Studies of the Yttrium Tantalate – Zirconium Oxide Quasi-Binary

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Studies of the Yttrium Tantalate – Zirconium Oxide Quasi-Binary

A dissertation presented

by

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ABSTRACT

For thermal barrier coating (TBC) applications, the high temperature tetragonal phase of ZrO\textsubscript{2} has been the widely used material for years due to its many favorable properties, including low thermal conductivity and high thermal expansion coefficient. It is known that the addition of Y\textsubscript{2}O\textsubscript{3} stabilizes the t-phase to room temperature, enabling its use in TBCs. However, as engine operating temperatures push to higher temperatures, challenges with phase stability and heat transport become apparent, leading to a search for new TBC materials. One promising candidate is the YO\textsubscript{1.5}-TaO\textsubscript{2.5}-ZrO\textsubscript{2} system. This dissertation explores the synthesis, structural characterization, and thermal and optical properties of compositions along the YTaO\textsubscript{4}-ZrO\textsubscript{2} quasi-binary.

Using a variety of characterization techniques, the phase diagram along the YTaO\textsubscript{4}-ZrO\textsubscript{2} quasi-binary is developed. The behavior of the crystal structures and the phase transformations within the YTaO\textsubscript{4} solid solution region is explored as a function of ZrO\textsubscript{2} content. The extent of the solubility limits for the YTaO\textsubscript{4} and ZrO\textsubscript{2} phases is established as a function of temperature, revealing a two-phase regime in the intermediate region of the YTaO\textsubscript{4}-ZrO\textsubscript{2} quasi-binary. The implications of this intermediate region include an extensive stable tetragonal phase field, small grain size with limited grain growth, and low thermal conductivity that is independent of temperature. The two tetragonal phases display structural
similarities, which when combined with the microstructural analysis of compositions in this intermediate region, suggests the presence of a higher temperature phase above 1600°C.

Next, the heat transfer behavior is investigated for compositions along the YTaO$_4$-ZrO$_2$ quasi-binary using thermal and optical techniques. The experimental results indicate compositions in the intermediate region are better thermal insulators than the current yttria-stabilized zirconia TBC coatings. Additionally, the thermochemical compatibility between the quasi-binary compositions and alumina is studied since alumina is the most commonly formed TGO in TBCs.
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CHAPTER 1

Introduction

Protecting gas turbine engine components from high temperature environments has been a challenging task for many years. To combat oxidation and provide thermal insulation for the metallic components, engineers have utilized a multilayered materials system known as a thermal barrier coating, or TBC. TBCs are typically composed of four different layers, as shown in Figure 1.1.

1. Topcoat: 100-400 micron thick thermally insulating and strain tolerant oxide, usually 3-4 mol% $\text{Y}_2\text{O}_3$ stabilized $\text{ZrO}_2$ which is equivalent to 7 wt% $\text{Y}_2\text{O}_3$ (known as 7YSZ)
2. Thermally grown oxide (TGO): 1-10 micron layer which forms during high temperature by oxidation and serves as an oxidation barrier, predominately $\text{Al}_2\text{O}_3$
3. Bond-coat: 100 micron metallic layer that acts as an aluminum reservoir for the formation of the TGO, resists creep/plastic yielding, and adheres to the topcoat
4. An internally cooled superalloy substrate: Ni-based superalloy, which sustains structural loads.

The combination of TBCs and cooling techniques has allowed engine operating temperatures to exceed the temperature limitations of the metallic components, leading to a substantial increase in engine efficiency over the years\(^1\) (see Figure 1.2). However, the next generation of engines is targeting operating temperatures upwards of 1500°C, which surpasses the temperature capabilities of current coatings. In particular, problems with the topcoat compromise the durability of the TBC.
Figure 1.1 – TBC Diagram
Schematic illustration of the thermal barrier coating system.

Figure 1.2 – Improvement of Engine Operating Temperatures
Advancement of temperature capabilities of Ni-based superalloys and thermal-barrier coating (TBC) materials over the past 50 years. The red lines indicate maximum allowable gas temperatures in engines. Reproduced from Clarke et al.\textsuperscript{1}
There are three critical limitations with using 7YSZ at these higher operating temperatures. First is phase stability over the entire temperature range. Known widely as t’-YSZ, the tetragonal phase field of zirconia is extended when doped with yttria, leading to a small compositional window in which the tetragonal phase is “nontransformable” for current engine operating temperatures. 7YSZ resides within the metastable region, shown in Figure 1.3. The temperature requirements for the next generation of TBCs exceed the \( T_0(c/t) \) line of the t’-phase, and prolonged exposure at elevated temperatures results in decomposition of 7YSZ to a Y-lean tetragonal phase and Y-rich cubic phase\(^2\). Upon cooling, the Y-lean tetragonal phase crosses the \( T_0(t/m) \) line and transforms to the monoclinic phase. The volume change accompanying the transformation causes cracking and delamination of the coating, thus reducing its durability.
Figure 1.3 – YSZ Metastable Phase Diagram

Metastable phase diagram of the zirconia-rich portion of the ZrO$_2$-YO$_{1.5}$ binary system. The equilibrium phase fields are delineated with solid lines, while the metastable phase fields are marked with dashed lines. The operating region of 7YSZ is indicated by the purple box. Adapted from Chevalier et al.\textsuperscript{3}

The second challenge with 7YSZ is its effectiveness as a thermal insulator at higher temperatures. The internal temperature the TBC, namely at the metal-oxide interface, is set by the external temperature of the hot gas in the engine and the heat that can be conducted away by internal cooling. As the external gas temperature increases, so does the interface temperature, which can cause deformation of the metal if the temperature is too hot. Since the thermal conductivity of 7YSZ at high temperatures is an intrinsic property, the only way to
reduce the internal temperature at higher engine operating temperatures is to increase the
thickness of the 7YSZ layer, thus increasing the temperature drop between the hot gas and
metal-oxide interface. However, the increased thickness results in extra weight on the rotating
engine components, reducing the performance of the engine. In the case of 7YSZ, the upper
temperature limit is set by the phase transformation of the t’-phase, and not its thermal
conductivity capabilities. However, any stable oxide with thermal conductivities comparable
to 7YSZ would require an increase in thickness at higher temperatures, thus the oxide’s
intrinsic thermal conductivity sets the maximum operating temperature. This indicates that
oxide materials with lower thermal conductivities are necessary for the next generation of
TBCs.

The final challenge facing current TBCs is high temperature corrosion by molten silicate
deposits, commonly referred to as CMAS (calcium-magnesium-alumino-silicate). During
operation, engines ingest fine particulates from the environment, such as sand and volcanic
ash. These particulates melt due to the temperatures within the engines being higher than their
melting points. This leads to wetting of the TBC, which readily reacts with the CMAS. The
penetration of the CMAS reduces the TBC’s ability to accommodate the strain incompatibility
of the oxide-metal interface, leading to cracking and delamination. Additionally, the reaction
between the CMAS and 7YSZ results in the precipitation of a modified oxide which lacks the
favorable properties of the t’-phase. This reduces the effectiveness of the TBC as an insulator.
To address the CMAS problem, the compositions and microstructures of future TBCs will
need to be tailored to resist the attacks, either through prevention of the wetting or the
formation of a sealing layer to restrict the penetration depth of the molten silicate into the coating.

The limitations of the current TBCs have led to a search for high temperature oxide materials that could replace 7YSZ. Many oxides have been previously explored, including Al₂O₃ and GdZrO₇, yet none of them have successfully met all the requirements of the topcoat (given in Table 1.1).

<table>
<thead>
<tr>
<th>Table 1.1 – Requirements for oxide materials used as topcoats in TBCs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low thermal conductivity</td>
</tr>
<tr>
<td>High thermal expansion coefficient</td>
</tr>
<tr>
<td>Highly compliant/strain tolerant</td>
</tr>
<tr>
<td>Resistant to erosion &amp; corrosion</td>
</tr>
<tr>
<td>High melting point</td>
</tr>
<tr>
<td>Low density</td>
</tr>
<tr>
<td>Chemically inert</td>
</tr>
<tr>
<td>Phase stability</td>
</tr>
<tr>
<td>High fracture toughness</td>
</tr>
</tbody>
</table>

Recently, oxide compositions in the YO₁.₅-TaO₂.₅-ZrO₂ system have demonstrated favorable attributes, which suggest they may satisfy the topcoat requirements.

