INVESTIGATIONS IN THE MECHANISM OF CARBOThERMAl REDUCTION OF
YTTRIA STABILIZED ZIRCONIA FOR ULTRA-HIGH TEMPERATURE
CERAMICS APPLICATION AND ITS INFLUENCE ON
YTTRIA CONTAINED IN IT

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Zirconium carbide (ZrC) is a high modulus ceramic with an ultra-high melting temperature and, consequently, is capable of withstanding extreme environments. Carbon-carbon composites (CCCs) are important structural materials in current commercial and future hypersonic aircraft; however, these materials may be susceptible to degradation when exposed to elevated temperatures during extreme velocities. At speeds of exceeding Mach 5, intense heating of leading edges of the aircraft triggers rapid oxidation of carbon in CCCs resulting in degradation of the structure and probable failure. Environmental/thermal barrier coatings (EBC/TBC) are employed to protect airfoil structures from extreme conditions. Yttria stabilized zirconia (YSZ) is a well-known EBC/TBC material currently used to protect metallic turbine blades and other aerospace structures. In this work, 3 mol% YSZ has been studied as a potential EBC/TBC on CCCs. However, YSZ is an oxygen conductor and may not sufficiently slow the oxidation of the underlying CCC. Under appropriate conditions, ZrC can form at the interface between CCC and YSZ. Because ZrC is a poor oxygen ion conductor in addition to its stability at high temperatures, it can reduce the oxygen transport to the CCC and thus increase the service lifetime of the structure.

This dissertation investigates the thermodynamics and kinetics of the YSZ/ZrC/CCC system and the resulting structural changes across multiple size scales. A series of experiments were conducted to understand the mechanisms and species involved in the carbothermal reduction of ZrO$_2$ to form ZrC. 3 mol% YSZ and graphite powders were uniaxially pressed into
pellets and reacted in a graphite (C) furnace. Rietveld x-ray diffraction phase quantification determined that greater fractions of ZrC were formed when carbon was the majority mobile species. These results were validated by modeling the process thermochemically and were confirmed with additional experiments. Measurements were conducted to examine the effect of carbothermal reduction on the bond lengths in YSZ and ZrC. Subsequent extended x-ray absorption fine structure (EXAFS) measurements and calculations showed Zr-O, Zr-C and Zr-Zr bond lengths to be unchanged after carbothermal reduction. Energy dispersive spectroscopy (EDS) line scan and mapping were carried out on carbothermaly reduced 3 mol% YSZ and 10 mol% YSZ powders. Results revealed Y$_2$O$_3$ stabilizer forming agglomerates with a very low solubility in ZrC.
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CHAPTER 1
INTRODUCTION

Today we live in the hypersonic age where aircraft hope to achieve speeds beyond Mach 5 (3,840 mph). These increasing speeds present challenges to every aspect of aerospace design from engine (power) to controls (response) to materials (light weight, high strength). Carbon-carbon composites (CCC) are important materials due to their light weight properties and good strength at temperatures of up to 1350 °C [1]. Due to these reasons, modern hypersonic aircrafts employ CCCs for their essential structural components such as, leading wing edges and nose cones [1]. As these planes travel at hypersonic speeds of Mach 5 and above [2]) they undergo aerothermal heating due to air resistance. The heating causes the temperature of the outer skin of the plane to approach 2000 °C [3] triggering the rapid oxidation of the carbon in CCC and formation of CO and CO₂ gases. This results in the loss of structural material and ultimately the failure of the plane.

Thermal barrier coatings (TBC)/environmental barrier coatings (EBC) are widely used to protect underlying substrate(s) in such harsh conditions. Yttria stabilized zirconia (YSZ) is one such important EBC material used popularly for protecting turbine blades [4] due to its versatile thermo-mechanical properties [5]. In a novel approach, 3 mol% YSZ is planned to be deposited as a protective coating on carbon-carbon composites (CCC), fig. 1.1. As temperatures exceed 1657 °C, the CCC and YSZ react (equation 1.1) to form zirconium carbide (ZrC) [6] at the CCC/YSZ interface. The ZrC formed may grow into the YSZ coating as the carbon is the mobile species. The novelty of this approach lies in the fact that since ZrC is a slower oxygen conductor and is less thermally conductive (20.5 W/m·°C at 20 °C) [7] than YSZ (2 W/m·°C at 20 °C), the performance of the protective coating will improve as it spends more time at elevated
temperatures. Because ZrC has a similar coefficient of thermal expansion to that of CCCs, it reduces the chance of coating failure during thermal cycling.

\[ \text{ZrO}_2 + 3\text{C} \rightarrow \text{ZrC} + 2\text{CO} \]  \hspace{1cm} \text{(1.1)}

Figure 1.1 Image showing proposed plan of depositing 3 mol\% YSZ (blue) on CCCs (black) and formation of ZrC (red) at the interface between YSZ and CCC during in service use of this adaptive coating.

An essential component of the above mentioned approach is the mechanism of carbothermal reduction, i.e., how ZrO\(_2\) to ZrC conversion occurs. The formation of ZrC (15.88 cc/mole) from ZrO\(_2\) (21.04 cc/mole) by carbonaceous (C or CO) species has been the subject of a number of investigations [8-14]. This information about the nature of dominant species driving this reaction is important as it would help control the amount of carbide formation at the interface and its influence on coating performance. Chapter 2 of the dissertation details current understanding of the mechanism of carbothermal reduction of zirconia from a theoretical and an experimental perspective.

Kinetics of ZrO\(_2\) to ZrC conversion is highly dependent upon the activity of the carburizing species. The direct relation of these parameters is of prime importance to identify the dominating species causing this transformation. Under actual service conditions, the activity of carburizing species would change according to the altitude of hypersonic flight and the temperature achieved by aerothermal heating. Chapter 3 is devoted to understanding the
influence of two carburizing species, C and CO, by thermochemical modeling of the system using FactSage software [15].

3 mol% YSZ powders primarily exhibits a tetragonal crystal structure with some monoclinic phase depending upon the processing temperature, fig. 1.2, and lattice parameters of 3.64 Å × 5.27 Å. ZrC (Rocksalt crystal structure) has a lattice parameter of 4.69 Å. Therefore, due to a difference in crystal structure, lattice parameter and density mismatch, inherent strains could arise at the atomic level in the matrix. In our application, formation of ZrC in the YSZ lattice presents a unique problem that can influence the stability of the deposited coating during its service. X-ray absorption spectroscopy (XAS) was utilized to probe this phenomenon at the atomic level. The XAS results and analysis are presented in Chapter 4.

![3 mol% YSZ XRD scan showing tetragonal and monoclinic phases](image)

Figure 1.2 XRD scan of 3 mol% YSZ powder showing primarily tetragonal zirconia with some monoclinic phase.

Zirconia is seldom used without a stabilizer like CeO₂, MgO, CaO and Y₂O₃ for engineering applications [16,17]. The additions of these binary compounds help stabilize the
high temperature phases of ZrO₂, tetragonal and cubic, at ambient temperature. Yttria stabilized zirconia (YSZ) is employed in many current use ranging from biomedical to engineering applications [4,18-24]. Carbothermal reduction of 3 mol% YSZ converts the ZrO₂ into ZrC, but the eventual disposition of the Y₂O₃ present in the ZrO₂ lattice after ZrC formation is unknown. Energy dispersive spectroscopy (EDS) and transmission electron microscopy (TEM) have employed to determine what happens to the yttrium as a result of ZrC formation. These novel findings are discussed in Chapter 5.

This PhD work focuses on various aspects of carbothermal reduction of yttria stabilized zirconia ranging from the mechanism of this reaction to its impact on the bond lengths of the parent oxide and the formed carbide. In addition, I have studied the effects of carbothermal reduction on on a zirconia stabilizer. These results strongly suggest a potential future application of 3 mol% YSZ as EBC on CCCs used in hypersonic airplanes. This dissertation seeks to help further advance the human endeavor for faster and reliable air travel by understanding various aspects of an EBC coating in the high temperature regime with potential incorporation.
CHAPTER 2
CHARACTERIZATION AND MATERIAL PREPARATION TECHNIQUES

2.1 Introduction

Various characterization procedures have been utilized in this dissertation to analyze material properties and the related phenomena. This also includes sample preparation methods like Focused Ion Beam (FIB) lift out processes to prepare samples for Transmission Electron Microscopy (TEM) studies. The characterization methods used in my investigations include x-ray diffraction (XRD) with Rietveld phase quantification, extended x-ray absorption fine structure (EXAFS) methods for measuring bond lengths and relative atomic positions, scanning transmission electron microscopy (STEM), and energy dispersive spectroscopy (EDS) for acquiring images and conducting chemical analyses.

2.2 Rietveld Phase Quantification Technique

2.2.1 Introduction

The Rietveld method of refinement was first discussed by H.M. Rietveld in 1966 [25] when he discussed the x-ray and neutron diffraction pattern refinement for alkaline earth metal uranates. The method of refinement relates to the adjustment of parameters used for fitting the computational model to the experimental results. The proper mathematical framework for this was not realized until an article on refinement of neutron diffraction pattern for nuclear and magnetic structures was published [26]. Although initially applied only for the refinement of neutron diffraction patterns, it was soon successfully extended to the x-ray diffraction.
One of the major strengths of the Rietveld refinement over other techniques is the use of actual experimental intensity values for carrying out calculations rather than the use of integrated intensities [27]. The systems with multiple overlapping peaks can also be refined with this technique. Currently, this technique is heavily used to carry out phase quantification of a multiphase mixture.

2.2.2 Fundamentals

First step to Rietveld refinement is to build a single phase using its corresponding crystallographic information. This information includes—type of crystal, occupation number, oxidation state of atoms, atomic coordinates, symmetry points, values of isotropic factors and anisotropic temperature [28]. Equation 2.1 shows the mathematical framework given by Rietveld et al.[26] that employs these values. The model building step is then followed by a least square fit to the actual experimental pattern. This is continued in cycles until a desired fit with satisfactory model parameter values are obtained. Since this approach uses crystallographic inputs thus overlapping peaks in the system are also resolved and refined.

\[ y_i(2\theta) = t S_k^2 J_k L_k \frac{2\ln 2}{H_k \sqrt{\pi}} \times \exp\left[-4 \ln 2 \left(\frac{2\theta_i - 2\theta_k}{H_k}\right)^2\right] \times \{1 - P(2\theta_i - 2\theta_k)^2 \times \frac{s}{\tan \theta_k}\} \]  \hspace{1cm} (2.1)

where,

\[ t = \text{step width of the counter}, \]

\[ S_k^2 = \text{square of the square of the structure factor}, \]

\[ J_k = \text{multiplicity factor for a particular reflection}, \]

\[ L_k = \text{Lorentzian factor}, \]
$2\theta_k$ = angular position corresponding to the calculated Bragg peak and corrected for the zero-point shift of the counter,

$H_k$ = Full width at half maximum,

$\theta_k$ = Bragg angle for the $k$th reflection,

$\exp[-4 \ln 2 \left(\frac{2\theta_i - 2\theta_k}{H_k}\right)^2] = $ Gaussian peak shape function but other functions like Lorentzian can also be used,

$P$ = Asymmetry parameter due to a number of issues like sample sizes and slit sizes so used, and

$s = +1, 0$ or $-1$ depending on whether $(\theta_i - \theta_k)$ is positive, zero, or negative respectively.

2.2.2.1 Full Width and Half Maximum Function

Caglioti et al. [29] gave the formula (equation 2.2) that describes the relation between Bragg angle, $\theta_k$, and halfwidth ($H_k$) of the corresponding diffraction peak. This relation also takes care of the peak broadening effects that occur due to particle and slit size effects. $U$, $V$, and $W$ are the halfwidth parameters.

$$H_k^2 = U \tan^2 \theta_k + V \tan \theta_k + W$$ (2.2)

2.2.3 Method of Calculation

Least squares refinement method relies on minimization of the square of the difference between observed values and scaled calculated values. These are carried out by computer programs where an initial starting value is given by the user for the first refinement cycle and subsequently refined after every fitting cycle.
Equation 2.3 shows a function, let say $M$, minimized during Rietveld refinement. This process is carried out for the full diffraction pattern [26].

$$M = \sum_i w_i (y_i^{\text{observed}} - \frac{1}{c} y_i^{\text{calculated}})^2$$

(2.3)

where $c$ = overall scale factor such that $y^{\text{calculated}} = c \cdot y^{\text{observed}}$, and

$$w_{i,k} = t_{J_{k}} \frac{2\sqrt{\ln 2}}{H_k \sqrt{\pi}} \times \exp\left[-4 \ln 2 \left(\frac{2\theta_i - 2\theta_k}{H_k}\right)^2\right] \times \left\{1 - P(2\theta_i - 2\theta_k)^2 \times s / \tan \theta_k\right\}$$

Following are the list of parameters refined during the fitting process,

$U, V, W = \text{halfwidth parameters,}$

$Z = \text{counter zero point}$

$A, B, C, D, E, F = \text{cell parameters according to } 1/d^2 = Ah^2 + Bk^2 + Cl^2 + Dkl + Ehl + Fhk$

$P = \text{asymmetry parameter}$

$c = \text{overall scale factor}$

$Q = \text{overall isotropic temperature parameter}$

$x_i, y_i, z_i = \text{co-ordinates of the } i\text{th atom}$

$B_i = \text{atomic isotropic temperature parameter,}$

$n_i = \text{occupation number}$
2.2.4 Phase Quantification

Hill et al. [30] describes the process of phase quantification using the Rietveld refinement approach in considerable detail. Equation 2.1 can be re-written as equation 2.4 with \( y_i \) (calculated) being the contribution of a particular peak (occurring at \( 2\theta_i \)) to the overall spectra,

\[
y_i \text{ (calculated)} = S \times J_k \times L_k \times S_k^2 \times G_{ik}
\]

2.4

where,

\( G_{ik} = \) normalized Gaussian profile function, but other functions like the Lorentzian can also be used

\[
S = (\rho' N_c^2 \nu / \rho) C = m/(Z M V) C = \text{scaling factor obtained from Rietveld analysis. It is used to match the } y_i \text{ (calculated) values to those of } y_i \text{ (observed) values}
\]

\[
C \text{ (constant)} = (f_o \lambda^3 h w t) / (8 / \pi r^2)
\]

\( f_o = \) x-ray flux,

\( \lambda = \) x-ray wavelength,

\( r = \) specimen-to-counter distance,

\( h, w, t = \) aperture height and width and the counting time,

\( \rho', \rho = \) the actual and theoretical densities,

\( \nu = \) specimen volume,

\( N = \) is the number of unit cells per unit volume.
$\rho'v = m$ = mass of a phase present in the sample

$\rho'v = ZM$, where $M$ is the mass per formula unit of a phase, and $Z$ is the number of formula units per unit cell.

