and superior coking resistance over YSZ, therefore, are heavily investigated for a variety of electrochemical applications. A major challenge when using BZY for applications is that processing is difficult, often requiring transition metal dopant sintering aids, but still the powders are prone to hydration that degrades the mechanical integrity. Powders and pellets of BZY15 having 0 to 8.0 molar percent NiO dopant were prepared using high purity chemical synthesis in order to quantify the solubility limit of NiO dopant. For the first time, SQUID magnetometry was used to quantify the distribution of Ni\(^{2+/3+}\) ions in the perovskite structure. The results show that Ni dopant is incorporated into BZY powders as excess barium nickel, BaNiO\(_x\). Upon sintering of these powders, the excess phase at grain boundaries is entirely BaNiO\(_{2.5}\). By careful processing and selective reduction it is possible to take advantage of the core/shell/surface to design nanocomposite powders. This work provides greater insight to the mechanism by which NiO dopant acts as a sintering aid in BZY, since BaNiO\(_{2.5}\) is a low melt phase but is also prone to hydration. This work highlights the importance of optimizing the dopant concentration when Ni is added.
as a sintering aid to prevent degradation of anodes.
This work demonstrates that internal reduction of polycrystalline Ni-doped YSZ is influenced by microstructural features. Polycrystalline pellets containing approximately 5% porosity were synthesized. A custom built furnace was assembled to perform all of the reduction experiments, equipped with control and monitoring devices recording temperature, $P_{O_2}$, and humidity. In general, higher temperatures increase mass transport and result in a faster reaction rate. A lower oxygen partial pressure increases the thermodynamic driving force for the reduction reaction. Humidity effectively increases the oxygen partial pressure, thus decreases the chemical gradient driving the reaction. The mechanism for internal reduction depends upon microstructural features that act to lower the nucleation energy need to form metallic Ni$^0$ and have space charge effects that influence mass transport. The results support that the Ni$^{2+}$ ions must substitute on Zr$^{4+}$ sites, since Ni$^{2+}$ segregation was not observed in APT analysis of as-sintered pellets.

The internal reduction reaction occurs in three stages. A geometric model is presented to describes the stage 1 reduction kinetics, and account for the extra time and flux of reactant species needed to fill pre-existing pores. The last stage two stages of reduction are dependent on diffusion of Ni$^{2+}$ ions to nucleation sites and sinks. A counter flux of oxygen vacancies and vacant zirconium sites results in order to maintain charge neutrality, and provides the nucleation sites for stage 3 reduction in the grain interior. Internal reduction of polycrystalline Ni-doped YSZ results in a complex microstructure with a large size distribution of metallic Ni$^0$ particles. The size of particles is unique to the microstructural features where metallic Ni$^0$ forms. The reduced microstructure contains a combination of > 100 nm Ni$^0$ particles in pre-existing pores, 20 - 50 nm Ni$^0$ particles along the grain boundary, and < 20 nm Ni$^0$ particles in the grain interiors. A particle free zone is observed adjacent to the grain boundary region that is explained by space charge effects. Diffusion due to electrical potential must be considered in internal reduction studies. Redox cycling of internally reduced pellets shows that the internally reduced microstructure is stable under the chosen oxidation conditions, but the < 20 nm metallic Ni$^0$ particles convert to < 20 nm NiO particles.

This work also provides greater insight to the distribution of Ni-dopant in BZY15 powders and pellets. In powders, the Ni exists as excess BaNiO$_x$, where the stoichiometry depends upon the particle size and Ni content. This work identifies the ideal calcination temperature of 900°C which enables synthesis of powders having a stoichiometric BZY core and BaNiO$_{2.1}$ shell structure with optimized Ni content up to 2.0 molar percent. Higher concentrations of Ni content result in the formation of BaNiO$_{2.5}$ nodules that are selectively reduced to prepare catalysts having Ni bonded to the core/shell powder. In sintered pellets, the Ni exists
entirely as \( \text{Ni}^{3+} \) either substituted on \( \text{Zr}^{4+} \) sites or as excess \( \text{BaNiO}_{2.5} \) at grain boundaries. An improved understanding of the distribution of Ni-dopant in BZY15 provide a foundation for future reduction studies of BZY15 pellets.
CHAPTER 9
RECOMMENDATIONS FOR FUTURE WORK