The primary goal of this work was to investigate oxide compositions in the YO₁.₅-TaO₂.₅-ZrO₂ system that could potentially replace 7YSZ in the next generation of TBCs. Compositions along the YTaO₄-ZrO₂ quasi-binary are very promising and thus served as the focus of this work. Interest in the quasi-binary also stems from the displacive phase transformations observed in the end compositions. Due to the importance of phase stability for TBCs, the
phase evolution of these compositions was investigated as a function of temperature, leading to the development of the YTaO₄-ZrO₂ quasi-binary phase diagram. The thermal and optical properties were also explored to address issues with heat transport through the oxide materials. Lastly, the thermochemical compatibility between compositions along the quasi-binary and alumina was studied because the TGO in TBCs is most commonly alumina¹⁰.

The chapter following this introduction presents a review of the current understanding of the phases in the YO₁.₅-TaO₂.₅-ZrO₂ system, including the phase stability of tetragonal YSZ, as well as the previous work, to which I contributed, investigating compositions along the YTaO₄-ZrO₂ quasi-binary. In Chapter 3, the experimental methods are summarized, including sample preparation and characterization techniques. Chapter 4 presents the results from the phase studies of the YTaO₄ solid solution, establishing the limits of the phase field and exploring changes in the YTaO₄ structures. In Chapter 5, the phase behavior is examined in the intermediate region of the YTaO₄-ZrO₂ quasi-binary, accumulating in the development of the YTaO₄-ZrO₂ quasi-binary phase diagram. As a method of assessing heat transport through the materials, the thermal and optical properties along the YTaO₄-ZrO₂ quasi-binary are explored in Chapter 6. In Chapter 7, the compatibility between compositions along the YTaO₄-ZrO₂ quasi-binary and alumina is evaluated since use of these materials as TBCs necessitates thermochemical compatibility with the TGO layer. Lastly, conclusions and recommendations for future work are presented in Chapter 8.
CHAPTER 2

Background

The push for higher operating temperatures and more efficient gas turbine engines has brought to light the limitations of current TBC systems, particularly regarding the chemical and phase stability of YSZ at high temperatures. Improvements in the capabilities of current coatings continue to be made, but it is evident that the next generation of turbines will require new TBC systems. The search for high temperature TBC materials to replace YSZ has led to an interest in the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ system, which has revealed several promising attributes for TBC applications, including the presence of a non-transformable tetragonal region. This chapter reviews the current understanding of the end points of the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ system and the binary systems between them. The work in the Zr-rich end which led to the interest in this system is also discussed.

2.1 The ZrO$_2$-Y$_2$O$_3$ System

2.1.1 Phases of Zirconia

Under ambient pressure, zirconia exhibits three polymorphs: monoclinic (m, P2$_1$/c), tetragonal (t, P4$_2$/nmc), and cubic (c, Fm$ar{3}$m). Their structures are illustrated in Figure 2.1. The monoclinic phase exists up to 1170°C, at which point it undergoes a transformation to the tetragonal phase. The tetragonal phase is stable over the 1170-2370°C temperature range. At 2370°C, the cubic phase becomes the equilibrium phase until the melting point at 2710°C.
The crystallographic information for the three phases is given in Table 2.1. The primitive t-phase unit cell is one-half the volume of the m-phase and c-phase unit cells.

The monoclinic structure is characterized by a seven-fold coordination of the Zr\(^{4+}\) ions and a layering of triangular coordination polyhedral of O\(_7\)Zr\(_3\) and distorted tetrahedral of O\(_{12}\)Zr\(_4\). The tetragonal structure demonstrates eight-fold coordination of the Zr\(^{4+}\) ions\(^{13}\), with two sets of Zr-O distances, while the cubic structure adopts a fluorite-type structure with eight-fold coordination of the Zr\(^{4+}\) ions\(^{14}\). Although the Zr\(^{4+}\) has eight-fold coordination in the tetragonal and cubic phases, its ionic radius is smaller than the ideal eight-fold coordination radius ratio minimum\(^{15}\), resulting in a distortion of the oxygen sublattice in the tetragonal phase and seven-fold coordination in the monoclinic phase.

---

**Figure 2.1 – Polymorphs of ZrO\(_2\)**

*The unit cells of the polymorphs of ZrO\(_2\) under ambient pressure*
The reversible transformation between the monoclinic and tetragonal phases is a martensitic transformation which is governed by a diffusionless shear mechanism\textsuperscript{16,17}. There is considerable hysteresis between the m→t (1170°C) and t→m (950°C) transition temperatures in polycrystalline materials, creating a coexistence region where both monoclinic and tetragonal phases occur simultaneously. By heating monoclinic Zirconia to a temperature in this region, the formation of tetragonal Zirconia is triggered, and domains will form within the monoclinic matrix. The coexistence of two phases produces a large strain energy, which halts any further transformation. Therefore, the temperature must be changed in order to continue the transformation. Experiments have confirmed that the amount of transformation is only a function of temperature, for both the forward and reverse reactions\textsuperscript{18}.

2.1.2 Stabilization of Zirconia

The tetragonal and cubic phases can be stabilized to lower temperature by doping ZrO\textsubscript{2} with lower-valent oxides\textsuperscript{19–22}, such as Y\textsubscript{2}O\textsubscript{3} or CeO\textsubscript{2}, or by decreasing the grain size to nanometer values\textsuperscript{23,24}. The addition of allovalent cation dopants creates oxygen vacancies to compensate for excess charge, which can be expressed using the Kroger-Vink notation
\[
R_x O_y \xrightarrow{ZrO_2} x \cdot R_{Zr}^{\frac{2y}{4}} + y \cdot O^2_0 + (y - 2x) \cdot V^+_0
\]  
(Equation 2.1)

assuming that the dopants are lower-valent oxides. The dopants also cause a dilation of the cation sublattice sites, which results in the Zr\(^{4+}\) ions having an environment closer to seven-fold coordination. The combination of the anion vacancies and the distortion of the cation environments allows the high temperature phases to be retained to lower temperatures. Typically, the cations used for the stabilization of the t- and c-phases have larger ionic sizes and lower charge states than the Zr\(^{4+}\) ion. Moreover, the dopant choice determines if stabilization of the cubic phase is possible since not every dopant stabilizes both high temperature phases.

In the case of state of the art TBCs, the dopant of choice has been Y\(_2\)O\(_3\). The phase diagram for the ZrO\(_2\)-Y\(_2\)O\(_3\) system (see Figure 2.2) has been studied extensively\(^{25-28}\). There is almost no solubility of Y\(_2\)O\(_3\) into m-ZrO\(_2\), while t-ZrO\(_2\) will incorporate a modest amount of Y\(_2\)O\(_3\). However, the c-ZrO\(_2\) solid solution is extensive, even stabilizing down to low temperatures. This enables the use of the c-phase in an equilibrium form in room temperature conditions. Unfortunately, the same does not hold true for the t-phase, which is limited by the m-t transformation and can only exist in a metastable form at low temperatures. Because the kinetics of the m-t transformation is limited by the slow cation diffusion in this system, the metastable t-phase is stable at low temperatures\(^{29,30}\). Unfortunately, the metastable tetragonal form decomposes to the m- and c-phases after long exposure at high temperatures.
The m-t transformation in yttria-stabilized zirconia is accompanied by a 4% volume change. This volume change is important for two reasons: (1) it is the basis of transformation toughening in ZrO$_2$\cite{31-35} and (2) it leads to cracking in the TBCs which is detrimental to their durability. Transformation-toughened ZrO$_2$ is fabricated such that discrete transformable tetragonal grains exist at room temperature, meaning the transformation temperature has been suppressed. When stress is applied to the system, such as in a propagating crack, the particles transform to their monoclinic phase. The change in volume associated with the transformation reduces the crack’s driving force, leading to toughening of the material. Unfortunately, this

\textit{Figure 2.2 – ZrO$_2$-YO$_{1.5}$ Phase Diagram}

\textit{Phase diagram of the ZrO$_2$-YO$_{1.5}$ binary. Adapted from Fabrichnaya et al.\cite{28}}
toughening mechanism is only applicable at temperatures lower than the current desired engine operating temperatures since the t-m transformation is thermodynamically prohibited at these high temperatures.