This mathematical approach gives the relative amount of a particular phase in the material by utilizing Rietveld refinement strategy for phase quantification. The results are in terms of individual weight fractions of the phases. To determine actual amounts of a phase, an internal standard with known weight is mixed with the sample [30].

A correction factor was introduced by Rietveld [26] to account for preferred orientation, but the March function [31], being correctly normalized, does a better job for Rietveld phase quantification analysis on samples with preferred orientation. Detailed discussions of the Rietveld technique and its applications can be found in a number of references [32-34].

2.3 Extended X-ray Absorption Fine Structure (EXAFS)

2.3.1 Introduction

EXAFS was first explored as a characterization method in the 1930’s after Kronig published an article titled “Quantum Mechanics Calculations for Electrons in Crystal Lattices” [35,36]. These findings were later advanced by Sayers, Stern and Lytle in the early 1970’s, and led to the establishment of this technique for structural findings [37]. Over the years, high energy synchrotron radiation facilities have also greatly contributed to the improvement in quality of EXAFS data acquisition. Many science and engineering fields utilize it to understand structure-property relationships for various material systems. This technique is especially useful in
systems where diffraction measurements cannot be carried out e.g. liquids, solutions, polymers, and amorphous materials.

2.3.2 Fundamentals

2.3.2.1 Characteristic X-rays

X-ray radiation is produced as a result of sudden slowing down of fast moving electrons. In a laboratory XRD, electrons are produced by thermionic emission from a heated filament. These emitted electrons are then accelerated by an external electrical potential from a cathode. When these fast moving electrons hit the surface of a target material, x-rays are produced that can then be used for carrying out diffraction experiments. The energy of these x-rays depend upon the accelerating voltage. When this applied voltage reaches a critical value, the accelerated electrons can knock out electrons from the inner atomic shells of the target material leading to the formation of a vacancy or a hole in that shell. Electrons from the outer shells of the atom can then drop down into the empty orbital filling the hole so as to maintain minimum electron energy configuration. As a result of this process, the descending electron loses energy and produces x-rays which are known as the characteristic lines or x-rays, fig. 2.1. These appear as sharp spikes on the x-ray emission spectra of the target material. The energies of these characteristic x-rays depends upon the energy difference between the two shells involved in the process and have a corresponding fixed value, fig. 2.2. The characteristic x-rays are labeled as $K_\alpha$, $K_\beta$, $K_\gamma$ in increasing energy order. The labeling is based on the shell (K, L, M……) to which electrons transition and the shell from which they start (L, M, N……). Similarly L series would be termed for electrons dropping down from higher shells into unoccupied L shell. $\alpha$, $\beta$ and $\gamma$ subscripts relate to the energy of the x-rays emitted in decreasing order respectively which
is directly related to the energy difference between the shell containing hole and the shell descending electron. These characteristic x-rays are used in the laboratory XRD where we need a fixed energy x-ray while EXAFS needs a range of x-ray energies [38].

Figure 2.1 X-rays with enough energy can knock out an electron from an inner shell (1); An outer shell electron replaces it (2); and subsequently releases an x-ray with a known energy (3) [39].
2.3.2.2 Photoelectric Effect

The photoelectric effect, discovered by Albert Einstein, involves the ejection of an electron (i.e., photoelectron) from an atom as it absorbs a photon. The maximum kinetic energy of this photoelectron upon emission from a material is given as follows,

\[ \text{K.E.} = \frac{1}{2} m v^2 = E - E_0 \]  \hspace{1cm} (2.5)

where,

\( E = h\nu = \text{quantized energy of the incident photon}, \) and

\( E_0 = e\phi = \text{threshold energy with } \phi \text{ being the work function}. \)

Using de Broglie relation, \( \lambda = h/mv \), wave vector, \( k = 2\pi/\lambda \), and equation (2.5) following expression for photoelectric wave vector could be derived,

\[ k = \frac{2m}{\sqrt{h^2 (E - E_0)}} \]  \hspace{1cm} (2.6)
2.3.2.3 Absorption Coefficients and Edges

X-rays when traveling through matter interact in numerous ways resulting in some part of the beam getting transmitted, reflected and absorbed. The resulting intensity due to absorption can be mathematically described as [38]:

\[ I = I_0 \exp(-\mu x) \]  

Where,

\( \mu = \) linear absorption coefficient,

\( I_0 = \) incident x-ray intensity, and

\( I = \) transmitted x-ray intensity

The absorption coefficient is usually expressed as a mass absorption coefficient (\( \mu/\rho \)) because the amount of x-rays absorbed is directly related to the quantity of interacting matter.

The absorption edge is defined as the sudden increase of the absorption coefficient of the material as the x-rays pass through it. This sudden jump in absorption coefficient is due to the ejection of a core electron from an atom, fig. 2.3.

2.3.3 Theory of EXAFS

Fig. 2.3 shows the absorption spectrum of a material. EXAFS is the oscillating part of this function beyond the absorption edge. In isolated atoms as the absorption edge is exceeded the absorption coefficient decreases monotonically as a function of increasing energy. In real world materials, this event rarely occurs as molecules and condensed matter exhibit “wigging” variations in the absorption coefficient due to the local atomic environment in an energy range of
40-1000 eV above the absorption edge. The pre-edge region of a spectrum contains valuable information about the bonding, electronic configuration, and site symmetry while the edge position contains information about the oxidation state of the atom as it is compared with a standard. This region between pre-edge and EXAFS is termed as x-ray absorption near edge structure (XANES). EXAFS measurements are done in transmission and fluorescence modes. X-ray fluorescence radiation is measured at right angles to the incident beam fig. 2.4 [38].

Figure 2.3 Image showing the pre-edge, edge and EXAFS region of a transmission mode absorption acquisition [38].
Oscillations in the EXAFS spectra are a result of the interference effects due to outgoing photoelectron waves and interactions with neighboring atoms. As an electron is ejected from the x-ray absorbing atom, it travels as an outgoing spherical wave. This wave interacts with neighboring atoms and is backscattered. The backscattered wave and incoming spherical waves interfere constructively and destructively giving rise to the sinusoidal (or oscillatory) nature of $\mu$ (absorption coefficient) vs $E$ (incident photon) variation. This oscillation is sinusoidal with an associated amplitude and frequency. These wave parameters are related to the type of and bond lengths of the neighboring atoms and their distances from the absorber, respectively. This model is termed as short-range single-electron single-scattering theory [38].

For high energies ($\gtrsim 60$ eV), equation 2.8 gives the modulation of the EXAFS absorption rate, $\chi$. $\mu_o$ is the “background” absorption in the spectrum [38]

$$\chi (E) = \frac{\mu (E) - \mu_o(E)}{\mu_o(E)} \quad 2.8$$
Absorption data as a function of energy, $\chi(E)$, can be converted to absorption as a function of phase space, $\chi(k)$, using the photoelectron wave vector $k$, equation 2.6:

$$\chi_i(k) = \frac{(N_iS_0^2)}{kr_i^2} F_{\text{eff}}(k) e^{-2\sigma^2_i k^2} \frac{R_i}{e^{\lambda(k)}} e^{-2R_i} \sin[2kR_i + \phi_i(k)]$$  \hspace{1cm} (2.9)

The following describes these parameters and their significance in the EXAFS equation [40],

(a) $\phi_i(k)$: phase shift of the photoelectron;

(b) $F_{\text{eff}}(k)$: the effective scattering amplitude of the photoelectron;

(c) $\lambda(k)$: the mean free path of the photoelectron;

(d) $R_i$: Half path length of the photoelectron i.e., for a single-scattering event, the straight line distance between the absorber and one of the coordinating atom;

(e) $N_iS_0^2$: This modifies the amplitude of the EXAFS signal and is independent of the k values. The subscript i means that this value can be different for each path of the photoelectron. For single scattering event, $N_i$ is the number of coordinating atoms within a particular shell while for multiple scattering event, $N_i$ represents the number of identical paths. $S_0^2$ is defined as the passive electron reduction factor and accounts for the slight relaxation of the remaining electrons in the presence of the core hole formed due to generation of photoelectron. Its value ranges between 0.7 and 1.0[41]. Its value is generally the same between different species of the same element and the edge.

(f) $F_{\text{eff}}(k)$: This term is called as the effective scattering amplitude and accounts for the element sensitivity in EXAFS. It takes the form of the atomic scattering factor used in X-ray diffraction for single scattering path events. For multiple scattering paths, $F_{\text{eff}}(k)$ relates to effective
scattering amplitude expressed as a combination of single scattering events [42]. Since $F_{\text{eff}}(k)$ depends on the number of electrons, it is similar between elements with nearly the same number of electrons.

(g) $1/R_i^2$: This parameter explains that the contribution of EXAFS from a shell of atoms at a distance $R_i$ reduces as a function of increasing distance from the absorber.

(h) $\sin[2kR_i + \phi_i(k)]$: This term applies the oscillations in the EXAFS signal with a phase of $2kR_i + \phi_i(k)$. $2kR_i$ is the phase difference arising due to a difference in the path length $(2R_i)$ of the photoelectron. $\phi_i(k)$ is the phase shift of the photoelectron due to the interaction of the photoelectron with the nuclei of the absorber atom and the nuclei of the coordinating atoms that lie in the photoelectron’s path. Since the oscillations are sinusoidal, the Fourier transform (FT) of the EXAFS signal can describe the atomic structure within the material. These distances are related to $R_i$. The peaks in the FT window are not precisely at $R_i$ due to a phase shift $\phi_i(k)$, causing a shift in a distance of $\sim 0.5$ Å.

(i) $\exp(-2\sigma_i^2k^2)$: This term accounts for the differences that arise due to static and thermal disorders that causes the atoms to be shifted from their distance $R_i$ relative to the central absorber atom. $\sigma_i^2$ is the mean-square displacement of the bond length between the absorber atom and the coordination atoms in a shell. EXAFS phenomenon occurs in the femtosecond ($10^{-15}$ sec) time scales while thermal vibrations occur at a much longer time scale of $10^{-10}$ to $10^{-12}$ sec. Therefore, the EXAFS spectra measures the distance between absorber atom and backscattering atom in terms of $\sigma_i^2$ values.

(j) $\exp(-2R_i/\lambda(k))$: $\lambda(k)$ is the mean free path of the photoelectron (i.e. the average distance that a photoelectron travels after excitation). $2R_i$ is the path length that the photoelectron travels to
interact with surrounding atoms. The negative exponential of the photoelectron path length divided by the photoelectron mean free path defines the range about which an EXAFS can define the local structure.

(k) \( \Delta R_i \): This denotes the change of interatomic distance relative to the initial path length \( R_i \). Ideally the path length can should change only slightly (<0.1 Å) so as to get a good fit between the model and the data.

(l) \( \Delta E_i \): This term is the change in the photoelectron energy that is needed to align the theoretical spectrum and the measured spectrum on the energy scale.

2.3.4 Data Processing and Refinement in Practice

There are many methods available for analyzing the EXAFS data. These include – curve fitting, lee and beni method, the r space method, parameter correlation and the FABM method and many more. Today the ab-inito method is rather popular due to its simplicity and standardized procedures that are available easily. To carry out these ab-initio calculations, the IFEFFIT[43] suite of programs is used (as mentioned in Chapter 4). This software package is open-source that can be downloaded freely for use on various computer platforms. Athena is one of the modules in the IFEFFIT suite that is used to refine the data, fig. 2.5. The following sections describe various details about data refinement using Athena.
Figure 2.5 Image showing main window of the ATHENA module. The section on the upper right corner displays the list of files imported, and section on the left displays the analysis parameters for the selected (or highlighted) data set.