Additional reduction times in smaller time increments at each temperature used in this study are recommended to improve the kinetic models describing the reduction reaction and quantify activation energies associated with each step. The geometric model presented in this work only applies to stage 1 reduction and can only be used to correlate the magnetometry data to the extent of the reduction reaction. Smaller time increments between stage 2 and 3 reduction could also provide valuable insight to the nucleation event leading to the formation of metallic Ni\textsuperscript{0} particles in voids. This research does not adequately investigate the nucleation event leading up to stage 3 reduction. The majority of APT analysis in this work was focused on grain boundary chemistry, versus bulk grain chemistry during the reduction reaction. It is unclear if the nucleation event is triggered by clustering of vacancies and/or a critical nucleus of Ni\textsuperscript{2+} ions.

Further analysis of the grain boundaries using APT is suggested to model the space charge layer in Ni-doped YSZ. Since the reduction of Ni-doped YSZ is an electrochemical reaction, performing reductions under and applied bias or measuring the conductivity during the reduction reaction could also provide greater insight to how charged species diffuse along grain boundaries during the reaction. The use of single crystal Ni-doped YSZ species is suggested to study how charged species diffusion through the bulk of the grain interiors.

The internal reduction behavior of Co-doped YSZ and Fe-doped YSZ is recommended as a follow-up to this study. Preliminary experiments show that Co-doped YSZ results in Co\textsuperscript{0} particles, however, Fe-doped YSZ showed no metallic Fe\textsuperscript{0} even after 120 h reduction in 2% H\textsubscript{2}. This outcome is supported by the Ellingham diagram which shows iron has more stable redox behavior than cobalt, which has greater redox stability over nickel.

Internal reduction studies of Ni-doped BZY could be interesting since the majority defects are quite different from YSZ. Before internal reduction studies are performed, detailed chemical analysis of BZY15 powders and pellets using techniques like EXAFS, chemical mapping in STEM, or APT is recommended to supplement the magnetometry findings presented in this work.
REFERENCES CITED


W. Kobsiriphat, B. D. Madsen, Y. Wang, L. D. Marks, and S. A. Barnett. $La_{0.8}Sr_{0.2}Cr_{1-x}Ru_xO_3-\delta$ - $Gd_{0.1}Ce_{0.9}O_{1.95}$ solid oxide fuel cell anodes: Ru precipitation and electrochemical performance. *Solid State Ionics*, 180(2-3):257–264, March 2009.


APPENDIX A - GAS MIXTURE CALCULATIONS

Representative Mathematica code used to perform calculations to determine hydrogen compositions to maintain oxygen partial pressure across a range of temperatures.

dH = -241830;

dS = -44.34;

dG = -228610;

R = 8.3145;

n = 2;

F = 96485.5;

Keq[T_] = \[E^\wedge{(dH/(R*(T + 273.15)) - dS/R)}\];

pH2c[pH2O_, pO2_, T_] = Log[10, 10^\wedge{pH2O/(10^\wedge{(pO2/2)Keq[T]})}];

pO2c[pH2O_, pH2_, T_] = Log[10, 10^\wedge{(2pH2O)/(10^\wedge{(2pH2)Keq[T]^2})}];

pH2Oc[pH2_, pO2_, T_] = Log[10, 10^\wedge{pH210^\wedge{(pO2/2)Keq[T]}}];

pO2c[{-3.49, -1.7, 900}]

pO2c[{-3.49, -2, 900}]
pO2c[−3.49, −2.74, 900]

pO2c[−3.49, −2.74, 900]

−20.4824

−19.8824

−18.4024

−16.4824

pO2c[−3.49, −2.54, 900]
\[-18.8024\]

\[10^\wedge - 18.8024\]

\[1.57616 \times 10^\wedge - 19\]

\[\text{pO}_2c[-3.49, -3.54, 800]\]

\[-18.8091\]

\[10^\wedge - 18.8091\]

\[1.55203 \times 10^\wedge - 19\]
APPENDIX B - GAS CALIBRATION FACTOR

The properties for mono atomic Ar and diatomic H₂, O₂, and N₂ gases are presented in Table B.1. The molecular structure factor, $s_n$ is 1.030 for mono atomic gases and 1.000 for diatomic gases. Three compositions of gas are used in this work and the calculations of GCF are shown.

Table B.1: Thermal gas properties for mass flow controller gas GCF calculations.