2.1.3 Addition of Ta$_2$O$_5$ to YSZ

In an attempt to overcome the high temperature limitations of YSZ, other dopants have been added to the system, including HfO$_2$, Nb$_2$O$_5$, and Ta$_2$O$_5$ \cite{36-38}. One prospective candidate that has garnered attention is Ta-doped YSZ, which is stable up to 1500\degree C. Like HfO$_2$, Ta$_2$O$_5$ serves as a destabilizer of both the t- and c-phases in the ZrO$_2$-Y$_2$O$_3$ system. The Ta$_2$O$_5$-alloying results in an increase in the distortion of the lattice, leading to an increase in the tetragonality (c/a) of the YSZ phase \cite{36}. This is counter to the incorporation of stabilizing oxides, such as Y$_2$O$_3$, which decrease the tetragonality of the ZrO$_2$ phases. The addition of Ta$_2$O$_5$ also increases the m-t transformation temperature, as well as the fracture toughness of the YSZ. This is consistent with an increase in tetragonality. Unfortunately, the solubility of Ta$^{5+}$ into ZrO$_2$ is quite small (\~2 mol\% Ta$_2$O$_5$), but the co-doping of ZrO$_2$ with Y$^{3+}$ and Ta$^{5+}$ gives rise to solubility limits that are larger than that of Y$^{3+}$ or Ta$^{5+}$ alone, thus leading to an interest in YTaO$_4$.

2.2 The Y$_2$O$_3$-Ta$_2$O$_5$ System

2.2.1 Phases along the Binary

The Y$_2$O$_3$-Ta$_2$O$_5$ system is the next best explored binary in the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ system \cite{39-41}. There are five established phases along the binary: Y$_2$O$_3$, Y$_3$TaO$_7$, YTaO$_4$, YTa$_3$O$_9$, and
Ta$_2$O$_5$ (see Figure 2.3). Another phase YTa$_7$O$_{19}$ also exists towards the Ta-rich end, but this phase disappears once heat treated above 1650°C$^{42}$.

![Figure 2.3 – Y$_2$O$_3$-Ta$_2$O$_5$ Phase Diagram](image)

*Figure 2.3 – Y$_2$O$_3$-Ta$_2$O$_5$ Phase Diagram*

Phase diagram of the Y$_2$O$_3$-Ta$_2$O$_5$ system at high temperatures. Additional work shows the existence of orthorhombic phases in the Y$_3$TaO$_7$ phase field. Adapted from Bondar et al$^{41}$.

Y$_2$O$_3$ exhibits a cubic structure with a small tolerance for Ta$_2$O$_5$ and has the highest melting point (~2400°C) of the binary. Additional work has shown that Y$_2$O$_3$ exists as a hexagonal structure over the temperature range 2300-2400°C. At the other end of the binary, Ta$_2$O$_5$
exists in its orthorhombic low temperature $\beta$-Ta$_2$O$_5$ form up to 1360°C, where it undergoes a reversible phase transition to its tetragonal high temperature $\alpha$-Ta$_2$O$_5$ form$^{43}$. The solubility of Y$_2$O$_3$ into Ta$_2$O$_5$ is quite limited at high temperatures, and the melting point of Ta$_2$O$_5$ ($\sim$1875°C) is much lower than that of Y$_2$O$_3$, leading to low melting points for all the phases on the Ta-rich side in the binary system. This is a stark contrast to the ZrO$_2$-Y$_2$O$_3$ system for which the phases all melt at similar temperatures.

There remains some uncertainty over the structure of the Y$_3$TaO$_7$ compound and its compositional range. At lower temperatures, Y$_3$TaO$_7$ adopts an orthorhombic weberite structure over the 75-80 mol% Y$_2$O$_3$ compositional range. The weberite phase undergoes a reversible transformation to a defect fluorite structure at 1600°C$^{44}$. Another orthorhombic phase exists up to 1700°C for the 70-72 mol% Y$_2$O$_3$ compositions, which is regarded as Y$_{10}$Ta$_4$O$_{25}$. This orthorhombic phase coexists with the defect fluorite phase at high temperatures for the Y$_3$TaO$_7$ composition, even though Y$_3$TaO$_7$ is a single phase at lower temperatures$^{39,45}$. Unfortunately, due to the weak intensity of the ordered peaks of the orthorhombic phase$^{46}$, there is difficulty establishing phase boundaries for the Y$_3$TaO$_7$ phase field. The YTa$_3$O$_9$ and YTaO$_4$ phases exist over a much smaller compositional range, demonstrating much less tolerance for excess Y$^{3+}$ and Ta$^{5+}$. YTa$_3$O$_9$ adopts an orthorhombic perovskite structure$^{47}$ and melts at 1800°C. The last composition, YTaO$_4$, has been a major focus of this work.
2.2.2 Behavior of YTaO₄

YTaO₄ exhibits three crystal structures: high-temperature tetragonal form (T) and two room-temperature monoclinic forms (M and M’). These two monoclinic phases exhibit distinct structural differences, the most significant being the coordination of the Ta atoms and the unit cell size (see Figure 2.4 and Table 2.2). In the M’-phase, the cations arrange themselves in separate layers, with the Y³⁺ assuming eight-fold coordination and the Ta⁵⁺ assuming six-fold coordination. However, in the M-phase, the cations occupy different sites within each layer, and the Ta⁵⁺ ions have assumed a tetrahedral configuration. Given that one M-phase unit cell is approximately equal to two M’-phase unit cells, there is almost no difference in the volume of these two phases.

![YTaO₄ Monoclinic Structures](image)

**Figure 2.4 – YTaO₄ Monoclinic Structures**
Comparison of the room temperature M’-YTaO₄ (left) and M-YTaO₄ (right) structures. One unit cell is drawn in black for each phase. The difference in coordination number of the tantalum is shown by the polyhedrons.
During heating, the M’ structure undergoes an irreversible, very sluggish first-order transformation to the T structure, which exhibits a scheelite-type structure (space group: I \textit{4}_{1}/a), at temperatures above 1450°C. Upon cooling, the M’-phase cannot be recovered, and instead the T-phase undergoes a reversible second-order possibly ferroelastic phase transformation, distorting slight to form the M-phase\textsuperscript{52}. Because of the transformations, the M’ structure can be synthesized only at temperatures below the M-T transition temperature, approximately 1450°C, while the M-phase can only be obtained as a transformation product of the T-phase. The transformation from the M’-phase to the T-phase cannot be explained by a simple transformation mechanism. However, an argument has been made that the two structures are related by rotational twinning and that the M’-phase is the true low temperature phase, with the M-phase serving as an intermediate phase\textsuperscript{53}.

Because of the displacive nature of the M-T transformation, an orientation relationship exists between the M- and T-phases (see Figure 2.5). During the transformation, the c-axis of the T-phase corresponds to the b-axis of the M-phase. The unit cell undergoes a uniform shear
parallel to the [100], which is accompanied by an extension parallel to [010]. The volume change at the transformation temperature is continuous, while the thermal expansion coefficient is discontinuous, indicating that the transformation is second order in nature. Additionally, the spontaneous strain accompanying the transformation expresses the same temperature dependence as the order parameter for a second-order phase transformation given by Landau’s theory. The nature of the spontaneous strain also indicates that the transformation is ferroelastic, which presents the possibility for ferroelastic toughening in YTaO₄.

Figure 2.5 – M-T Crystallographic Relationship
2.3 The ZrO$_2$-Ta$_2$O$_5$ System

Prior to this thesis, little information was available on the phase relations along the ZrO$_2$-Ta$_2$O$_5$ binary. Although there is almost no solubility of Ta$_2$O$_5$ into ZrO$_2$, the addition of ZrO$_2$ to Ta$_2$O$_5$ creates a solid solution region up to about 10 mol% ZrO$_2$ for the different Ta$_2$O$_5$ phases. Based on the cation charge differences, there should exist few stable phases. However, the only observed phase is the Ta$_2$Zr$_6$O$_{17}$ orthorhombic phase. Ta$_2$Zr$_6$O$_{17}$ exists over the compositional range 11-33 mol% Ta$_2$O$_5$, but there has been some dispute over this range.