2.3.4.1 Conversion of Experimental Variables

The first step in data reduction is to generate the experimental spectrum using measured values (like voltage or intensity). The y-axis in these cases should be the total linear absorption coefficient i.e.

\[ \mu (E) x = \ln \left( \frac{I_o}{I} \right) \text{ for transmission mode and} \]

\[ \mu (E) x = \frac{F}{I_o} \text{ for fluorescence mode} \]

where \( F \) is the fluorescent x-ray intensity.
2.3.4.2 Background Removal

Background in EXAFS is considered to be that part of the spectrum that yields no information about the local structure of the material. Equation 2.8 gives the interference function \( \chi(E) \) with \( \mu(E) \) as the absorption coefficient of an element while \( \mu_o(E) \) the absorption coefficient of the isolated atom, fig. 2.6 [38]. \( \mu_o(E) \) is the absorption coefficient of an isolated atom, and it monotonically decreases if in transmission mode as a smooth curve (or increases if in fluorescence mode). This smooth curve is often generated by a background function using splines that are fixed with knots [40].

![Diagram](image1.jpg)
More recently the AUTOBK algorithm is used for background removal. This algorithm was developed by Newville et al. [44] and is an integral part of the IFEFFIT suite of programs being built into ATHENA and ARTEMIS. The background function is constructed by employing third order (cubic) splines constructed using low R range values [40].

2.3.4.3 Normalization

Normalization brings all the spectra to a single absorption coefficient (usually matching the value of several spectra to one “parent” spectrum). This allows comparison among spectra from not just one system, but from other materials. The variations in spectra for similar materials or even the same samples can be due to effects from an absorber element concentration, sample preparation, thickness, or the detector response. In addition to this, spectra collected in transmission mode and fluorescence mode would slope differently. Normalization compensates for this by making the final normalized absorption coefficient or edge step as 1 and flat [40].
Various steps in the normalization process involves regressing a line in the pre-edge region (−200 to −30 eV before the edge) and a linear or quadratic function in the post-edge region (50–1000 eV above the edge energy). These lines are extended beyond the absorption edge, E₀. The difference in the y-value at the intersection with the edge is used to define edge height or step height. All the data points in the spectrum are divided by the value of the edge height which is followed by the subtraction of the pre-edge line. Usually, the pre-edge region lies along zero absorption, and the edge step value is 1[40].

2.3.4.4 Conversion of E to k

All the photon energy E is converted to the photoelectron wave vector k via equation 2.6. The edge energy, E₀, is roughly chosen as a value in and around the actual physical edge. This would be varied in the fitting procedure thus needs not to be very accurate. The value of E₀ is usually selected based on the position of the first inflection point of the dE/dk.

2.3.4.5 Weighting Scheme

Many a times the χ(k) values show higher amplitude oscillations for one part of the spectrum than for the other side. To compensate for this, χ(k) is multiplied by some power of k, kⁿχ(k). This results in giving more weight to the higher k region of the χ(k) spectrum. This helps determining accurate bond length values as their calculations is more dependent on the frequency rather than amplitude [38].

Teo and Lee [45]suggested weighting schemes of n = 1, 2 and 3 for backscatterers with Z > 57, 36 < Z < 57 and Z > 36, respectively. This weighting scheme has a profound effect on the peak heights and positions in the data Fourier transforms. Thus when comparing unknown
models, special care should be taken in assigning k weights. Parameters can be compared amongst each other only if the data are analyzed in a similar fashion [38].

2.3.4.6 Aligning and Averaging Spectra

Edge energies of the spectra from the same samples can get misaligned because of a number of reasons. Some of these include monochromator mechanical instabilities, such as a missed step in the monochromator motor that changes the energy or any change in the monochromator temperature. In such cases, a reference standard is always run in parallel with the sample. Spectra are obtained from both a reference standard and the sample at the same time, so that any discrepancy in measurement would be similar to both the cases. Since the edge energy of the reference standard is known, we can know then by how much the actual measurement is off. This difference is then applied to that of sample edge energy and spectra are aligned. In most of the cases, this standard material is a foil of a pure metal of the core atom in the sample [40].

Multiple spectra from the same sample after the alignment procedure are merged into one to get an average EXAFS output of the sample. To merge the spectra, one should overlay all the absorption $\mu(E)$ spectra and check the edge region for any changes in the spectra. Damage to the sample during preparation or acquisition, can lead to a change in edge energy. If the spectra appear consistent, then they should be merged in $\mu(E)$ [40].

The merge operation is always carried out on $\mu(E)$. Weighting can be assigned for data sets which were acquired for longer durations and, thus, have higher quality as compared to others [40].
2.3.5 Building Theoretical Models for Fitting EXAFS Spectra

After the data is refined and processed, it is imported into the Artemis module, fig. 2.7. The new version of Artemis includes the Atoms module (for gathering structural inputs like atom coordinates and lattice parameters) module to carry out FEFF (effective atomic scattering amplitude) calculations.

Figure 2.7 Image showing main window of the ARTEMIS module. The section in the middle displays the list of paths used for building models.

Modeling EXAFS spectra to determine fine structure details involves various steps. FEFF uses information from a cluster of atoms and analyzes the scattering process. Currently, Artemis comes with the FEFF program built into it [46] for computing theoretical EXAFS models [40].

Inputs of atom coordinates and lattice parameters are required to generate various theoretical path lengths. These are then used for generating the computed curve, and least square
fit is carried out for the actual experimental pattern. If crystallographic information is not available, then values can also be estimated by density functional theory (DFT) calculations. These inputs are used by FEFF to calculate the theoretical EXAFS spectrum for that model [40].

2.3.5.1 Variables for EXAFS Fittings

The EXAFS equation is evaluated for each path, and a model is generated using each of these paths. Each path is defined by the parameters--N, $S_0^2$, $\sigma^2$ (amplitude of the EXAFS oscillations) and $\Delta E_0$ and $\Delta R$ (phase of the oscillations). Initial values for $N$, $S_0^2$, $\Delta E_0$, $\Delta R$ and $\sigma^2$ are required to begin the fitting process. These parameters are described below.

(a) $\Delta R$ is the difference in experimental and fit $R_i$ values of the paths. This is defined by $\alpha R_{\text{eff}}$ (isotropic expansion–contraction term) where $R_{\text{eff}}$ is the effective path length $R$ for each path. This parameter needs to be evaluated separately for each individual path [40].

(b) $\Delta E$ is the change required in the edge energy so to align the theoretical spectrum with the experimental one. Unlike $\Delta R$, one energy shift is applied to all paths. In general, these values should be less than 2 to 3 eV [40].

(c) $\sigma^2$ is the mean-square displacement between a central atom and the atoms in the coordination shell. These displacement values relate to the Debye or Einstein model for the contribution of phonons to specific heat capacity at a particular temperature [47]. Coordination shells that have same atoms and interatomic distances have similar thermal and static disorder [40].

(d) $S_0^2$: Only one value of $S_0^2$ is used for all paths used in the model. The optimal $S_0^2$ value is obtained by fitting the EXAFS spectrum of a known material measured under similar conditions.
2.4 Energy Dispersive Spectroscopy (EDS)

2.4.1 Principle

EDS makes use of the x-rays resulting from a sample bombarded by an electron beam. The energy of the x-rays provide chemical information about a region of interest, fig. 2.8. EDS can detect elements with atomic numbers 4 (Be) to 92 (U), but elements lighter than Ne require advanced detectors. Spatial resolution of the electron beam and sample quality highly influence the detection limits [48].

Qualitative analysis involves the identification of the emission lines (K, L, M….. series) in the measured spectrum. Quantitative analysis (determination of the concentrations of the elements present) involves measuring intensities corresponding to each element in the sample. When the electron beam is in a raster mode, elemental maps can be generated as the beam moves across a sample. [48].
Figure 2.8 Image showing various phenomena that occur when an electron beam hits the sample [48].

2.5 Focused Ion Beam (FIB)

The FEI Nova 200 nano lab dual beam system is a high resolution field emission electron gun column, and a gallium source focused ion beam column. The UNT instrument also has an Omniprobe Autoprobe™ nano manipulator and gas injection system for depositing Pt on the sample. The schematic diagram of the focused ion beam system is given in fig. 2.9. The electron beam column is normal to the sample surface while the Ga ion beam column is at an angle of 52° normal to the sample surface.
Figure 2.9 Schematic showing the angle between the two guns in the dual beam setup. The ion beam is at an angle of 52° normal to the surface [49].

2.5.1 TEM Sample Preparation

TEM sample preparation by liftout procedures are well detailed in literature [50]. Samples thicknesses must be 100 nm or less for it to be electron transparent. Foils of thickness less than 100nm foil were made using the following procedure,

(a) A conductive double sided carbon tape was pasted on to an SEM stub. The exposed face of this tape was dipped into the boat containing the powder sample to create an even coat. Excess powder is blown away using nitrogen purge gas. Fig. 2.10 shows a coated surface.
Figure 2.10 Secondary electron images (a) and (b) a carbon tape coated with powders.

(b) The sample was aligned to concentric and eucentric heights in the FIB system, and images were obtained from a random site on the sample using the electron beam and ion beam windows.

(c) Electron beam patterning was used to deposit a Pt layer of 15 to 20 microns in length (x), 4 micron in width (y) and about 100nm in thickness (z).

(d) Above was then followed by a 500nm thick Pt layer of similar x and y dimension was deposited using ion beam pattern after tilting the stage to 52 degrees.
(e) Two regular cross section trenches of same x dimension as above but 3.5 microns in the y dimension and 8 microns in depth were made on either side of the Pt layer. The ion beam was then used in steps such that the deepest part of both trenches was located close to the Pt deposited area.

(f) The stage was then titled back to 0 degrees and an undercut was made using ion beam at the bottom of the sample. Similarly one of the vertical sides was also milled.

(g) Omniprobe Autoprobe™ needle was then inserted and attached to the vertical side having the cut. Attaching of omniprobe was carried out using ion beam deposition of the Pt.

(h) The opposite uncut edge was also then cut and the Omniprobe nano manipulator was retracted so as to locate near TEM lift out grid as shown in fig 2.11.

Figure 2.11 An ion beam image showing a sample attached to omniprobe nano manipulator.

(i) The lifted out sample was attached to one of the sides of the Cu post of the TEM grid. This was followed by detaching the other end from the Omniprobe nano manipulator and retracting the transporter to its home location, fig. 2.12.
Figure 2.12 An ion beam image showing a sample attached to a copper post and ready for final stage of polishing.

(j) Sample lamella was then milled in FIB by successively reducing current capacity cycles. The current cycles started from 1 nano Amps to 50 Pico Amps at 30KV with stage tilt of 48 to 56 degrees.

(k) In the final step a milling with 5kV, 70 pico amps current at 56 degrees stage tilt resulted in sample becoming electron transparent, fig. 2.13.
Figure 2.13 Secondary electron images (a) and (b) showing a sample attached to copper post after being fully polished.

After all of the previous steps, the Omniprobe TEM lift-out grid with polished sample was cleaned in 30 watt Ar plasma for 5 minutes before inserting in the TEM column for analysis.
CHAPTER 3

EXPERIMENTAL AND THERMOCHEMICAL INVESTIGATIONS IN THE 
CARBOTHERMAL REDUCTION MECHANISM OF ZIRCONIA

3.1 Introduction

Carbothermal reduction is a common chemical process practiced commercially for the synthesis of many non-oxide ceramic powders. Zirconium carbide powders have long been produced by using carbothermal reduction under various conditions and surroundings [51,52]. Zirconium carbide is known for its high melting temperature, 3400-3540 ºC, high hardness, 2100 Knoop, and high modulus of elasticity, $380 \times 10^9$ Pa [5]. These properties enable it to be used in cutting tools, as a refractory material, and in composites to impart high strength. It has also found applications in electronic devices [53] and as a low neutron absorbing material in the nuclear industry [54].

3.2 Literature Review

The carbothermal reduction mechanism and the species involved leading to carbide conversion has been studied since the early 1980s when Vodop'yanov et al. [55,56] reported that at high temperatures zirconia (ZrO$_2$) reacts with carbon monoxide (CO) to form carbides on the surface of oxides under non-vacuum conditions. Maitre et al. [8] conducted experiments in inert atmospheres by reacting powder mixtures of ZrO$_2$ and graphite in a graphite furnace. These were followed by various thermo-gravimetric measurements and thermochemical modeling of the system including volatility diagrams. It was later inferred from these efforts that CO is the driving species for this reaction as it reacts with ZrO$_2$ to form an oxycarbide phase, ZrC$_{0.9}$O$_{0.06}$ that subsequently leads to ZrC. These equilibrium calculations were done on nonequilibrium and non-stoichiometric species. This may limit these results since no or limited data
is available for thermodynamics of non-stoichiometric phases. In another study [9], researchers attempted to compare results from carbothermal reduction of TiO$_2$ and SiO$_2$ with their work on zirconia. These assertions should be made carefully because Ti-O and Si-O compounds exist in different stoichiometries (e.g., TiO$_2$, Ti$_2$O$_3$, Ti$_3$O$_5$, Ti$_4$O$_7$, SiO$_2$, Si$_3$O$_4$) while ZrO$_2$ has only one oxide. Other investigations have been attempted using mass spectrometry [10,57] but instead of probing actual ZrO$_2$ reduction mechanism the results are assumed to be similar to that for TiO$_2$. Gruner et al.[11] carried out experiments using carrier gas hot extraction (CGHE) method, but assumes the mechanism discussed in above references and extends it to the results from experiments so conducted.