<table>
<thead>
<tr>
<th>Gas Type</th>
<th>Specific Heat, $c_{pn}$ (cal/gdeg C)</th>
<th>Density at 0deg C, $d_n$ (g/L)</th>
<th>Conversion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon, Ar</td>
<td>0.1244</td>
<td>1.782</td>
<td>1.39</td>
</tr>
<tr>
<td>Hydrogen, H₂</td>
<td>3.419</td>
<td>0.0899</td>
<td>1.01</td>
</tr>
<tr>
<td>Nitrogen, N₂</td>
<td>0.2485</td>
<td>1.250</td>
<td>1.00</td>
</tr>
<tr>
<td>Oxygen, O₂</td>
<td>0.2193</td>
<td>1.427</td>
<td>0.993</td>
</tr>
</tbody>
</table>

2 % H₂ - 98 % Ar

$$GFC_{2\%H_2,Ar} = \frac{0.3106 (0.02 \times 1.000 + 0.98 \times 1.030)}{0.02 \times 0.0899 \times 3.419 + 0.98 \times 1.782 \times 0.1244} = 1.4312 \quad (B.1)$$

1 % H₂ - 99 % N₂

$$GFC_{1\%H_2,N_2} = \frac{0.3106 (0.01 \times 1.000 + 0.99 \times 1.000)}{0.01 \times 0.0899 \times 3.419 + 0.99 \times 1.250 \times 0.2485} = 1.000 \quad (B.2)$$

21 % O₂ - 79 % Ar

$$GFCF = \frac{0.3106 (0.21 \times 1.000 + 0.79 \times 1.030)}{0.21 \times 1.427 \times 0.2193 + 0.79 \times 1.782 \times 0.1244} = 1.3202 \quad (B.3)$$

Conversion for 1 % H₂ - 99 % N₂ from 2 % H₂ - 98 % Ar

$$\frac{GFC_{1\%H_2,N_2}}{GFC_{2\%H_2,Ar}} = \frac{1.000}{1.4312} = 0.69871 \quad (B.4)$$

Conversion for 21 % O₂ - 79 % Ar from 2 % H₂ - 98 % Ar

$$\frac{GFC_{21\%O_2,Ar}}{GFC_{2\%H_2,Ar}} = \frac{1.3202}{1.4312} = 0.92242 \quad (B.5)$$
The following examples give sequences which are useful to obtain magnetic susceptibility measurements for this work.

C.1 MH Curve, DC Susceptibility

Set Temperature 100.000K at -10.000K/min.

Wait for Temp: Stable Delay: 60 secs

Set Magnetic Field 10000.00 Oe, No Overshoot, Hi Res Enabled

Wait for Temp: Stable Field: Stable Delay: 15 secs

Scan Field from 10000.00 Oe to 2000.00 Oe in -1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled

Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track: Yes, raw: No, diag: No

End Scan

Scan Field from 1000.00 Oe to 100.00 Oe in -100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled

Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track: Yes, raw: No, diag: No

End Scan

Scan Field from 50.00 Oe to -50.00 Oe in -50.00 Oe increments (3 steps), No Overshoot, Hi Res Enabled

Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track: Yes, raw: No, diag: No

End Scan

Scan Field from -100.00 Oe to -1000.00 Oe in -100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled

Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track: Yes, raw: No, diag: No
End Scan
Scan Field from -2000.00 Oe to -10000.00 Oe in -1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -10000.00 Oe to -2000.00 Oe in 1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -1000.00 Oe to -100.00 Oe in 100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -50.00 Oe to 50.00 Oe in 50.00 Oe increments (3 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from 100.00 Oe to 1000.00 Oe in 100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from 2000.00 Oe to 10000.00 Oe in 1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Set Temperature 35.000K at 10.000K/min.
Set Magnetic Field 0.00 Oe, No Overshoot, Hi Res Enabled
End Sequence