2.4 Compositions within the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ System

As mentioned before, both ZrO$_2$ and YTaO$_4$ exhibit monoclinic structures at low temperatures, which transform into tetragonal structures at high temperatures. These transformations, although controlled by different mechanisms, are both displacive in nature. The similarities between the ZrO$_2$ and YTaO$_4$ phases and transformations, as well as the noted strong synergism associated with co-doping of ZrO$_2$ with equal numbers of trivalent and pentavalent ions, created an interest in the phases within the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ system, particularly along the YTaO$_4$-ZrO$_2$ line. Most the previous work has focused on the Zr-rich end of the YTaO$_4$-ZrO$_2$ quasi-binary. Beginning with ZrO$_2$, the addition of YTaO$_4$ extends the t-phase to approximately 22 mol% YTaO$_4$ (see Figure 2.6) and creates a non-transformable region from 16-22 mol% YTaO$_4$. Unlike the non-transformable t’-phases in other ZrO$_2$ systems, including YSZ, this non-transformable region is not metastable. The addition of YTaO$_4$ suppresses the M-T transformation temperature below ambient temperatures, even
reaching below the temperature of liquid nitrogen for some compositions\textsuperscript{69}, and creates a thermodynamically stable tetragonal region stretching from ambient to 1500°C.

**Figure 2.6 – YO\textsubscript{1.5}-TaO\textsubscript{2.5}-ZrO\textsubscript{2} Phase Diagram**

Phase diagram of the YO\textsubscript{1.5}-TaO\textsubscript{2.5}-ZrO\textsubscript{2} system at 1500°C based on the work of Kim and Tien\textsuperscript{37} and Pitek and Levi\textsuperscript{9}. The dashed lines indicate tentative tie lines. Note: $C$ – cubic, $F$ – fluorite, $O$ – orthorhombic, $t$ – tetragonal
Additionally, when held at high temperatures for significant periods of time, the non-transformable t-phase remains tetragonal and does not decompose into a mixture of cubic and tetragonal, even at 1500°C. If the phase were metastable, then it would partition, as is seen in 7YSZ. In addition, the phase behavior of compositions to the left and right (Y-rich and Y-poor) of the YTaO₄-doped ZrO₂ tetragonal phase indicate that the non-transformable region has little tolerance for excess of either yttrium or tantalum. Given the limited compositional range of YTaO₄, there most likely exists a line compound between YTaO₄ and ZrO₂. Unlike with YSZ, the non-transformable region is caused by the local distortions associated with the substitution of the Y³⁺ ions and Ta⁵⁺ ions for the Zr⁴⁺ ions, and not by the presence of oxygen vacancies. The lack of vacancies results in lower diffusion rates, reducing the grain growth at higher temperatures. This is critical for the microstructure of TBCs since it affects the strain tolerance of the coatings with thermal cycling.

In addition to the improved phase stability, compositions in the t-phase exhibit properties that are comparable or better than 7YSZ. As with other stabilizers, the alloying of YTaO₄ with ZrO₂ improves the fracture toughness of ZrO₂ to levels that are at least comparable with YSZ. However, it also increases the tetragonality of the t-phase, which counters the behavior seen by the other stabilizers. This discrepancy indicates that the underlying toughening mechanism is different than the transformation toughening observed in YSZ. Additionally, these compositions exhibit low thermal conductivity that is independent of temperature. In YSZ, the low thermal conductivity is attributed to high concentrations of oxygen vacancies, which are very effective at scattering phonons. However, the low thermal conductivity
observed in these compositions is caused by the mass disorder associated with the replacement of Zr$^{4+}$ ions with Y$^{3+}$ ions and Ta$^{5+}$ ions.

Although extensive work has been performed on compositions at the Zr-rich end of the diagram, much less is known about the phases in the vicinity of YTaO$_4$ and their properties. In recent work, the phase behavior of YTaO$_4$ doped with ZrO$_2$ has been explored up to Y$_{0.8}$Ta$_{0.8}$Zr$_{0.4}$O$_4$. Similar to the behavior of ZrO$_2$, the YTaO$_4$ monoclinic-tetragonal transformation temperature decreases with ZrO$_2$ concentration from 1426°C to 821°C, and some of the tetragonal phase is retained to room temperature. However, it is unknown if an analogous non-transformable region is possible for YTaO$_4$ doped with ZrO$_2$ or what the conditions would be for the existence of such a region.

2.5 Summary

The metastable behavior of yttria-stabilized zirconia places upper temperature limitations on TBCs operating conditions, thus pressing the need for a new oxide material for the next generation of TBCs. ZrO$_2$ co-doped with YO$_{1.5}$ and TaO$_{2.5}$ has displayed many attractive properties for TBC applications, such as a non-transformable tetragonal region and fracture toughness and thermal conductivity values comparable with 7YSZ. However, the phase behavior and properties along the entire YTaO$_4$-ZrO$_2$ quasi-binary remains to be developed, which is focus of this thesis.
CHAPTER 3

Synthesis and Characterization Techniques

Previous chapters gave an overview of TBCs, describing their design challenges and material guidelines, and demonstrated why the YTZ system would be a strong potential candidate for the next generation of TBCs. However, in order to take the next step with these materials, a comprehensive understanding of the phase evolution of this system and the behavior of its material properties is necessary. Using a myriad of characterization techniques, compositions along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ quasi-binary were explored. A summary of these methods and instruments is given in this chapter, as well as a description of the synthesis process utilized to create the powders and pellets.

3.1 Sample Preparation

3.1.1 Powder Synthesis by Reverse Co-precipitation

Bulk powders were synthesized via reverse co-precipitation\textsuperscript{76}. Precursor solutions of zirconium oxynitrate hydrate (>99%) and yttrium nitrate hexahydrate (>99.8%) were prepared by dissolving the powders in deionized (DI) water, while Tantalum chloride (99.99%) was dissolved in ethanol, resulting in the following reactions

$ZrO(NO_3)_2 \cdot xH_2O \xrightarrow{H_2O} Zr(OH)_4 + 2HNO_3 + yH_2O$

$Y(NO_3)_3 \cdot xH_2O \xrightarrow{H_2O} Y(OH)_3 + 3HNO_3 + yH_2O$

$TaCl_5 \xrightarrow{C_2H_5O} Ta(C_2H_5O)_5 + 5HCl$

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The precursor solutions were calibrated using the gravimetric method, with a target concentration of 0.4mmol/g, and subsequently mixed in the proper proportions to yield the desired composition. The mixed solution was then dropped into a 2.5M ammonium hydroxide solution, NH₄OH, with an initial pH of 11.2 at room temperature, and the pH was maintained above 10 during the process. This pH was chosen based on the insolubility ranges of the individual elements (Table 3.1) as determined from their Pourbaix diagrams.

<table>
<thead>
<tr>
<th>Element</th>
<th>Co-precipitation Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>&lt; 8.7</td>
</tr>
<tr>
<td>Zr</td>
<td>&lt; 3.5 and &gt; 12.8</td>
</tr>
<tr>
<td>Ta</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>8.7 &lt; x &lt; 12.8</td>
</tr>
</tbody>
</table>

The resulting white precipitates were then separated by centrifugation and subsequently washed three times, twice with DI water and once with ethanol, before being dried overnight at 70°C. Finally, the powders were calcined in air at 700°C for 2 hours to create molecularly mixed metal oxides, as confirmed by thermal gravimetric analysis (TGA) measurements, shown in Figure 3.1. This calcination temperature was chosen based on the phase transitions of YTaO₄, which crystallizes at approximately 850°C. However, the differential scanning calorimetry (DSC) showed that the powders’ crystallization temperature decreased with increasing ZrO₂ content across the entire Yₙ₉(1-x)Taₙ₉(1-x)Zr₂xO₄ quasi-binary (Figure 3.2). Nonetheless, the desired phases were not achieved until after the higher temperature heat treatments, thus the calcined powders were either amorphous or in a transitional phase. This is evident by the presence of metal-oxygen stretching vibrations and the lack of the polyhedron vibrations in the Raman spectra of the calcined powders (not shown).
Figure 3.1 – Sample Preparation: TGA Measurements
TGA measurements showing sample weight as a function of temperature after the drying step of the co-precipitation method for YTaO₄ alloyed with ZrO₂.
Figure 3.2 – Sample Preparation: DSC Measurements
DSC measurements showing the crystallization temperatures of compositions along the YTaO$_4$-ZrO$_2$ quasi-binary. The measurements were performed on powder samples following the drying step of co-precipitation.