Absent from these studies is the dependence of CO partial pressure on this reaction. CO occurs as a reaction product during carbothermal reduction of zirconia at temperatures of 1657 ºC and above [6] according to reaction (3.1). This reaction shows that the CO available for reaction with zirconia is dependent on the prior carbothermal reduction of ZrO$_2$. Moreover, CO is a larger species than C precluding its diffusion into zirconia.

\[
\text{ZrO}_2(s) + 3\text{C}(s) \rightarrow \text{ZrC}(s) + 2\text{CO}(g) \quad (3.1)
\]

Thermodynamic reactions involving CO and ZrO$_2$ indicate that ZrC is unlikely to form from these reactants. Fig. 3.1 shows change in Gibbs free energy (\(\Delta G\)) plots for two different reactions (Equations 3.2 and 3.3) between ZrO$_2$ and CO:

\[
\text{ZrO}_2(s) + 4\text{CO}(g) \rightarrow \text{ZrC}(s) + 3\text{CO}_2(g) \quad (3.2)
\]

\[
\text{ZrO}_2(s) + \text{CO}(g) \rightarrow \text{ZrC}(s) + 1.5\text{O}_2(g) \quad (3.3)
\]
Figure 3.1 Graph showing variation of change in standard Gibbs free energy ($\Delta G^0$) as a function of temperature for reactions (3.1), (3.2) and (3.3).

The $\Delta G$ values are highly positive for a large temperature range confirming that under atmospheric pressure CO is unlikely to react with ZrO$_2$ to form ZrC [15,58]. Reactions (3.2) and (3.3) can go in the forward direction only (i.e., have a negative $\Delta G$ values) under non-equilibrium conditions. These values are governed by the following equation,

$$\Delta G = \Delta G^0 + RT\ln Q$$

(3.4)

where $\Delta G^0$ is change in Gibbs free energy at standard state, R is the gas constant, T is the absolute temperature, and Q is the reaction rate constant. Fig. 3.1 shows $\Delta G^0$ is always positive for both reactions. Thus for $\Delta G$ to be negative, $\Delta G^0 < -RT\ln Q$. Therefore, unless the partial pressures of CO are very high ($1.9 \times 10^{14}$ Pa at 25 ºC for reaction (3.2)), CO will not convert ZrO$_2$ to ZrC. Moreover, under equilibrium conditions and unit activity of solids in reaction (1), partial
pressure of CO is calculated to be $4 \times 10^5$ Pa at 1800 ºC. This makes it extremely difficult for CO to initiate any ZrO$_2$ to ZrC transformation.

In many reactions, such as (3.5), varied ratios of CO, CO$_2$ and O$_2$ can result in activity of carbon greater than one. Consequently, carbon would start depositing from atmosphere. The graphite furnace used in this work has a partial pressure of O$_2$ of ~0.09 Pa. A quick analysis would reveal that unless the partial pressure of O$_2$ is not less than $\sim 3.13 \times 10^{-9}$ Pa, the activity of graphite would not exceed a value of one according to reaction (3.5) [15,58]. Therefore, the main motivation of this study is to examine the extent of reaction and potential mechanisms of zirconia carbothermal reduction under differing exposures to carbonaceous species – namely CO and C.

$$2C(s) + O_2(g) \rightarrow 2CO(g)$$  \hspace{1cm} (3.5)

3.3. Materials and Methods

3.3.1. Sample Preparation

A composite pellet system was designed that consisted of two parts: upper and lower halves that were made separately by die pressing powders to form pellets. The YSZ powder was manufactured by Tosoh Corporation under product name TZ-3Y-E. The 3 mol% YSZ exhibited specific area of 15200 m$^2$/kg and crystallite size of ~26 nm. The graphite powder (300 mesh size) was produced by Alfa Aesar. The motivation behind constructing a composite system was to use the bottom half of the pellet as a carbon source (CO and/or C) for reactions to occur into and within the top half. Fig. 3.2 shows the two composite systems, MP and GP, and their sintered counterparts, MPs and GPs. The naming convention is based upon the nature of the bottom half of the pellet systems. MP and MPs have a mixed bottom pellet made from YSZ and
graphite. Thus a designation “MP” was used to abbreviate “mixed pellet”. Similarly GP and GPs pellet systems have their bottom half made up of graphite only, and thus the abbreviation “GP” stands for “graphite pellet”. MPs and GPs have an added suffix “s” since their top halves of YSZ were sintered before being put on its bottom half. Four pellet systems, with multiple repetitions have been tested which yielded reproducible results.

![Schematic of pellets](image)

Figure 3.2 Schematic of pellets (a) MP, (b) GP, (c) MPs, and (d) GPs. Shrinkage seen in the top halves of MPs and GPs is due to prior sintering of the YSZ pellet.

MP consisted of a bottom half made up of YSZ and graphite mixed using a mortar and pestle in a molar ratio of 1:3.3. This molar ratio was chosen so as to have carbon in excess which would leave no ZrO$_2$ unreacted. This powder blend was then die pressed at a uniaxial pressure of 34.4×10$^6$ Pa to form cylindrical pellet. The GP pellet consisted of a bottom half made only from 0.25 g graphite powder. Both top halves for MP and GP were made up of 1g of YSZ powder die pressed to a density of ~2940 kg/m$^3$. In MPs and GPs samples, the YSZ top halves were sintered after die pressing to a density of 5800 kg/m$^3$ (~96.7% dense) prior to heat treatment. The sintering temperature-time profile is shown in Fig. 3.3. In none of the samples discussed above were the top and bottom halves die pressed together. Top half of any pellet system was simply placed on top of its respective bottom half using tweezers.
3.3.2. Carbothermal Reduction Heat Treatments

Heat treatments were done under flowing helium in a Thermal Technology graphite furnace (Model 1000-2560-FP20). Prior to heat treatments, the chamber was pumped down to \( \sim 1.3 \times 10^{-4} \) Pa and then flushed with research grade He. Samples were heated to a temperature of 1800 °C under flowing He using the procedure shown in Fig. 3.4. This involved a ramp up from room temperature to 1350 °C at a rate of 300 °C/hr, from 1350 °C to 1650 °C at a rate of 1800 °C/hr, from 1650 °C to 1800 °C at a rate of 300 °C/hr, followed by a dwell of 1800 seconds, and cooling down to 20 °C at 300 °C/hr.

Figure 3.3 Heat treatment procedure for sintering top halves of GPs and MPs. Each labeled data point shows the corresponding temperature at various hold stages.
3.3.3. Characterization

Cu-Kα X-ray diffraction (XRD) was done using a Rigaku Ultima III diffractometer. Scans were acquired from top and bottom halves of all the pellets before and after heat treatments. These were then analyzed for the phases present and their respective mole fractions. Peak identification corresponding to YSZ, graphite and zirconium carbide were done using JCPDS files nos. 01-070-4426, 01-071-4630 and 01-073-0477, respectively. MDI Jade software was used for peak identification, and Rietveld refinement was employed on all XRD scans to obtain molar percentages of the various phases.
3.4. Results and Discussion

3.4.1. Characterization of Pellets Before and After Carbothermal Reduction Heat Treatment

XRD determined that the 3 mol% YSZ raw powder consisted of tetragonal and monoclinic zirconia phases shown in Fig. 1.1. The basic aim behind designing the four composite pellet systems was to differentiate the relative amounts of CO and C diffusing species into their respective YSZ top halves. Based on Reaction (1), the MP bottom half pellet would form ZrC and liberate CO at T > 1657 °C. This CO along with some C is then available to react with the top half of the pellet. Due to a mixed bottom half in MP, CO, in principle, is the primary diffusional species. GP has a bottom half composed only of graphite. Thus, C, in principle, would be the primary species causing conversion on the bottom face and CO on the top face of its top half. Therefore, CO generation due to the YSZ and graphite reaction at interface of top and bottom half would be considerably less in GP compared to the MP pellet. As a result, C would be a more abundant diffusional species in bottom face of GP top half than CO. Moreover, during heat treatment the top halves would undergo phase transformation, to ZrC, and sintering, to 80% density of zirconia, at the same time. This would concurrently reduce porosity and retard any CO diffusion owing to its bigger size.

MPs and GPs, have the same bottom halves as MP and GP, respectively, but the YSZ top halves are sintered to 98% of theoretical density before reaction heat treatment. CO gas diffusion would thus be limited in sintered YSZ since there is negligible porosity. Like in MP, the primary species available for reaction with ZrO₂ in MPs is CO while C is much less abundant. In GPs the primary abundant species for diffusion is C whereas CO would be the minor species on the bottom face but play a significant role for the top face of its top half.
At 1800 ºC, C and CO can diffuse from the bottom half of a pellet (source) into its respective top half (sink). Even with increased mobility of these species, carbothermal reduction will occur only at temperatures where reaction (1) has negative values of the Gibbs free energy. The bottom half of each pellet serves as an atomic carbon source for its respective YSZ top half in minor and major amounts depending on the pellet system. As previously mentioned, MP and GP have different dominant carbon species available to react with the top halves. MP has gaseous CO in abundance while GP provides only C as a reactant, for bottom face of its respective top half, at least initially. As the gaseous species becomes available, it can react with both faces and sides of the YSZ top half. However, in the GP pellet, solid carbon is in contact with YSZ and should result in a more solid diffusion-based reaction.

To differentiate amongst these possible reactions, separate XRD scans were acquired from the bottom and top faces of their corresponding bottom and top halves. Fig. 3.6 (a) and (c) shows XRD results acquired from the bottom half of MP (i.e., from reacted C + YSZ) and MPs. There are no peaks corresponding to YSZ confirming full conversion to ZrC. Conversely, XRD results on GP and GPs, shown in Fig. 3.6 (b) and (d), exhibited only graphite peaks with no peaks corresponding to YSZ or ZrC. To characterize the top halves of the MP, GP, MPs, and GPs pellets, both its top and bottom faces were analyzed according to the procedure shown in Fig. 3.5. The corresponding XRD scans in Fig. 3.7 all show the presence of tetragonal ZrO$_2$ and ZrC in varying percentages (no monoclinic ZrO$_2$). In Table 3.1, quantitative Reitveld refinement analyses show that the maximum ZrC conversion occurred on the bottom face of the GP pellet followed by the GPs, MP and MPs bottom faces. The reason for this trend is because the GP pellets are a greater source of C, and, thus show a larger amount of ZrC formation. Meanwhile, the sintered samples show less ZrC formation than their un-sintered counterparts because
sintering severely limits exposed interior surfaces as potential reaction sites. In addition, the lattice parameter for ZrC formed on various faces of the pellets is relatively constant, listed in Table 3.2, with an average around 4.673 Å and a standard deviation of 0.002 Å.

Figure 3.5 Flowchart showing the methodology in XRD analysis of pellets before and after the carbothermal reduction heat treatment. The cloud shape represents powder formed from bottom halves as they decompose after heat treatment.
Figure 3.6 XRD scans acquired from the bottom halves of (a) MP, (b) GP, (c) MPs and (d) GPs after carbothermal reduction heat treatment.

Table 3.1 Mole percentages of zirconium carbide formed on top and bottom faces of respective top halves of MP, GP, MPs and GPs. These mole percentages were calculated by doing Rietveld analysis on XRD data in figure 8.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Mole Percentages</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>Top face- 42% ZrC</td>
</tr>
<tr>
<td></td>
<td>Bottom face- 23% ZrC</td>
</tr>
<tr>
<td>GP</td>
<td>Top face- 45% ZrC</td>
</tr>
<tr>
<td></td>
<td>Bottom face- 74% ZrC</td>
</tr>
<tr>
<td>MPs</td>
<td>Top face- 15% ZrC</td>
</tr>
</tbody>
</table>
Bottom face- 18% ZrC

Top face- 18% ZrC

Bottom face- 57% ZrC
Figure 3.7 XRD data acquired from (i) bottom face and (ii) top face of (a) MP, (b) GP, (c) MPs, and (d) GPs top half pellets. Table 3.1 lists the various amounts of ZrC formed on respective faces.

Table 3.2 Lattice parameters of Zirconium carbide formed at various faces of top halves of MP, GP, MPs and GPs calculated from XRD data in Figure 3.7.