C.2 MT Curve, DC Susceptibility

Set Temperature 100.000K at -10.000K/min.
Waitfor Temp:Stable Delay:60secs
Set Magnetic Field 10000.00 Oe, No Overshoot, Hi Res Enabled
Waitfor Temp:Stable Field:Stable Delay:15secs
Scan Field from 10000.00 Oe to 2000.00 Oe in -1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from 1000.00 Oe to 100.00 Oe in -100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from 50.00 Oe to -50.00 Oe in -50.00 Oe increments (3 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -100.00 Oe to -1000.00 Oe in -100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -2000.00Oe to -10000.00 Oe in -1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -10000.00Oe to -2000.00 Oe in 1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -1000.00Oe to -100.00 Oe in 100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from -50.00Oe to 50.00 Oe in 50.00 Oe increments (3 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from 100.00Oe to 1000.00 Oe in 100.00 Oe increments (10 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Scan Field from 2000.00Oe to 10000.00 Oe in 1000.00 Oe increments (9 steps), No Overshoot, Hi Res Enabled
Multi-Measure 3x Measure DC: 6.00 cm, 60 pts, 1 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:No, diag:No
End Scan
Set Temperature 35.000K at 10.000K/min.
Set Magnetic Field 0.00 Oe, No Overshoot, Hi Res Enabled
End Sequence

C.3 AC Susceptibility

Set Cal Factor: Temp: Low Temp 4.230
Set Cal Factor: Temp: Fill Temp 3.950
Wait for Delay: 100secs
Measure DC: 4.00 cm, 41 pts, 3 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:Yes, diag:Yes
Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, diag:Yes, raw:No
Scan Temp from 100.0K to 10.00K at 2.000K/min in -5K increments (19 steps) Settle
Wait for Temp: Stable Delay: 20secs
Measure DC: 4.00 cm, 41 pts, 3 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:Yes, diag:Yes
Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, diag:Yes, raw:No
End Scan
Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, diag:Yes, raw:No
Scan Temp from 9.000K to 2.000K at 0.500K/min in -1K increments (8 steps) Settle
Wait for Temp: Stable Delay: 20secs
Measure DC: 4.00 cm, 41 pts, 3 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:Yes, diag:Yes
Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, diag:Yes, raw:No
End Scan
Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, diag:Yes, raw:No
Scan Temp from 6.000K to 50.00K at 1.000K/min in 1K increments (45 steps) Settle
Wait for Temp: Stable Delay: 20secs
Measure DC: 4.00 cm, 41 pts, 3 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:Yes, diag:Yes

Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, 
    diag:Yes, raw:No

End Scan

Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, 
    diag:Yes, raw:No

Scan Temp from 55.00K to 90.00K at 5.000K/min in 5K increments (8 steps) Settle

Wait for Temp: Stable Delay: 20 secs

Measure DC: 4.00 cm, 41 pts, 3 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:Yes, diag:Yes

Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, 
    diag:Yes, raw:No

End Scan

Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, 
    diag:Yes, raw:No

Scan Temp from 90.00K to 250.0K at 1.000K/min in 2K increments (81 steps) Settle

Wait for Temp: Stable Delay: 20 secs

Measure DC: 4.00 cm, 41 pts, 3 scans, AutoRng, Long, Iterative Reg., track:Yes, raw:Yes, diag:Yes

Measure AC: 1.0000 Oe, 7.098 Hz, 2 meas, 2 blks, 1E-006 Null, x 1, 0 s, AutoRng, track:Yes, 
    diag:Yes, raw:No

End Scan

Set Temperature 35.000K at 10.000K/min.

Set Magnetic Field 0.00 Oe, Oscillate, Hi Res Enabled

End Sequence
APPENDIX D - ATOM PROBE TOMOGRAPHY DATA

This appendix presents all APT reconstructions of various NiO-doped 10YSZ. Table D.1 summarizes the NiO-doped 10YSZ specimen and associated runs.

Table D.1: Summary of NiO-doped 10YSZ specimens and run number. (X) indicates that the tip was liberated during the run.

<table>
<thead>
<tr>
<th>Grid</th>
<th>Specimen Condition</th>
<th>Run Numbers</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>Dry Reduced at 1000°C for 20 h</td>
<td>2706, 2707, 2708, &amp; 2709</td>
</tr>
<tr>
<td>E</td>
<td>Wet Reduced at 1000°C for 50 h</td>
<td>2357(X), 2417, 2710, 2747, 2748, 2749, &amp; 2750</td>
</tr>
<tr>
<td>F</td>
<td>As-sintered</td>
<td>2355(X), 2356(X), 2388, 2389, 2390, &amp; 2391</td>
</tr>
<tr>
<td>I</td>
<td>As-sintered</td>
<td>2741, 2742(X), 2744, 2745, &amp; 2746</td>
</tr>
<tr>
<td>O</td>
<td>Dry Reduced at 1000°C for 25 h</td>
<td>2857, 2858, &amp; 2859</td>
</tr>
</tbody>
</table>