3.1.2 Formation of Dense Pellets

To form dense pellets, the calcined powders were ball-milled in ethanol at 200rpm for 2 hours, using an YSZ jar and 3mm YSZ balls$^{78}$. The suspension was transferred to centrifuge tubes and sat for 3.5 hours to allow particles larger than 1.2 microns to settle, leaving a fine powder suspension. The duration of the sedimentation was determined by the desired particle size and the medium, see Figure 3.3. The smaller particles were isolated from the suspension by centrifugation and dried overnight. Solid disk pellets were then made by mixing the fine

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powders with a binder (5wt% Poly(vinyl alcohol) in DI water) and cold, uniaxial pressing the slurry at 700 MPa. This procedure was adopted in order to make fully dense pellets since dense pellets could not be made by simply sintering without removing agglomerates.

Figure 3.3 – Powder Sedimentation
Schematic of the sedimentation of the ball-milled powders. The sedimentation time was calculated by applying Stokes’ Law and setting a minimum particle size of 1.2 microns. Variables: $L$ – particle’s minimum falling distance, $r$ – particle radius, $\eta$ – viscosity of the fluid, $\nu$ – particle velocity, $p_p$ – particle density, $p_f$ – fluid density

3.2 Heat Treatment

After calcination, samples were heat treated to obtain the desired crystallographic phases and to improve the resolution of the characterization measurements. The heat treatment temperatures were determined by the YTaO$_4$ phases, further examined in Chapter 4, with the
common temperatures being 1200°C for the M’-phase and 1600°C for the M-phase for phase studies on powders. The ramping rate was kept between 5-10°C/min, and the dwell time at high temperatures was either 2, 4, 40, or 100 hours. Specific heat treatments are presented in later chapters.

For microstructural studies and thermal diffusivity measurements of the M-phase, dense pellets were required. The heat treatment of the pellets varied slightly from that of the powders due to the use of a binder during pressing. Pellets were heated to 700°C at 2°C/min and held for 2 hours to burn off the binder and any water within the pellet, then continued ramping at 5°C/min to 1600°C and held for the desired number of hours.

3.3 Structural Characterization

3.3.1 X-ray Diffraction

Powder x-ray diffraction (XRD) was used to identify the phases present in the sample, determine the lattice parameters as a function of composition and temperature, and examine the phase transitions. Measurements were carried out at three different facilities.

Room temperature XRD measurements using Cu-Kα radiation ($\lambda_{K\alpha 1} = 1.54056\text{Å}$, $\lambda_{K\alpha 2} = 1.54439\text{Å}$) were conducted at the MIT Center for Materials Science and Engineering. A Bragg-Brentano configuration was used in a PANalytical X'Pert Pro Diffractometer with fixed divergence and scattering slits of 0.5, 0.04 radian Soller slits, a Nickel filter, and an X'Celerator position sensitive detector. For high temperature in-situ studies, an Anton Paar
HTK1200N furnace was used. Samples were heated at 50°C/min and allowed 5 minutes to equilibrate before the start of each scan.

In addition to laboratory x-ray diffractometers, experiments were conducted at two synchrotron facilities. To elucidate the phase behavior as a function of composition, high resolution room temperature XRD studies were made at the Advanced Photon Source (APS) at Argonne National Laboratory (in Argonne, Illinois, USA) using the 11-BM mail-in program. For these experiments, the calcined powders underwent heat treatments before being ground with a mortar and pestle and then passed through a 325 mesh sieve. The powders were packed in a rapidly rotating Kapton capillary, and the ends were sealed with glue. A multi-analyzer detector system was used to collect data over the range 0.5°≤2θ≤50° with a step size of Δ2θ=0.001° and a scan speed of 0.1 sec/step. The first set of samples used a wavelength of 0.459981Å (27 keV), while the second set used wavelength of 0.414166Å (30 keV).

To study the phase evolution with temperature, high-temperature in-situ XRD studies were performed at the European Synchrotron Radiation Facility (Grenoble, France) using beamline ID22. The powders were packed inside a platinum tube, and the ends were sealed with high temperature cement before being mounted in the alumina support tubes. A triple lamp furnace, shown in Figure 3.4, was used to heat the samples to roughly 1600°C, and diffraction patterns were acquired during subsequent cooling to room temperature. Samples were allowed 5 minutes to equilibrate at each temperature. An incidence x-ray energy of 42 keV (wavelength=0.29419355Å), calibrated using NIST Si 640c, was chosen to minimize the
absorption by the Tantalum. Each dataset was collected over the range $-4^\circ \leq 2\theta \leq 18^\circ$ with a step size of 0.002$^\circ$ and a scan speed of 2$^\circ$/min using a 9-channel Si 111 multianalyser stage detector system. The collection time for one scan was 11 minutes. Three datasets were taken at each temperature and averaged together to improve the signal-to-noise ratio. No variation with time was observed, thus allowing the collection and averaging of multiple scans at each temperature. The temperature of each measurement was determined from the thermal expansion of the platinum tube. A reference room temperature measurement was collected before heating to determine the initial Pt lattice parameter and to check the effect of the in-situ heating on the phase composition. The Pt lattice parameter for each measurement was refined using the Fullprof suite$^{79}$, and the actual sample temperature was calculated using the thermal expansion of Pt$^{80}$ given by

$$\frac{\delta a}{a_{293.15}} = 7.03139 \times 10^{-6} \times T + 5.44686 \times 10^{-9} \times T^2 - 7.00236 \times 10^{-12} \times T^3 + 5.91557 \times 10^{-15} \times T^4 - 2.41456 \times 10^{-18} \times T^5 + 3.90366 \times 10^{-22} \times T^6 - 2.39164 \times 10^{-3}$$

where T is in Kelvin and $a(293.15) = 3.9236\text{Å}$. 
3.3.2 Rietveld Refinement

Whole pattern fitting and Rietveld analysis\textsuperscript{81} of the acquired synchrotron XRD data was conducting using the GSAS software\textsuperscript{82} with the EXPGUI graphical interface\textsuperscript{83}. The line profiles were fit using the pseudo-Voight function, and the background was fit using a 6-term shifted Chebyshev polynomial. For the high temperature in-situ measurements, a larger number of terms were required for the background fit due to the odd tails formed by the platinum peaks. Accurate determination of the lattice parameters was possible for each phase using the Rietveld method, but extracting phase percentages was difficult due to multiple overlapping peaks, variation in peak intensities, and the partial stabilization of high temperature phases. Moreover, orientation relationships between the phases skewed the intensities of certain reflections. For measurements involving a laboratory diffractometer, the
XRD data were analyzed using the Rietveld software as part of the X’pert HighScore Plus analysis package.

### 3.3.3 Raman Spectroscopy

Raman spectroscopy was used to probe the local structure of samples and to explore the effect of oxide alloying. The Raman scattering from vibrational modes is dependent on the material’s bonding and symmetry, meaning it is material specific and can be used to characterize materials. Moreover, the vibrational modes observed in Raman spectroscopy provide information about the short range order in the crystal, which serves as a complement to XRD. Raman spectra were recorded using LabRAM Aramis Raman system (Horiba Jobin Yvon, Edison, NJ) equipped with 325nm and 532nm laser beams. To explore the phase transitions, in-situ measurements were obtained using a Linkam heating stage (Scientific Instruments Ltd., Waterford Surrey, England) with temperature capabilities up to 1500°C. The ramping rate was 20°C/min, and samples were allowed time to equilibrate at each temperature step. Spectra were acquired during both heating and cooling, as well as at room temperature before and after the temperature sweeping. Analysis of the spectra, including background subtraction, normalization, and peak fitting, was performed using the LabSpec Spectroscopy Suite Software (Horiba Jobin Yvon, Edison, NJ).

### 3.3.4 TGA/DSC

TGA and DSC measurements were made using a Netzsch Netzsch STA 449 F5 Jupiter system (Burlington, MA). Approximately 15μm of powder were loaded into an Al2O3 crucible and
heated to 1550°C with a heating and cooling rate of 10°C/min. Calcination studies were run under flowing air, while phase transitions were measured under flowing Argon.

3.4 Electron Microscopy

Microstructural studies were conducted on pellets using Field Emission Scanning Electron Microscope (FE-SEM, Zeiss), and energy dispersive x-ray spectroscopy (EDS) analysis was carried out by JEOL using their JSM-7200F Schotky FE-SEM. To reduce charging effects, the pellets were coated with Pt-Pd or carbon, and low voltages (≤ 5kV) were used.

Transmission electron microscopy (TEM) measurements were conducted at the Center for Nanoscale Systems (Harvard University, Cambridge, MA) at 200kV using the JEOL ARM200F FEG TEM/STEM system equipped with EDS capabilities and a double-tilt holder. A TEM sample was prepared using a dual beam, focused ion beam (FIB) and scanning electron microscope (FIB-SEM, FEI Helios 660) via the lift-out method. Damage caused by the Ga ion beam during FIB was removed using the Fischione NanoMill 1040. The microstructures were imaged using both bright and dark field conditions, and electron diffraction patterns were obtained to study orientation effects between different phases.