<table>
<thead>
<tr>
<th>Top half</th>
<th>a (Å)</th>
<th>Bottom Face</th>
<th>Top Face</th>
</tr>
</thead>
<tbody>
<tr>
<td>MP</td>
<td>4.669</td>
<td>4.675</td>
<td></td>
</tr>
<tr>
<td>GP</td>
<td>4.676</td>
<td>4.672</td>
<td></td>
</tr>
<tr>
<td>MPs</td>
<td>4.669</td>
<td>4.672</td>
<td></td>
</tr>
<tr>
<td>GPs</td>
<td>4.676</td>
<td>4.675</td>
<td></td>
</tr>
</tbody>
</table>

3.4.2. Bulk Diffusion of C in YSZ Pellets

The carbon diffusion coefficient in zirconia has been reported to be six orders of magnitude less than oxygen self-diffusion [59]. This would indicate several orders of magnitude difference in diffusivity between C and CO through YSZ due to the gaseous nature of CO. Based on the recent work of Vykhodets et al [59] and utilizing their data, the diffusion coefficient of C in YSZ at 1800 °C is calculated to be 3×10⁻¹⁴ m²/sec [59]. Using Fick’s second law and this
diffusion coefficient, the effective diffusion length of C in YSZ can be approximated to 25 μm for 1800 seconds at 1800 °C (calculated plots shown in Fig. 3.8). According to these results at distances greater than 25 μm, there should not be any ZrC formation due to lack of diffusing carbon. To confirm this experimentally, the top halves of MP, GP, MPs, and GPs were sliced radially to half their heights (~1.5 mm), shown in Fig. 3.9. After slicing, XRD scans were acquired from the exposed faces, namely Face A and Face B while keeping the X-ray beam close to the geometric center. Fig. 3.10 shows the XRD scans obtained from Face A and Face B for all of the pellets. None of the scans show the dominant ZrC (111) peak at 2θ=33.2°. On the contrary, all the peaks correspond to YSZ tetragonal phase confirming that no ZrC formed in the center, at least to these 1.5-2 mm depths. Fig. 3.8 shows the penetration depth for diffusion times of 3600 seconds (circles) to 5400 seconds (triangles), and that C cannot diffuse further than 50 μm. These results further confirm that carbothermal reduction is more C driven than CO driven due to the slow solid-state diffusion of carbon. X-ray penetration depth calculations indicate that the diffraction analysis only examines approximately the first 16-20 μm of ZrO₂/ZrC.
Figure 3.8 Variation of carbon concentration as a function of diffusion distance (x) in YSZ at 1800 °C. Curves are plotted for various diffusion times of 1800, 3600 and 5400 seconds. The vertical dotted line shows maximum distance to which X-rays penetrated based on diffraction data acquired from bottom and top faces of MP, GP, MPs and GPs top halves.

Figure 3.9 Schematic of the methodology of slicing top halves of MP, GP, MPs and GPs along with approximate dimensions of original and sliced pellets. Face A and Face B are labeled according to their geometric locations on sliced halves.
3.4.3. Surface Diffusion of C on YSZ Pellets

As mentioned earlier, the bottom half of MP acts as a strong source of CO and a weak source of C for diffusion into the bottom face of the top half. In contrast, GP acts as a strong C source and a weak CO source for its bottom face of the top half. During the course of the carbothermal reduction reaction, it is feasible that CO can be liberated as a reaction product and form an envelope the top YSZ pellet leading to radially inward diffusion. Similarly, C due to being a small and a relatively mobile species can also diffuse to the top from surface sites on the pellet edges. Relative to gaseous envelopment, surface diffusion is slow and could lead to a gradient of YSZ conversion to ZrC along the sides of the pellet. Given the differences between
gaseous and surface diffusion rates, one would expect that surface diffusion would have a more observable time dependence.

Examination of these surface effects is important to understand details of the diffusion mechanism(s). To this end, a series of XRD spot scans were performed on one of the sliced faces (Face A or Face B) of the MPs and GPs pellets. These spot scans, when stitched together, form a line that connects the pellet edge to its center as shown in Fig. 3.11. Such a line scan can reveal a possible transition from ZrC to YSZ along the radial direction of the pellet. These rectangular X-ray beam cross-sections were made spatially large enough to cover considerable areas near the edge and center of the pellet’s face.

Figure 3.11 Schematic of the various points for XRD measurements along the sliced face (A or B) of a top half pellet. Dark rectangular slab represents XRD stage on which the pellet rests during acquisitions. The rectangular regions, designated by numbers 1 to 8, represent areas from where XRD scans were obtained. Point 1 is on the XRD stage which provides no diffraction, and points 2 to 8 span from the very edge of the pellet to near the pellet center.

XRD line scan results obtained from this procedure are shown in Fig. 3.12 (a) for MPs and Fig. 3.12 (b) for GPs. For both pellets, only YSZ peaks were detected with no evidence of ZrC reflections on all the XRD scans obtained from points 1 to 8. Since XRD has spatial limitations to detect small phase regions, XPS was employed to help determine the composition
of the periphery of the pellet. These XPS results confirmed the presence of ZrC and a small concentration of yttrium within the ZrC layer.
Figure 3.12 Stacked XRD scans acquired from radially distributed points on Face A (or Face B) of sliced top halves of (a) MPs and (b) GPs pellets. No ZrC formation was detected along Points 1 to 8. Point 1 corresponds to region near sample stage and Point 8 corresponds to region near center of the sliced pellet. Optical images showing superimposed images of sliced (c) MPs and (d) GPs top halves with fluorescent streaks (denoted by arrows). Fluorescent streaks represent area where X-rays were falling on the sample during one of the acquisitions of points 1 to 8 on Face A or Face B. These were captured separately using same scale as that for the sliced sample images and then superimposed on them.

Any surface diffusion formation of ZrC is significantly less than the previously observed bulk diffusion formation in the top and bottom faces of the MP, GP, MPs, and GPs top halves.
Corresponding optical images of the X-ray spot streaks superimposed on actual samples are shown for MPs (Fig. 3.12(c)) and GPs (Fig. 3.12(d)).

3.4.4. Discussion on the Mechanism of Carbothermal Reduction of Zirconia

During the carbothermal reduction heat treatment, the bottom face of the MP top half (YSZ) is exposed to more CO than GP because of its mixed ZrO$_2$ and C bottom half. Based on previous research [8-10,12,55,56,60] where CO is thought to be the reaction driver for ZrC conversion, the bottom face of the MP top half should produce more ZrC formation than GP. However, it was determined that GP bottom face exhibits significantly more ZrC conversion (70%) than MP (23%). The pellet systems studied have CO and C as the only likely species capable of carburizing YSZ to ZrC. The top halves of MP and GP densify to 80% (4.8 g/cm$^3$). During this treatment, enough porosity exists for both species to diffuse; therefore, it is difficult to discern the dominating species driving carbide formation. To study this effect, sintered versions of these samples, GPs and MPs, were exposed to the same heat treatments and carbonaceous exposures as their porous counterparts. In both sintered samples, the top and bottom faces still show ZrO$_2$ to ZrC conversion, albeit less mole percent than the corresponding non-sintered pellets. These sintered YSZ top halves should restrict or minimize any gaseous CO diffusion through them and only react through direct contact or gaseous species emanating from the lower halves. However, carbon because of its very small size can diffuse via grain boundaries, interstitial sites and lattice defect sites. Because reduction of YSZ to ZrC is still observed in the sintered GPs and MPs pellets, it is reasonable to conclude that carbon is the key reactant on the bottom face of the YSZ.
As stated previously, diffusion measurements [59] show that kinetics of carbon diffusion in zirconia are rather slow ($D_C$ in YSZ = $3 \times 10^{-14}$ m$^2$/sec at 1800°C). Thus, any YSZ to ZrC conversion occurring because of carbon will be highly localized. This effectively means that carbon diffusion in YSZ is so slow that it causes the diffusion front to extend to similar depths as that of the conversion front of ZrO$_2$ to ZrC transformation. Experimental XRD results on Face A and B of MPs and GPs top halves confirms this since no ZrC was detected on the sliced faces.

3.5. Summary and Conclusions

Experiments and calculations were performed to study carbothermal reduction mechanisms and determine whether CO is the dominant species driving the ZrO$_2$ to ZrC conversion. A series of experiments using pellet systems were conducted in which major and minor amounts of CO and C were exposed to YSZ, and the reaction products were analyzed to confirm the reaction driver. If CO is the source of C for ZrC formation then the sample with the most available CO, MP, would exhibit the highest conversion; however, this was not observed. Instead, GP, which has a bottom half of graphite acts as a weak source of CO, shows maximum ZrC formation at the interface between top and bottom half due to solid-solid reaction of zirconia and graphite. In addition, top halves of MP and GP undergo sintering and reaction at the same time. This restricts CO diffusion through the bulk as the top pellets are sintered to 80% of theoretical density of zirconia during heat treatment. To form ZrC, a carbonaceous species must transport into ZrO$_2$, thus, C is a much more likely species to diffuse through a sintered sample than CO. In support of this mechanism, theoretical calculations indicate partial pressures of CO needed to drive zirconium carbide formation from zirconia are far beyond the environment in the reaction furnace. Since most of the commercial processing is done under normal atmospheric
pressures, formation of ZrC by reaction between ZrO$_2$ and CO appears less likely than carbon diffusion.

In addition, carbon diffusion in zirconia is slow even at elevated temperatures due to which the diffusion rate would be similar to reaction rate. Thus any ZrC formation is highly localized as seen experimentally in all the top halves as well as in diffusion depth calculations. These results indicate carbothermal reduction to be C driven as CO would be expected to be orders of magnitude faster than C and cause unlocalized diffusion (within the sample pores). Based on these results, carbothermal reduction of zirconia is more dependent on solid-solid reactions than gas-solid reactions. This finding is in disagreement with previous research findings that suggest carbothermal reduction of zirconia to be only a CO driven reaction mechanism.
CHAPTER 4
MECHANISTIC INSIGHTS INTO THE CARBOThERMAL REDUCTION OF ZIRCONIA

4.1 Introduction

Carbothermal reduction of zirconia can proceed by three primary pathways—reactions (3.1), (3.2) and (3.3) as discussed in Chapter 3. Activity and partial pressure values are important characteristics of a solid and gaseous reacting species in these chemical reactions. Thus depending upon these values, the reaction can proceed favorably in a certain direction even when the equilibrium temperature (calculated by thermodynamic tables) is not reached. We experimentally demonstrated in previous chapter that carbon is the major species driving ZrO₂ to ZrC conversion, but based on the above discussion the partial pressure values of carbon monoxide can still play a dominant role in this reaction. This chapter is focused on understanding the influence of carbon activity and CO partial pressure on the extent of carbothermal reduction of zirconia.

4.2 Material and Methods

The thermochemical modeling software Factsage [15,61] was chosen to investigate the mechanism of carbothermal reduction of zirconia by varying the activities and partial pressures of C and CO respectively at 1800 °C.

4.2.1 FactSage Modelling

FactSage is a computational thermochemistry software widely used in industry and academia for conducting chemical thermodynamics analysis of several systems. In our study, the chemical equilibrium module was utilized to calculate the concentrations of various chemical
species under a range of conditions. This software uses the Gibbs energy minimization approach when constituents react (partially or fully) to reach a chemical equilibrium [61]. To study the impact of carbon and CO as reacting species we created two separate representative models for the system—ZrO$_2$ + CO + Ar and ZrO$_2$ + C + Ar.

Using partial pressure values of CO (P$_{CO}$) from 0.1 to 1.0, and the fraction of ZrC was calculated for the ZrO$_2$ + CO + Ar system. A similar procedure was carried out varying the activity of C (a$_C$) for the ZrO$_2$ + C + Ar system. The resulting ZrC fractions were compared to the corresponding a$_C$ or P$_{CO}$. Argon was used as buffer gas to maintain a total system pressure of 1 atm. Table 4.1 lists the initial conditions for the models.

Table 4.1 Initial and test conditions used for the two models.

<table>
<thead>
<tr>
<th>Model</th>
<th>Total pressure</th>
<th>Temperature</th>
<th>Partial pressure/activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZrO$_2$ + CO + Ar</td>
<td>1 atm</td>
<td>1800 ºC</td>
<td>P$_{CO}$ varied from 0.1 to 1.0 with increments of 0.01</td>
</tr>
<tr>
<td>ZrO$_2$ + C + Ar</td>
<td>1 atm</td>
<td>1800 ºC</td>
<td>a$_C$ varied from 0.1 to 1.0 with increments of 0.01</td>
</tr>
</tbody>
</table>

4.2.2 Experimentation

In order to verify computational results, a sintered pellet was heat treated in a flowing CO gas environment under ambient pressure. The heat treatment procedure, XRD phase identification and quantification were similar to those described in Chapter 3.
4.3 Results and Discussion

4.3.1 ZrO$_2$ + CO + Ar

Fig. 4.1 shows the variation of moles of ZrC formed as a function of partial pressure of CO gas in the system at 1800 °C. The maximum amount of ZrC (0.08 moles) occurred at a partial pressure of 1 atm of CO leaving 0.92 moles of ZrO$_2$ unreacted. These calculations also showed a graphite activity of 0.39 at 1 atm CO, formed at the equilibrium. The activity of carbon formed at the equilibrium increased with increasing partial pressures of CO even though the amount so formed is very small.

![Moles of ZrC(s) formed as a function of CO partial pressure at 1800 °C](image)

Figure 4.1 Plot showing the moles of ZrC formed as a function of partial pressure of CO in the ZrO$_2$ + CO + Ar system at 1800 °C. The inset graph shows the highlighted region in much detail with corresponding ZrC formation amounts.
4.3.2 ZrO$_2$ + C + Ar

As the activity of carbon was varied from 0.1 to 1.0, complete reaction of ZrO$_2$ to ZrC was observed at a carbon activity of 0.31 and greater. Fig. 4.2 shows the variation in ZrC amounts as a function of carbon activity in the system. At equilibrium maximum amounts of CO formed amounts were limited to a partial pressure value of 0.67 atm (2 moles). This was realized at a carbon activity of 0.31 and above.