3.5 Thermal and Optical Properties

3.5.1 Thermal Diffusivity

For thermal diffusivity measurements, samples were coated with gold and then graphite on both sides. The measurements were conducted every 100°C from room temperature to
1000°C under flowing Argon using a laser flash system (Micro Flash LFA 457, Netzsch, Selb, Germany). Three data points were obtained at each temperature and then averaged together. One measurement step was added during cooling to check for hysteresis in the data as a function of temperature. The thermal conductivity was then calculated using the thermal expansion coefficient, the sample density, and the heat capacity. More details given in Chapter 6.

3.5.2 Diffuse Reflectance

Diffuse reflectance and transmittance measurements were performed at room temperature using a UV-VIS-NIR spectrophotometer (Hitachi U-4100, Japan) equipped with a 60mm integrating sphere coated with BaSO₄. Tungsten and deuterium lamps were used as the light sources to irradiate the sample (normal to the surface), and the hemispherical reflected light over the range 250nm to 2500 nm was collected by two types of detectors: PMT for the UV-VIS region and PbS for the NIR region.

3.6 Composition Nomenclature

The compositions along the YTaO₄-ZrO₂ quasi-binary were made using the ratios of the individual oxides given by the formula \( x \cdot ZrO₂ + \left( \frac{1-x}{2} \right) \cdot YO_{1.5} + \left( \frac{1-x}{2} \right) \cdot TaO_{2.5} \) where x refers to the mol% ZrO₂. All compositions in this work are named using this molar percentage system, which relates half of one YTaO₄ unit to one full ZrO₂ unit. Every figure, including the YTaO₄-ZrO₂ quasi-binary phase diagram, is expressed in terms of x for the Y₀.₅Ta₀.₅O₂-ZrO₂ scale. Table 3.2 gives the conversion between the Y₀.₅Ta₀.₅O₂ and YTaO₄ scale systems. The
The full molar scale is plotted on the top axis of the YTaO$_4$-ZrO$_2$ quasi-binary phase diagram for comparison (Figure 5.8).

**Table 3.2 – Conversion of compositions from the Y$_{0.5}$Ta$_{0.5}$O$_2$-ZrO$_2$ molar scale in the ZrO$_2$-YO$_{1.5}$-TaO$_{2.5}$ ternary system to the YTaO$_4$-ZrO$_2$ molar scale for the YTaO$_4$-ZrO$_2$ Quasi-Binary Phase Diagram**

<table>
<thead>
<tr>
<th>ZrO$<em>2$-YO$</em>{1.5}$-TaO$_{2.5}$ Ternary Phase Diagram</th>
<th>YTaO$_4$-ZrO$_2$ Binary Phase Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mol% ZrO$_2$</td>
<td>X</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>10</td>
<td>0.1</td>
</tr>
<tr>
<td>20</td>
<td>0.2</td>
</tr>
<tr>
<td>30</td>
<td>0.3</td>
</tr>
<tr>
<td>40</td>
<td>0.4</td>
</tr>
<tr>
<td>50</td>
<td>0.5</td>
</tr>
<tr>
<td>60</td>
<td>0.6</td>
</tr>
<tr>
<td>70</td>
<td>0.7</td>
</tr>
<tr>
<td>80</td>
<td>0.8</td>
</tr>
<tr>
<td>90</td>
<td>0.9</td>
</tr>
<tr>
<td>100</td>
<td>1</td>
</tr>
</tbody>
</table>

For ease of description, the cubic, tetragonal, and monoclinic forms of the zirconia-solid solution phases are indicated by the lower case $c$, $t$, and $m$, respectively, whereas those of the yttrium-tantalate solid solution are indicated by the upper case $T$ and $M$. 
CHAPTER 4

**YTaO$_4$ Solid Solution**

Within the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ system, oxide compositions containing equimolar YO$_{1.5}$ and TaO$_{2.5}$ have demonstrated attractive properties for TBC applications, including the existence of a non-transformable tetragonal region. Much of the previous work has focused on the ZrO$_2$-rich end of the quasi-binary between ZrO$_2$ and YTaO$_4$, yet the YTaO$_4$-rich end of the quasi-binary remains underdeveloped. This chapter explores the phase behavior of YTaO$_4$-rich compositions and establishes the limits of the YTaO$_4$ solid solution regime.

4.1 **Room Temperature Phase Field of YTaO$_4$**

4.1.1 **Solubility Limit**

X-ray diffraction patterns and Raman spectra were obtained for compositions up to x=0.3 to understand the effect of ZrO$_2$ on the YTaO$_4$ crystal structures and establish the solubility limits. To obtain the M'-phase, samples were treated at 1200°C for two hours with an approximate ramping rate of 5°C/min. For the M-phase, the same ramping rate was used, but the samples were treated at 1600°C for two hours to safely clear the M'-T transition temperature for YTaO$_4$.

From the XRD patterns (Figure 4.1), it’s evident that the solubility limit of ZrO$_2$ into YTaO$_4$ is quite large for both monoclinic phases. Compositions treated at 1200°C contain only the M'-phase until x=0.2. In the x=0.2 and x=0.3 samples, the Zirconia solid solution tetragonal...
(t) phase appears, with the most noticeable peak occurring at $2\theta=30^\circ$. The amount of ZrO$_2$ t-phase present is very small, suggesting that the solubility limit is close to the $x=0.2$ composition. In the case of the 1600°C heat treatment, the samples contain the M-phase until the $x=0.3$ composition. Based on the percentage of t-phase present in the $x=0.3$ scan, the solubility limit is between the $x=0.2$ and $x=0.3$ compositions. To approximate the actual limit, the lattice parameters were extracted from the XRD scans using the Rietveld refinement method. By plotting the volume of the phases as a function of composition, the solubility limit was determined to be around $Y_{0.75}Ta_{0.75}Zr_{0.5}O_4$. However, there are errors using this method since the lattice parameters of the phases change slightly depending upon the heat treatment, particularly in the two-phase region. This will be further discussed in the next chapter.

![Figure 4.1](image)

**Figure 4.1 – YTaO$_4$ Solid Solution XRD Measurements**

X-ray diffraction scans of YTaO$_4$ doped with ZrO$_2$ for two different heat treatments, corresponding to the $M'$-phase (left) and M-phase (right). The ZrO$_2$ t-phase peaks are marked by yellow squares.
Another notable feature of the XRD scans is that there is a systematic broadening and shifting of the peaks with increasing ZrO₂ content, which is indicative of a decrease in the crystallite size and a change in the unit cell size, respectively. However, the crystal symmetries do not change for either monoclinic phase. This suggests that the ZrO₂ is fully incorporated into the YTaO₄ structures, regardless of the treatment temperature.

The behavior of the Raman spectra also supports this conclusion (see Figure 4.2). For both the M’- and M-phase, there is no significant change in the spectra with increasing ZrO₂ concentration, apart from minor peak shifts. All the peaks can be indexed as either M’ or M (see Table 4.1), and the number of peaks and their locations agree with those in the literature. Moreover, the Raman peaks broaden slightly but individual peaks remain distinguishable, indicating that there is little distortion in the local structure. This confirms that the local symmetries are preserved as ZrO₂ is alloyed with YTaO₄.
Figure 4.2 – YTaO₄ Solid Solution Raman Measurements
Raman spectra of YTaO₄ doped with ZrO₂ for two different heat treatments, corresponding to the M’-phase (left) and M-phase (right). In both cases, no significant changes in the spectra occur with respect to the ZrO₂ concentration, apart from peak broadening.

Table 4.1 – Raman spectra of the YTaO₄ monoclinic structures and their vibration assignments

<table>
<thead>
<tr>
<th>Free TaO₄ ion</th>
<th>TaO₄ ion in YTaO₄</th>
<th>Exp. Data (cm⁻¹)</th>
<th>Assigned Vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>M’</td>
<td>M</td>
</tr>
<tr>
<td>n₁: A₁</td>
<td>A</td>
<td>815</td>
<td>823</td>
</tr>
<tr>
<td>n₃: T₂</td>
<td>A+2B</td>
<td>663</td>
<td>703</td>
</tr>
<tr>
<td>n₄: T₂</td>
<td>A+2B</td>
<td>506</td>
<td>486</td>
</tr>
<tr>
<td></td>
<td></td>
<td>414</td>
<td>455</td>
</tr>
<tr>
<td></td>
<td></td>
<td>346</td>
<td>426</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-</td>
<td>378</td>
</tr>
<tr>
<td>n₂: E</td>
<td>2A</td>
<td>296</td>
<td>347</td>
</tr>
<tr>
<td></td>
<td></td>
<td>281</td>
<td>325</td>
</tr>
<tr>
<td>External Modes</td>
<td>External Modes</td>
<td>&gt;250</td>
<td>&gt;260</td>
</tr>
</tbody>
</table>
4.1.2 Evidence of Line Compound

Preliminary work by Clarke and Levi has suggested that a line compound exists between YTaO$_4$ and ZrO$_2$, and that this line has very little tolerance for excess Y$^{3+}$ and Ta$^{5+}$ ions$^{9,69,73}$. Studies conducted at the ZrO$_2$-rich end have demonstrated this behavior, but information at the YTaO$_4$-rich end is sorely lacking. To confirm the existence of a line compound, compositions 5% to the left and right of the Y$_{(1-x)}$Ta$_{(1-x)}$Zr$_{2x}$O$_4$ line were studied by XRD at the YTaO$_4$-end of the line. Experiments were performed on samples treated at 1200°C (M’-phase) and 1600°C (M-phase) to account for the two different monoclinic structures, and the results for the 18 mol% ZrO$_2$ samples are shown in Figure 4.3.
Figure 4.3 – Evidence of Line Compound: XRD Measurements

X-ray diffraction scans comparing compositions to the left and right of the YTaO₄-ZrO₂ quasi-binary for 18 mol% ZrO₂. The results for the lower heat treatment (M’-phase) samples are shown at the top, while the higher heat treatment (M-phase) samples are at the bottom. Individual peaks are marked by symbols corresponding to the different phases, and the phase legend is displayed to the right of each graph.
All the compositions demonstrated the same trend: compositions with more YO$_{1.5}$ contained a secondary Y-rich phase and compositions with more TaO$_{2.5}$ contained a secondary Ta-rich phase. However, the secondary phases varied depending on the heat treatment. In the case of the 18 mol% ZrO$_2$ samples, the compositions that are Y-rich separate into the YTaO$_4$ phase and Y$_3$TaO$_7$ phase, regardless of heat treatment. However, the Ta-rich compositions display two different excess phases (YTa$_3$O$_9$ and TaO$_{2.5}$). Since only the YTa$_3$O$_9$ phase was observed for both heat treatments of the Y$_{0.45}$Ta$_{0.55}$O$_{2.05}$ composition, it’s possible that the tie lines are different at the lower temperatures, causing the 18 mol% ZrO$_2$ composition to sit in a multi-phase field which contains TaO$_{2.5}$. However, the lack of information on the TaO$_{2.5}$ side of the ZrO$_2$-YO$_{1.5}$-TaO$_{2.5}$ ternary phase diagram makes determination of this currently impossible. Regardless, the behavior observed in the off-compositional samples confirms that the Y$_{(1-x)}$Ta$_{(1-x)}$Zr$_{2x}$O$_4$ line is a line compound up to 18 mol% ZrO$_2$ independent of treatment temperature.

4.2 Substitution of Zr$^{4+}$ into YTaO$_4$ Structures

As previously described in Chapter 2, YTaO$_4$ exhibits three distinct crystal structures (M’, M, and T), and the coordination number of the trivalent and pentavalent ions vary greatly within the phases. The Y$^{3+}$ ion sits in a deformed polyhedron with eight-fold coordination for all three phases, while the Ta$^{5+}$ ion adopts four-fold coordination in the M- and T-phases and six-fold coordination in the M’-phase. As YTaO$_4$ is alloyed with ZrO$_2$, this creates the possibility of the Zr$^{4+}$ being placed in three different coordination configurations. However, the three cations have drastically different ionic radii (see Table 4.2).
Typically, the Zr$^{4+}$ ion prefers eight-fold coordination, which is observed in both tetragonal and cubic Zirconia$^{13,14}$, or seven-fold coordination, as seen in monoclinic Zirconia$^{12}$. It is also possible for Zr$^{4+}$ to have six-fold coordination in perovskite structures$^{88}$, but it won’t assume that coordination in its oxide form. However, Zr$^{4+}$ is not known to adopt four-fold coordination. To determine where the Zr$^{4+}$ ion is going into the YTaO$_4$ structures, the pros and cons of three cases must be considered:

1. Zr$^{4+}$ replaces only Y$^{3+}$

   Based on coordination number only, this substitution is possible since Zr$^{4+}$ prefers eight-fold coordination. However, the replacement of Y$^{3+}$ with Zr$^{4+}$ would result in excess positive charge, leading to the creation of cation vacancies (Y$^{3+}$ or Ta$^{5+}$). Given the large solubility limits observed in both the M’- and M-phases, it is unlikely that the structures could accommodate so many cation vacancies. Moreover, the displacement of the Y$^{3+}$ would lead to the formation of secondary Y-rich phases due to the limited tolerance for excess Y$^{3+}$ or Ta$^{5+}$, yet no extra phases are observed in the XRD scans, suggesting that the Zr$^{4+}$ is not favoring only the Y$^{3+}$ site.

### Table 4.2 – Ionic Radii of the Cations$^{87}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Charge</th>
<th>Ionic Radius (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y</td>
<td>3</td>
<td>0.1019</td>
</tr>
<tr>
<td>Zr</td>
<td>4</td>
<td>0.084</td>
</tr>
<tr>
<td>Ta</td>
<td>5</td>
<td>0.074</td>
</tr>
</tbody>
</table>
2. \( \text{Zr}^{4+} \) replaces only \( \text{Ta}^{5+} \)

This substitution seems possible for the M’-phase since \( \text{Zr}^{4+} \) can adopt a six-fold coordination in certain situations, but it’s improbable that the \( \text{Zr}^{4+} \) ion would tolerate the four-fold coordination in the M-phase without highly distorting the structure. Such a distortion would change the vibrational modes of the local structure, causing shifts in the peaks in the Raman spectra. However, no change in the Raman spectra of the M-phase is observed. In addition, the replacement of \( \text{Ta}^{5+} \) with \( \text{Zr}^{4+} \) would create excess negative charge, causing \( \text{O}^{2-} \) vacancies to form. As with the previous case, the M’ and M structures would not be able to accommodate the large number of vacancies occurring at the solubility limits, and no secondary Ta-rich phases are observed in the XRD scans, suggesting the \( \text{Zr}^{4+} \) isn’t replacing only the \( \text{Ta}^{5+} \).

3. \( \text{Zr}^{4+} \) equally replaces \( \text{Y}^{3+} \) and \( \text{Ta}^{5+} \)

Although the ionic radii of the three cations greatly differ, the ionic radius of the \( \text{Zr}^{4+} \) ion is only 3.5% larger than the average of the ionic radii of \( \text{Y}^{3+} \) and \( \text{Ta}^{5+} \), which is 0.087nm. The equal substitution of \( \text{Y}^{3+} \) and \( \text{Ta}^{5+} \) by \( \text{Zr}^{4+} \) would then only slightly distort the crystal structures. This means the structure would be stable even with an extensive number of the atomic sites filled with \( \text{Zr}^{4+} \). In the case of the M- and T-phases, if the \( \text{Zr}^{4+} \) ions are replacing neighboring \( \text{Y}^{3+} \) and \( \text{Ta}^{5+} \) ions, then the local distortion of the \( \text{Ta}^{5+} \) site would be countered by that of the \( \text{Y}^{3+} \) site, thus allowing the \( \text{Zr}^{4+} \) ion to adopt four-fold coordination. Moreover, by replacing the \( \text{Y}^{3+} \) and \( \text{Ta}^{5+} \) ions equally, the charge neutrality is preserved, so no vacancies form.
Given the trends observed in the XRD patterns and Raman spectra, it can be surmised that the Zr$^{4+}$ ions are equally replacing the Y$^{3+}$ and Ta$^{5+}$ ions. Moreover, the Zr$^{4+}$ ions are most likely replacing neighboring Y$^{3+}$ and Ta$^{5+}$ sites.