![Figure 4.2 Plot showing the moles of ZrC formed as a function of carbon activity in the ZrO$_2$ + C + Ar system at 1800 ºC.](image)

4.3.3 Heat Treatment of Sintered 3 mol% YSZ Pellet in Flowing CO Gas

A 3 mol% YSZ sintered pellet was heat treated in a pure CO gas environment using the heat treatment profile mentioned in Chapter 3. Fig. 4.3 shows the XRD patterns from the top and bottom faces of the pellet. Rietveld phase quantification was done using MDI Jade 9.0 revealed
formation of about 15 mole% ZrC on the top face of the pellet. The x-ray penetration depth was calculated to a depth of 16 μm using integrated intensity approach as described in reference [62].

Figure 4.3 XRD scans acquired from the top and bottom faces of the heat treated 3 mol% YSZ sintered pellet.

4.3.4 Discussion on Comparison Between Thermodynamic Modeling Results and Experimental Results

\[ \text{ZrO}_2 + \text{CO} + \text{Ar} \]

model results show that the fraction of ZrC formed is far less than that formed for \( \text{ZrO}_2 + \text{C} + \text{Ar} \). Rietveld phase quantification values from XRD patterns of the heat treated pellet indicate the conversion amounts at 15 mol% ZrC on the top face. This is comparable to those obtained for top face of MPs (15 ± 1.5 mol% ZrC) and GPs (18 ± 1.8 mol% ZrC) top half pellets. These numbers confirm our hypothesis from the previous chapter that any ZrC formed on the top face of MP, GP, MPs and GPs pellets is due to interaction with CO gas.
only. Also, this value is far less than that formed at the bottom face of GPs pellet proving CO to be incapable of causing considerable ZrC conversion.

The ZrO₂ + C + Ar model also demonstrated that a carbon activity of 0.31 was able to completely convert 1 mole of ZrO₂ to ZrC as compared to 1 atm of CO in ZrO₂ + CO + Ar model. This means that assuming ideal behavior carbon-carbon composite does not need to be all carbon to initiate this reaction. At equilibrium, 0.67 atm partial pressure of CO (2 moles) is realized in the former model which from the results of latter model renders it incapable of any substantial ZrC formation. Thus from this and above mentioned results CO is not the major species for formation of ZrC from ZrO₂.

Graphite forms as a product at equilibrium in the case of ZrO₂ + CO + Ar in obscured amounts but with a finite activity (0.39 at 1 atm CO). As seen in ZrO₂ + C + Ar model, any activity of carbon (greater than 0) is capable of ZrC formation. Thus in actual practice the top faces of MP, GP, MPs and GPs experience more ZrC formation than calculated from modeling results because of this carbon formed at the end of prior reaction that reacts with exposed or next set of ZrO₂ available in the pellet. This indicates that C is the primary species for the carbothermal reduction of ZrO₂.

4.4 Summary and Conclusions

Chemical thermodynamic modeling was conducted to understand the carbothermal reduction mechanism of zirconia under varying activities and partial pressures of the carburizing species at 1 atm total pressure. Results showed far less ZrC formation (0.08 moles) in a CO rich environment as compared to the C rich environment (1 mole of ZrC). A mere activity of C at 0.31 was found sufficient to cause complete conversion of 1 mole of ZrO₂ to ZrC.
Experiments were done by heat treating a sintered 3 mol% YSZ at a CO partial pressures values of 1 atm to compare conversion amounts with those obtained from modeling. Reitveld phase quantification of XRD patterns suggested formation of 15 mol% ZrC on the top face of the pellet. This value is similar to those formed on the top face of MP, GP, MPs and GPs top half pellets. In addition to this, the measured values from Chapter 3 follows the logic of those obtained from modeling as graphite left at equilibrium would cause more conversion by reacting with next layer or exposed ZrO₂ units in the sample.

The equilibrium partial pressure of CO in the ZrO₂ + C + Ar model was found to be 0.67 atm (2 moles). Results from the ZrO₂ + CO + Ar model suggest the CO present is not enough to convert ZrO₂. Thus from the thermochemical modeling results, we conclude that C is the primary species responsible for the carbothermal reduction of zirconia than CO.
CHAPTER 5
X-RAY ABSORPTION SPECTROSCOPY STUDIES ON THE CARBOThERMAL
REDUCTION REACTION PRODUCTS OF 3 MOL% YSZ

5.1 Introduction

Zirconia (ZrO$_2$) is an important ceramic material recognized for its unique mechanical, ionic and thermal properties. The three polymorphs of zirconia occur at successive temperature ranges — monoclinic (below 1170 ºC) [63,64], tetragonal (1170 ºC to 2370 ºC) [65] and cubic (2370 ºC to 2680 ºC) [66]. Ceria, magnesia, calcia and yttria stabilize the tetragonal or cubic phases well below the tetragonal to monoclinic transformation temperature [16,17]. Yttria (Y$_2$O$_3$) stabilized zirconia (YSZ) has found a broad range of applications from biomedical implants [18,19], oxygen sensors[20-24] to thermal barrier coatings on jet engine turbine blades [4].

The formation of ZrC from ZrO$_2$ and carbon species has been the subject of a number of investigations [8-12,14,55-57,60] as discussed in Chapter 3. However, the atomic structure of composite ZrO$_2$/YSZ and ZrC after carbothermal reduction is unknown and is the main focus of this chapter.

5.2 Literature Review

X-ray absorption spectroscopy (XAS) is a powerful tool widely employed to describe local structure and short range order in materials irrespective of their crystallinity [38]. Much work has been done using XAS to explore the chemistry of pure and stabilized zirconia. Results
have shown marked differences between tetragonal phases of pure ZrO$_2$ and YSZ due to their different defect chemistries [67,68].

Previous research has also explored the extended x-ray absorption fine structure of pure and stabilized zirconia [67-76]. Li et al. [67,69-73] extensively investigated undoped and doped ZrO$_2$ systems. These studies found that the EXAFS patterns were phase and not dopant dependent and that the distortion of Zr-O and Zr-Zr shells is caused due to oxygen vacancies and it increases with increasing symmetry. The mechanism of tetragonal or cubic phase stabilization by Y$_2$O$_3$ along with static and thermal distortions that influence characteristic EXAFS patterns and structure have also been demonstrated successfully. Catlow et al. [74] conducted EXAFS experiments and computer simulations to understand the vacancy-cation interactions and found vacancies to be concentrated more in near Zr$^{+4}$ than Y$^{+3}$ ion for a yttria doped zirconia system. This is an interesting result as it contends that positively charged oxygen vacancies are found near electropositive Zr$^{4+}$ cation rather than the negatively charged yttrium dopant ($Y_{Zr}^{-}$). Along similar lines, Cole et al.[75] studied the location of vacancies in the zirconia lattice as a function of dopant size. It was shown that in the case of a relatively small dopant cation the vacancies like to locate themselves near to the host Zr$^{+4}$ cation whereas in case of a much larger impurity cation, the oxygen vacancies like to stay around the dopant cation. Rush et al. [76] conducted EXAFS acquisitions on YSZ films with nano-grain sizes and found their Fourier transform patterns similar to the bulk counterparts. The only noticeable difference was observed in the heights of various shells that were attributed to difference in nearest neighbors different nearest neighbors between nano grain sized YSZ films (more grain boundaries) and bulk samples (less grain boundaries).
In contrast, limited work has been performed on ZrC [77-79] so much so that absorption patterns are used for comparison and were not used to calculate bond lengths in the system. No studies were found describing fine structure changes that occur during carbothermal reduction of YSZ into ZrC. Thus, the aim of this research is to understand and interpret the change in various bond lengths that occur due to the formation of ZrC in an YSZ matrix using Zr K-edge x-ray absorption fine structure.

5.3 Materials and Methods

5.3.1 Sample Preparation

EXAFS acquisitions were carried out on four samples. Two were powders: 3 mol% YSZ powder (Tosoh Corporation with a crystallite size of ~26 nm) and pure ZrC powder (Sigma Aldrich with a particle size of 10 μm and 99% purity). Standard preparation methods were followed to prepare powder samples for acquiring EXAFS data. This included the application of the desired powder on a piece of regular scotch tape and placing them in an X-ray beam path for pattern collection. The remaining two samples were sintered YSZ and GPs top half pellet as described in Chapter 3. For GPs pellet, ZrC formed on the face in direct contact with the graphite is of interest here due to its higher conversion amounts.

5.3.2 Characterization

5.3.2.1 X-ray Diffraction

Cu-Kα X-ray diffraction (XRD) experiments of pellets were performed using a Rigaku Ultima III diffractometer at a rate of 0.5 deg/min. Peak identification and phase quantification corresponding to YSZ, graphite and ZrC were done using procedure described in section 3.3.3.
5.3.2.2 X-ray Absorption Measurements

Zr K edge x-ray absorption measurements were done at the 10-ID-B beamline of the Advanced Photon Source, Argonne National Laboratory. Typical data acquisition window varied from \( k \) (photoelectron wave vector) = 0 to 14 Å\(^{-1}\) and spectra were collected with a fast scanning mode at various locations on a sample. Typically a 300(vertical) ×400(horizontal) μm\(^2\) beam was used and the spectra were taken with 400 μm steps vertically at all the sample faces. Powder samples were examined in transmission mode while solid samples were scanned in fluorescence mode using ion chamber with Stern Heald geometry. A pure Zr-foil (edge position of 17998 eV) was used as a reference with every scan to account for any shift in edge energy during acquisitions.

Since the spectra at different positions within a sample are the same within the noise level, the spectra from the same samples were averaged. The IFEFFIT suite of programs [43] were used to carry out the ab-initio calculations.

Data analysis was carried out using the standard EXAFS equation [38],

\[
\chi(k) = \sum_{j} \frac{N_j}{kR_j^2} F_j(k) e^{-2\sigma_j^2k^2} e^{-2R_j \lambda} \sin[2kR_j + \phi_j(k)]
\]  

(5.1)

where \( F_j(k) \), \( \phi_j(k) \) and \( \lambda(k) \) are the effective scattering amplitude, the phase shift and the mean free path of the photoelectron respectively. The factor \( k^2 \) is the square of photoelectron wave vector and is defined as follows,

\[
k^2 = \frac{2m_e(E-E_0)}{\hbar}
\]  

(5.2)
The threshold energy $E_0$ was assigned based on the value(s) of the highest inflection point obtained after aligning the scans. The data were imported into the Athena data analysis software [43] for deglitching, normalizing and background reduction [40]. We used Artemis [43] to model the structures where theoretical paths were generated using FEFF6 [43,80]. These paths (Zr-O, Zr-C and Zr-Zr) are listed in Table 5.1 and were calculated from references [81] and [82]. These data were used to model experimental FT (Fourier transform) magnitude patterns.

Fitting parameters included the amplitude reduction factor ($S_0^2$), energy shift ($\Delta E_0$), change in path length ($\Delta R$), and thermal and static disorder in the path lengths ($\sigma^2$). The $S_0^2$ value was determined by fitting the Zr foil. This value of $S_0^2$ was used for fitting the sample results. Data were iteratively fit until an R-factor (measure of absolute misfit between data and theory) of less than 10% was obtained. A two shell model was employed to accommodate NN (nearest neighbors, cation-anion) and NNN (next nearest neighbors, cation-cation) and to determine detailed atomic arrangements. Table 5.2 shows values of fitting parameters for various samples that will be discussed in further detail in the results and discussion section. These fitting processes are in accordance with methods described by Ravel et al. [43], Kelly et al. [40] and Newville [80].

Table 5.1 Crystallographic data of tetragonal zirconia and ZrC.

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<tr>
<th>Composition</th>
<th>ZrO$_2$</th>
<th>ZrC</th>
</tr>
</thead>
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<td>Phase</td>
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<td>Cubic</td>
</tr>
<tr>
<td>Zr-X</td>
<td>Zr-O$_I$</td>
<td>Zr-O$_{II}$</td>
</tr>
<tr>
<td>Path length (Å)</td>
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<td>2.39</td>
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<tr>
<td>Coordination</td>
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<td>4</td>
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Table 5.2 EXAFS fitting results for all the samples.

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<th>Coordination number</th>
<th>R ± dR (Å)</th>
<th>σ² ± dσ² (Å²)</th>
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</thead>
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<tr>
<td>3 mol% YSZ powder</td>
<td>Zr-O₁</td>
<td>4</td>
<td>2.13 ± 0.059</td>
<td>0.009 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Zr-Zr</td>
<td>12</td>
<td>3.62 ± 0.011</td>
<td>0.014 ± 0.002</td>
</tr>
<tr>
<td>3 mol% YSZ sintered (pellet)</td>
<td>Zr-O₁</td>
<td>4</td>
<td>2.13 ± 0.066</td>
<td>0.009 ± 0.002</td>
</tr>
<tr>
<td></td>
<td>Zr-Zr</td>
<td>12</td>
<td>3.62 ± 0.003</td>
<td>0.008 ± 0.001</td>
</tr>
<tr>
<td>ZrC (powder)</td>
<td>Zr-C</td>
<td>6</td>
<td>2.32 ± 0.032</td>
<td>0.004 ± 0.002</td>
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<tr>
<td></td>
<td>Zr-Zr</td>
<td>12</td>
<td>3.33 ± 0.007</td>
<td>0.003 ± 0.001</td>
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<tr>
<td>GPs</td>
<td>Zr-O₁</td>
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<td>2.13 ± 0.053</td>
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<tr>
<td></td>
<td>Zr-Zr (from t-ZrO₂)</td>
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<td>3.63 ± 0.002</td>
<td>0.009 ± 0.001</td>
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<tr>
<td></td>
<td>Zr-C</td>
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<td>2.34 ± 0.007</td>
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<tr>
<td></td>
<td>Zr-Zr (from ZrC)</td>
<td>12</td>
<td>3.28 ± 0.027</td>
<td>0.005 ± 0.001</td>
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5.4 Results and Discussion

5.4.1 X-ray Diffraction

Fig. 5.1 shows the X-ray diffraction pattern of the sintered YSZ pellet that confirms the presence of only the tetragonal phase. Following the carbothermal reduction heat treatment, XRD peak identification confirms the presence of ZrC and YSZ on the sample face in direct contact with graphite (Fig. 3.7 (d)). Based on Rietveld analysis, the sample is 57 mol% ZrC to a calculated [62] depth of ~16 μm.
5.4.2 EXAFS of 3 mol% YSZ Powder and Sintered Pellet

Crystallographic data for tetragonal ZrO$_2$, listed in Table 5.1, shows first and second shell (I and II) Zr-O and Zr-Zr distances. Previous efforts have used a simplified model to describe this system using fewer subshells [67,69,70,76]. Therefore only a single Zr-Zr path (Zr-Zr) with a coordination number of 12 was used to model the NNN shell (Zr to adjacent Zr) instead of two paths. A previous study [70] determined that for 3 mol% YSZ the EXAFS contribution of the Zr-O$_{\Pi}$ subshell decreases with increasing acquisition temperature—becoming negligible at room temperature. Therefore only the Zr-O$_{\Pi}$ subshell with a coordination number of 4 was employed in modeling the NN shell (Zr to adjacent O).

Fig. 5.2(a) shows the normalized EXAFS pattern for 3 mol% YSZ powder and corresponding $k^2\chi(k)$ (Fig. 5.2(b)) and Fourier transform magnitude (Fig. 5.2(c)). Since the two shell model gave a satisfactory fit, multiple scattering paths were not included. A similar methodology was followed for the sintered YSZ pellet, and the resulting fits are shown in fig. 5.3
Table 5.2 lists the values of the fitted parameters. For the 3 mol% YSZ powder, the NN shell comprised of the Zr-O₁ path was fitted to 2.13 Å as the bond length. The NNN shell consisting of the Zr-Zr bond was fitted to a bond length of 3.62 Å. These values are in agreement with Li et al. [67,69-71] and Rush et al. [76] for 3 mol% YSZ powders. Using the same procedure, Zr-O₁ and Zr-Zr bond lengths for the sintered YSZ pellet are 2.13 Å and 3.62 Å, respectively. Because the fit bond lengths are identical, it is reasonable to assume that sintering does not have any effect on the atomic structure (inter-atomic bond distances) and thus any existence of voids do not disrupt the structure.
Figure 5.2 Plots showing (a) normalized X-ray absorption spectra, (b) EXAFS or $k^2 \chi(k)$ pattern, (c), (d) and (e) Magnitude, real part and imaginary part of FT of EXAFS pattern for Powder 3 mol% YSZ. (b), (c), (d) and (e) are compared with their corresponding fitted curves generated using FEFF.
Figure 5.3 Plots showing (a) normalized X-ray absorption spectra, (b) EXAFS or $k^2\chi(k)$ pattern, (c), (d) and (e) magnitude, real part and imaginary part of FT of EXAFS pattern for sintered 3 mol% YSZ pellet. (b), (c), (d) and (e) are compared with their corresponding fitted curves generated using FEFF.

5.4.3 EXAFS of Pure ZrC Powder

Fig. 5.4(a) shows the normalized absorption spectrum with a corresponding $\chi(k)$ plot (Fig. 5.4(b)) and the modulus of the Fourier transform (Fig. 5.4(c)). Standard Zr-C and Zr-Zr path lengths (Table 5.1) were used to generate theoretical spectra. Fitting results gave Zr-C and Zr-Zr bond lengths of 2.32Å and 3.33Å for the pure ZrC powder that are in agreement with the values listed in Table 5.1.
Figure 5.4 Plots showing (a) normalized X-ray absorption spectra, (b) EXAFS or $k^2\chi(k)$ pattern, (c), (d) and (e) magnitude, real part and imaginary part of FT of the EXAFS pattern for pure ZrC powder. (b), (c), (d) and (e) are compared with their corresponding fitted curves generated using FEFF.

5.4.4 EXAFS of the GPs Pellet

The previously shown XRD pattern in fig. 3.7 confirmed the concurrent presence of ZrC in the YSZ matrix due to carbothermal reduction reaction. Fig. 5.5 shows the corresponding EXAFS standard path lengths of Zr-O$_1$ and Zr-Zr in tetragonal ZrO$_2$ and Zr-C and Zr-Zr in ZrC used to generate the theoretical spectra. The resultant fits determine Zr-O$_1$, Zr-Zr, Zr-C and Zr-Zr bond length values of 2.13 Å, 3.63 Å, 2.35 Å, and 3.28 Å, respectively. On comparing these values with those of the sintered YSZ pellet and the pure ZrC powder, there are no significant differences in bond length values with respect to the pure/standard phases. This implies there is no apparent strain or thermal effects produced in the pellet during the carbothermal reduction process.
5.5 Summary and Conclusions

EXAFS analysis was conducted on the Zr-K edge of 3 mol% YSZ powder, pure ZrC powder, sintered and GPs pellets. The magnitude of FT patterns from both powders and the sintered YSZ pellet served as standards to compare bond lengths to the carbothermally reduced pellet. It was determined that all the fitted bond length values are in excellent agreement when comparing the pure standards to the GPs sample. Sintering did not affect the inter-atomic bond distances. The results also imply that ZrC formed does not affect the cation-oxygen and cation-cation bond lengths of the parent YSZ phase. In addition, the Zr-C bond length remains unchanged from its standard value suggesting there is no apparent strain or thermally-induced effects on the near fine structure resulting from the carbothermal reduction process.
CHAPTER 6
INFLUENCE OF CARBOThERMAL REDUCTION REACTION ON YTTRIA STABILIZER
IN YTTRIA STABILIZED ZIRCONIA

6.1 Introduction

Carbothermal reduction of pure zirconia proceeds as previously mentioned in reaction (3.1). In a thermal protection application, we require conversion of 3 mol% YSZ to ZrC at the interface between the coating and the CCC. This presents a unique problem. When Y$_2$O$_3$ is doped in ZrO$_2$, Y$^{3+}$ ions replace some of the Zr$^{4+}$ ions. A 3+ yttrium in a 4+ zirconium site creates a net negative charge and, to maintain electroneutrality, positively charged oxygen vacancies are created in the matrix, equation 6.1. This stabilizes the high temperature phase(s) of ZrO$_2$ based on oxygen concentrations [16,83,84]. Y$_2$O$_3$ will not form a separate phase in Y$_2$O$_3$-ZrO$_2$ until the yttria content exceeds 30 mole% [85]. Due to this, the incoming carburizing species could interact with not just Zr but also with Y. This presents an interesting situation that needs a more thorough examination. Thus, the aim of this chapter is to understand the interaction of yttrium with carbon species and speculate on the consequent implications of using YSZ as a protective coating on CCCs.

\[ \text{Y}_2\text{O}_3 \rightarrow 2\text{YZr}^\prime + \text{VO}^\cdot\cdot + 3\text{O}_\text{O}^\cdot \quad (6.1) \]

6.2 Literature Review

Y$_2$O$_3$ is known to phase segregate in YSZ during annealing. The extent of this phenomenon is dependent on a combination of time and temperature and the amount of stabilizer present in the matrix. Numerous studies have attempted [86-92] to understand the mechanism
behind this behavior. Brandon et al. [86], Ilavsky et al. [87,89], Witz et al. [92] conducted experiments on plasma spray deposited YSZ coatings of varied dopant amounts. These were annealed for various times and temperatures, and the corresponding XRD patterns were recorded. These efforts found that depending on Y$_2$O$_3$ content the tetragonal phase decomposed into two phases--a yttrium rich cubic phase or yttrium enhanced tetragonal phase and a yttrium depleted monoclinic phase.

Ridder et al. [90] conducted studies using the time-of-flight low-energy ion scatter (LEIS) technique. The samples were prepared by precipitation method and then calcined at various temperatures. Results indicated the segregation of Y$_2$O$_3$ in the subsurface region of the samples, and the phenomenon was shown to be not influenced by the presence of any (additional) impurities in the system.

Schulz et al. [88] did similar heat treatments on electron-beam-physical vapor deposited (EB-PVD) YSZ films. X-ray fluorescence (XRF) and XRD examinations confirmed results similar to the ones mentioned above. Most of the studies have described the degradation phenomenon while very few have addressed the actual mechanism. In one such case, Ridder et al. [90] speculate that subsurface segregation of Y$_2$O$_3$ might be driven by strain relaxation and different bonding of Y$_2$O$_3$ particles with the contaminants in the matrix.

Hughes [93] suggested a mechanism by calculating the segregation enthalpy of Y$_2$O$_3$ in ZrO$_2$ using XPS results. The net free energy of Y$_2$O$_3$ segregation in ZrO$_2$ was found to be positive due to surface phase formation despite a negative free enthalpy contribution from the binary heat of mixing and solute strain energy contributions. Guo [94,95] proposed a space charge model for Y$_2$O$_3$ segregation in ZrO$_2$. The space-charge potential is defined as the
compensating charge developed in regions adjacent to the grain boundaries as the segregation of ions create excess electric potential in the grain boundary region. The space-charge potential of YSZ is negative due to a $\text{VO}^{2+}$ depletion in the space-charge layers and its very low grain-boundary conductivity. To ensure the bulk conductivity by the optimal dopant additions of $\text{Y}_2\text{O}_3$, segregation of $\text{Y}_2\text{O}_3$ would increase grain boundary conductivity and create a positive effective charge, and consequently, neutralize the negatively-charged contribution of oxygen vacancy depletion.

One of the important insights gained from these studies is that regardless of the degree of $\text{Y}_2\text{O}_3$ segregation, no separate yttria phase formation has been reported.

As discussed in previous chapters, our application requires formation of ZrC near the interfacial region between the 3 mol% YSZ and the CCC substrate. The resultant ZrC could either have Y either retained within the rocksalt structure or be excluded due to solubility limits. The resultant compound could have its crystal structure and/or the lattice parameter modified as we know from the case of YSZ. Limited amount of work has been cited for effect of Y doping in ZrC. Samsonov et al. [96,97] studied Y-ZrC made by sintering ZrC with 5 wt% metallic yttrium. Spectral emission analysis of the samples revealed that the yttrium content in ZrC did not exceed 1.5 to 2 wt% where the remaining Y formed $\text{Y}_2\text{O}_3$. Moreover, x-ray diffraction patterns of this material showed only ZrC with a lattice parameter similar to the pure phase.

The literature suggests that few studies focused on the mechanism of yttria segregation from YSZ. No work was found describing the influence of carbothermal reaction on the yttrium stabilizer in zirconia or a phase diagram for the Y-ZrO$_2$-ZrC.
6.3 Materials and Methods

6.3.1 Sample Preparation

Samples were prepared by mixing 3 mol% and 10 mol% YSZ with graphite using a mortar and pestle in a 1:3.3 molar ratio. This sample was heat treated in a graphite furnace using the procedure described in Chapter 1.

6.3.2 Characterization

XRD was employed to identify various phases present in the pure and reacted powder mixtures. A standard PDF file was used to index ZrC peaks as mentioned in Chapter 1. Y₂O₃ and 10 mol% YSZ phases were indexed with PDF file nos. 01-079-1257 and 01-070-4436. To create transmission electron microscope (TEM)/ energy dispersive spectroscopy (EDS) samples, these powders were sectioned and lifted out using a focused ion beam (FIB) on the NOVA dual beam tool.

6.4 Results and Discussions

6.4.1 X-ray Diffraction

The XRD pattern of 10 mol% YSZ, fig. 6.1, showed only the cubic zirconia phase. 3 mol% YSZ exhibits a mixed tetragonal (major) and monoclinic (minor) phase, fig. 1.2. Carbothermal reduction of the two powders yielded the formation of ZrC, but, in case of 10 mol% YSZ, Y₂O₃ was also present, fig. 6.2.
In Fig. 6.3, XRD patterns of the ZrC peaks formed from 3 and 10 mol% Y$_2$O$_3$-ZrO$_2$ were essentially the same suggesting that the initial yttria content had no impact on the carbothermal reduction product.

Figure 6.1 XRD pattern of 10 mol% YSZ powder showing cubic phase zirconia.
Figure 6.2 XRD pattern of carbothermally reduced 10 mol% YSZ powder showing ZrC formation with $Y_2O_3$ phase.

Figure 6.3 Graph comparing the spectra obtained from the ZrC powders made by carbothermal reduction of 3 mol% YSZ and 10 mol% YSZ samples.
6.4.2 Energy Dispersive Spectroscopy

The x-ray diffraction pattern for carbothermally reduced 10 mol% YSZ, fig.6.2, shows a presence of both ZrC and Y₂O₃. XRD does not describe how the Y₂O₃ is distributed within the ZrC; consequently, EDS elemental mapping and line scans were carried out on carbothermally reduced 3 and 10 mol% YSZ. These maps would yield more insight into the yttrium distribution in the samples. The TEM lift out samples were typically about around 20 μm in length. 3 mol% YSZ has almost a third of the amounts of yttria in it as compared to 10 mol% YSZ. Due to size constraints, a 20 μm lift out sample from reduced 3 mol% YSZ powders would further reduce the chances of any Y₂O₃ detection. Thus EDS on reduced 10 mol% YSZ powders were done to get better insights.

6.4.2.1 Carbothermally Reduced 3 mol% YSZ

As discussed in section 6.1, in YSZ, Y⁺³ ions reside on Zr⁺⁴ ion sites and oxygen vacancies are created to maintain electroneutrality. Based on the literature, yttrium would be evenly distributed with a 3 mol% YSZ powder. EDS elemental mapping of the carbothermally reduced powder showed most regions to be ZrC rich and Y free. The EDS scan in Fig. 6.4 shows a small circular-shaped Y-rich region.
Figure 6.4 (a) STEM image showing the area of interest on the lift out sample of ZrC formed from 3 mol% YSZ. The mapped region is marked using green arrow. (b), (c), (d) and (e) show the elemental maps so acquired for Zr, Y, C and O elements. (f) and (g) show the elemental composition(s) from spot A and spot B on the sample.

6.4.2.2 10 mol% YSZ Powder

Fig. 6.5, 6.6 and 6.7 show EDS line scans from various locations in the sample. As dictated from the defect chemistry, equation 6.1, for $\text{Y}_2\text{O}_3$ in $\text{ZrO}_2$, the Y was found to be evenly distributed with Zr along the scan lengths. These results are further cemented by the elemental area maps in fig. 6.8, 6.9 and 6.10 where Y is evenly distributed in the YSZ matrix. The respective average O, Y and Zr atomic percentages were found to be approximately 70%, 5%
and 25% from various locations on the sample. These are in reasonable agreement with the approximate stoichiometric values of 65, 7, and 28%.

Figure 6.5 STEM Images and EDS line scans from one of the locations on the 10 mol% YSZ sample. (a) and (b) STEM and corresponding BF images respectively. (c), (d) and (e) show the location of the beam marker (red cross) relative to the sample and (i), (j) and (k) show the
obtained atomic spectra from these locations. (f), (g) and (h) show the variation of Zr, Y, C, Cu and O elements along the length of the scan.

Figure 6.6 STEM Images and EDS line scans from one of the locations on 10 mol% YSZ sample. (a) and (b) STEM and corresponding BF images respectively. (c), (d) and (e) show the location of the beam marker (red cross) relative to the sample and (i), (j) and (k) show the
obtained atomic spectra from these locations. (f), (g) and (h) show the variation of Zr, Y, C, Cu and O elements along the length of the scan.

Figure 6.7 STEM images and EDS line scans from one of the locations on 10 mol% YSZ sample. (a) and (b) STEM and corresponding BF images respectively. (c), (d) and (e) show the location of the beam marker (red cross) relative to the sample and (i), (j) and (k) show the obtained
atomic spectra from these locations. (f), (g) and (h) show the variation of Zr, Y, C, Cu and O elements along the length of the scan.

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<th>Element</th>
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<td>Y</td>
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<tr>
<td>O</td>
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Figure 6.8 Images showing the EDS area map results from one of the locations on 10 mol% YSZ sample. (a) and (b) show BF and corresponding STEM images respectively. (c), (d) and (e) show the distribution of Zr, Y and O elements in the scanned area. The red cross shows the location of the beam relative to the atomic spectra obtained and shown in (f).
Figure 6.9 Images showing the EDS area map results from one of the locations on 10 mol% YSZ sample. (a) and (b) show BF and corresponding STEM images respectively. (c), (d) and (e) show the distribution of Zr, Y and O elements in the scanned area. The red cross shows the location of the beam relative to the atomic spectra shown in (f).

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Figure 6.9 Images showing the EDS area map results from one of the locations on 10 mol% YSZ sample. (a) and (b) show BF and corresponding STEM images respectively. (c), (d) and (e) show the distribution of Zr, Y and O elements in the scanned area. The red cross shows the location of the beam relative to the atomic spectra shown in (f).
Figure 6.10 Images showing the EDS area map results from one of the locations on 10 mol% YSZ sample. (a) and (b) show BF and corresponding STEM images respectively. (c), (d) and (e) show the distribution of Zr, Y and O elements in the scanned area. The red cross shows the location of the beam relative to the atomic spectra shown in (f).

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6.4.2.2 Carbothermal Reduction of 10 mol\% YSZ Powder

EDS mapping of carbothermally reduced 10 mol\% YSZ powder shows various pockets of $\text{Y}_2\text{O}_3$ segregations. Figs. 6.11, 6.12, 6.13, and 6.14 present the obtained images from various parts of the sample. These elemental pictures suggest that the pockets are formed by Y diffusing out along the grain boundaries of the Zr rich matrix and then segregating at the nexus of several grain boundaries.

Average Y and Zr atomic percentages in Y rich regions were found to be 66.9\% and 7.7\%, respectively, and average Y and Zr atomic percentages in Zr rich regions were found to be 2.3\% and 84.6\% respectively. The 2.3\% Y in the ZrC compares well to the solubility limit of 1.5-2\% proposed by Samsonov et al. Elemental quantification carried out on the overlapping regions showed average Y and Zr atomic percentages to be approximately 34.4\% and 43.0\%, respectively.
Figure 6.11 Images showing the EDS area map results from one of the locations on carbothermally reduced 10 mol% YSZ sample. (a) and (b) show the STEM and corresponding BF images respectively with the area of acquisition marked by the green arrow. (c), (d) and (e) show the distribution of Zr, Y, C and O elements from the scanned area. The red cross (spot A and spot B) in these images show the location of the beam relative to atomic spectra shown in (f) and (g).
Figure 6.12 Images showing the EDS area map results from one of the locations on carbothermally reduced 10 mol% YSZ sample. (a) shows the STEM image with the area of acquisition marked by the green arrow. (b), (c) and (d) show the distribution of Zr, Y, C and O elements from the scanned area. The red cross (spot A and spot B) in these images show the location of the beam relative to atomic spectra shown in (e) and (f).
Figure 6.13 Images showing the EDS area map results from one of the locations on carbothermally reduced 10 mol% YSZ sample. (a) shows the STEM image with the area of acquisition marked by the green arrow. (b), (c) and (d) show the distribution of Zr, Y, C and O elements from the scanned area. The red cross (spot A and spot B) in these images show the location of the beam relative to atomic spectra shown in (e) and (f).
6.4.3 Discussion on the Phase Separation of Y$_2$O$_3$ from ZrC

XRD results show Y$_2$O$_3$ with ZrC in carbothermally reduced 10 mol% YSZ powders. These yttria peaks are not observed for the case of reduced 3 mol% YSZ due to low Y content. As mentioned previously, ZrC peak positions for both 3 and 10mol% yttria samples have the
same 2 theta values. Fig. 6.3 compares the XRD spectra from the two reduced powders. This indicates a very low solubility of $Y_2O_3$ in ZrC. Moreover, amounts of Y are left in ZrC grains has no influence on the crystallography of itunlike Y in YSZ that is known to alter the crystal structure and lattice parameter which is not observed in our studies. Similar results have been found for Y metal in ZrC by Samsonov et, al. [96,97].

EDS mapping conducted on the samples found grains of $Y_2O_3$ at various locations on the sample. In 3 mol% YSZ, the size and distribution of $Y_2O_3$ rich pockets are small for the carburized powder. 10 mol% YSZ powders have a higher Y content and thus form bigger yttrium-rich regions. These grains were found to be uniformly distributed within the sample and amidst ZrC grains. The ZrC grains were devoid of any Y. Based on the EDS elemental maps, Y is diffusing via ZrC grain boundaries and forming yttria at grain boundary junctions. EDS elemental quantification has limits at low concentrations; therefore, the exact solubility limit of the two phases ($Y_2O_3$ and $ZrO_2$) cannot be determined precisely.

6.5 Summary and Conclusions

The XRD and EDS analyses were carried out on carbothermally reduced 3 mol% and 10 mol% YSZ. In the reduced 10 mol% YSZ powder, $Y_2O_3$ peaks were observed in the XRD spectra while no such peaks were seen for the 3mol% sample. The ZrC phase in both samples had the same diffraction peaks suggesting that $Y_2O_3$ has no effect on the crystal structure and lattice parameter of the resultant matrix. These results are supported by the findings of Samsonov et al.[96,97] who discovered similar results for the case of Y metal in ZrC sintered powders. EDS mapping showed the formation of $Y_2O_3$ grains in the two reduced samples within the ZrC. $Y_2O_3$ pockets were found to be larger for reduced 10 mol% YSZ because of the
much higher Y concentration in starting powder and the limited solubility of Y in ZrC. Elemental images suggest that yttrium diffuses by grain boundaries and coalesces at the grain boundary junctions to form Y$_2$O$_3$ grains. Because of the low solubility of yttrium in ZrC, carbothermal reduction of yttria-stabilized zirconias will result in Y$_2$O$_3$ precipitates.
7.1 Summary and Conclusion

The carbothermal reduction mechanism of YSZ was investigated experimentally and computationally. Theoretical investigations showed that any reaction of ZrO2 with CO and CO2 would form negligible amounts of ZrC at equilibrium. Experimental studies using quantitative x-ray diffraction confirmed that more ZrC formation in the samples (GP and GPs) where C was the major carburizing species (74% maximum ZrC formation). On the other hand, samples in which CO is more available for reaction showed lesser amounts of conversion and thus CO was identified as a minor player for driving carbothermal reduction reactions. Two separate thermochemical models—ZrO2 + C + Ar and ZrO2 + CO + Ar were studied using FactSage thermochemical modeling software. At 1800ºC, the C activity and CO partial pressure were varied from a value of 0.1 to 1.0 in these models and reaction products were compared. An activity of 0.31 was found to completely convert ZrO2 to ZrC. In contrast, a partial pressure of 1 atm of CO formed only 0.08 moles of ZrC leaving 0.92 moles of ZrO2 unreacted. From these calculations and not neglecting the role of CO in the GP, MP, GPs and MPs samples, it is reasonable to conclude that C is the major species driving the carbothermal reduction mechanism of ZrO2.

Zr K-edge EXAFS studies on a mixed phase sample showed both ZrO2 and ZrC present. Results showed that the formation of ZrC within YSZ does not affect the bond lengths of either compound (Zr-O, Zr-C, Zr-Zr). There is no evidence of strained bonds resulting from carbothermal reduction. STEM-EDS analysis was carried out on carbothermally-reduced 3 mol%
YSZ and 10 mol% YSZ powders to understand the influence on Y\textsubscript{2}O\textsubscript{3} stabilizer. Yttrium (or yttria) was found to diffuse through ZrC grains and form yttria regions at grain boundary junctions. This phenomenon has not been previously reported.

7.2 Future Work

The work entailed in this dissertation is a stepping stone towards using 3 mol% YSZ as an EBC/TBC for carbon-carbon composites. The following framework could lead to successful application of this idea.

(1) CO and CO\textsubscript{2} mixtures can cause activity of C to change drastically. This can potentially lead to precipitation of C from this mixture and thus trigger carbothermal reduction of ZrO\textsubscript{2}. Thus various CO/CO\textsubscript{2} gas ratios need to be tested at high temperatures. Mass spectrometry of the product gases should be used in these experiments to determine the threshold temperature of the reduction reaction. Further, mass spectroscopy could be used to better understand the thermodynamics of this reaction.

(2) ZrO\textsubscript{2} is known as a fast oxygen ion conductor with a diffusion coefficient of the order of \( \sim 10^{-10} \) m\(^2\)/sec. Surprisingly, C diffusion in ZrO\textsubscript{2} has been found to follow very slow kinetics \( (3 \times 10^{-14} \) m\(^2\)/sec at 1800 °C). This is unusual as C and O sit in periodic table in the same row and thus have same number of shells and slightly different atomic number. Few of the reasons that cause this difference could be that oxygen transport is realized through oxygen vacancies which would be relatively faster than carbon diffusion via oxygen vacancies. In addition to this, C\textsuperscript{4-} has an ionic radius of 2.6Å whereas O\textsuperscript{2-} is only 1.38Å. This difference in size could be another benefactor in the faster mobility of oxygen ion. A more intricate investigation into this problem should be made because this could help us potentially understand the C reaction mechanism with ZrO\textsubscript{2}.
Previous researchers have described the formation of a stable zirconium oxycarbide (ZrC$_{0.9}$O$_x$, $x = 0.04-0.08$) phase with a lattice parameter (4.688 Å) smaller than that of ZrC (4.693 Å). To better understand oxygen incorporation into ZrC, we propose to conduct high resolution XRD and EXAFES on carbothermally reduced powders at a synchrotron facility.

To create a more viable thermal protection coating, 3 mol% YSZ has to be infiltrated in the CCCs. A suitable process like sol-gel needs to be employed, and experiments need to be conducted to determine the extent of infiltration and the conditions to optimize this process.
BIBLIOGRAPHY


48. 'micron.ucr.edu/public/manuals/EDS-intro.pdf'.


96. G. V. Samsonov, V. A. Lavrenko, V. S. Neshpor, L. N. Okhremchuk, T. A. Podchernyaeva, V. S. Fomenko and A. I. Chekhovskii, 'Reaction of hydrogen atoms with the surface of yttrium-