### 4.3 Effect of ZrO$_2$-Alloying on the Phase Transitions

YTaO$_4$ displays two very distinct phase transitions (M’-T and M-T), which both occur around 1425°C. In the case of YTaO$_4$, the material will form the M’-phase as long as it never surpasses the M-T transition temperature. It’s known from the XRD studies that doping YTaO$_4$ with ZrO$_2$ produces both monoclinic phases, depending on the heat treatment. This raises interest in the behavior of the phase transitions with ZrO$_2$ content.

#### 4.3.1 M to T Transition

Building on previous work, the M-T transition was investigated via in-situ XRD for x=0.25-0.3 compositions in order to explore the remainder of the solid solution region. The samples were treated at 1600°C for 40 hours to reach their equilibrium state. Measurements were done from room temperature to 1000°C, with scans taken every 50°C during heating and every 100°C during cooling. The unit cell parameters as a function of temperature were determined from the X-ray diffraction patterns using Rietveld analysis. As can be seen in Figure 4.4, the transformation is reversible at the solubility limit, and there is no discontinuity in the volume at the transformation. However, since T-phase is present at every temperature for both heating and cooling, the transformation temperature is not immediately clear. The monoclinic angle $\beta$
was used to calculate the transformation temperature (Figure 4.4c). The variation of the monoclinic angle $\beta$ with temperature could be fitted with the power law

$$\beta = A(T_{Tr} - T)^n + 90$$  
(Equation 4.1)

where $A$ is a scaling factor, $T_{Tr}$ is the transformation temperature, and $n$ is the exponent. A value of $n=0.34$ was used to fit the monoclinic angles for all compositions, and the intercept of the extrapolated fitted curves with the temperature axis gave the transformation temperature. This $n$ value was chosen based on previous work characterizing the M-T transition in ZrO$_2$-doped YTaO$_4$ for lower ZrO$_2$ content$^{75}$. From these fits, the M-T transition temperatures were determined to be $498\pm3^\circ C$ for the $x=0.25$ composition and $419\pm7^\circ C$ for the $x=0.3$ composition. There is some hysteresis between the heating and cooling data, which results in the cooling monoclinic angles giving M-T transition temperatures that are approximately $50^\circ C$ lower than that of the heating scans. Using the data from previous work and the heating data from this work, the M-T transformation temperature as a function of ZrO$_2$ concentration was plotted for the entire solid solution regime (Figure 4.4d). The transformation temperature decreases with increasing ZrO$_2$ concentration and can be fit with a quadratic equation.
Figure 4.4 – YTaO₄ Solid Solution M-T Transformation

Results of the in-situ XRD measurements of the x=0.25 composition. (a) Selected scans showing the reversibility of the transformation during heating and cooling. (b) Variation of the volume of the unit cells as a function of temperature during heating. (c) Variation of the monoclinic angle as a function of temperature during heating and cooling. The dashed lines correspond to the best fit using a power law. (d) The M-T transformation temperature as a function of ZrO₂ concentration. The open circles correspond to measurements performed by Shian et al., while the filled circles represent work performed for this thesis.

Although the addition of ZrO₂ lowers the transformation temperature, it does not change the mechanisms of the transformation. The M-T transformation in YTaO₄ exhibits features which are consistent with a ferroelastic transformation. First, the transformation is a reversible,
stress-induced transformation that can be characterized by an order parameter\textsuperscript{55}. Second, domain switching, as indicated by twin domains with (2 0 -9.1) and (9.1 0 2) boundary planes\textsuperscript{75}, is observed in the microstructures.

As ZrO\textsubscript{2} is alloyed with YTaO\textsubscript{4}, the same characteristics are observed throughout the solid solution regime. The transformation is reversible, and the continuous volume change confirms its displacive nature. At the solubility limit, the volume change is only 0.2\%. Additionally, the behavior of the monoclinic angle with temperature follows the same power law for all the compositions. This n value (0.34) is lower than the mean field exponent (n=0.5) for a second order transformation because the fit covers a large temperature range. Away from the transformation, the monoclinic angle is only affected by the thermal expansion of the unit cell. If the lower temperature data is excluded, then the mean field exponent n=0.5 does fit the data well. Also, using n=0.5 results in transformation temperatures that are about 40-50 degrees higher. Lastly, twins are observed in the ZrO\textsubscript{2} doped samples (see Figure 4.5). Their size decreases with increasing ZrO\textsubscript{2} content, which agrees with the decrease in crystallite size seen in the XRD. The twins can be observed by SEM for the x=0-0.2 compositions, but TEM is required for compositions with great ZrO\textsubscript{2} concentration.
4.3.2 \textit{M’ to T Transition}

Although the addition of ZrO$_2$ to YTaO$_4$ greatly changes the M-T transition temperature, it has little effect on the transformation between the M’- and T-phases. DSC measurements show that the transformation retains its endothermic nature as the ZrO$_2$ concentration increases, while the transformation temperature increases slightly (see Figure 4.6). The increase in temperature is not linear, and the most pronounced difference occurs between the x=0.1 and x=0.2 compositions. This temperature jump is probably a result of the difference in the solubility limits observed in the M’-phase (x < 0.2) and M-phase (x > 0.2). Moreover, the DSC measurements are swept at a rate of 10°C/min, and this transformation is very sluggish, as demonstrated by the broadness of the DSC peaks.

\textit{Figure 4.5 – Evidence of Twinning}

\textit{SEM images showing twin domains on the surface of the grains for the x=0 and x=0.2 compositions. The twins are present in the top grain for the x=0.2 sample.}
Since the M’-T transformation is slow, the effect of sintering time and temperature were investigated as a function of ZrO₂ content. Six sets of pellets were pressed for compositions with x=0-0.2. Three sets of pellets were sintered for 40 hours at 1400°C, 1450°C, or 1500°C, and the other three sets were sintered for 100 hours using the same three temperatures options.
The same heating and cooling rate of 5°C/min was used for all samples. Phase identification was possible using Raman spectroscopy since the M’- and M-phases have distinct Raman spectra, and the presence of the M-phase means that the sample has transformed to the T-phase at high temperature.

Regardless of composition or sintering time, all the samples treated at 1400°C contained only the M’-phase. Likewise, all samples treated at 1500°C contained only the M-phase, agreeing with the DSC results that the M’-T transformation must occur between 1400°C and 1500°C even when YTaO₄ is alloyed with ZrO₂. The samples treated at 1450°C contained both monoclinic phases, depending on the sintering time and composition. A comparison of the Raman spectra of individual compositions for the different heat treatments is given in Figure 4.7. YTaO₄ treated at 1450°C for 40 hours is mostly composed of the M’-Phase, but part of the sample has begun to transform to the M-Phase, as demonstrated by the presence of the M-Phase Raman peak at ~320cm⁻¹. The same phase behavior is observed for the x=0.2 composition. However, the YTaO₄ sintered for 100 hours is completely M-phase, whereas the x=0.2 composition still contains a small fraction of the M’-phase, represented by the peak at ~415cm⁻¹. From these results, it appears that the M’-T transformation temperature is independent of ZrO₂ content but slightly effected by sintering time. This trend is very different from the M-T transformation temperature, which decreases with ZrO₂ content in the solid solution regime.
Figure 4.7 – $M'$-T Transformation Raman Spectra

Raman spectra comparing the effect of composition and sintering time and temperature on the transformation from the $M'$-phase to the T-phase for (a) $x=0$ sintered for 40 hours, (b) $x=0.2$ sintered for 40 hours, (c) $x=0$ sintered for 100 hours, (d) $x=0.2$ sintered for 100 hours
4.4 Stabilization of High Temperature Phases

It is known in the YSZ system that the high temperature tetragonal and cubic phases can be retained down to room temperature through quenching or constraining the particle size. A similar process occurs in the YTaO$_4$-ZrO$_2$ system. Starting with $x=0.1$, the addition of ZrO$_2$ to YTaO$_4$ stabilizes a small amount of the T-phase to room temperature.

It’s evident from the in-situ XRD measurements that the cooling rate does affect the amount of T-phase that is retained. During heat treatments, every sample was cooled at a rate of 5-10 °C/min, whereas in the in-situ measurements, cooling rates of 50°C/min or more were used. Additionally, higher amounts of the T-phase were observed in samples that were quenched from high temperature to room temperature. Interestingly, the duration of the heat treatment of the samples impacted the phase ratios. Two sets of samples were made for the $x=0.2$ and $x=0.3$ compositions; one set was treated at 1600°C for 2 hours and the other for 40 hours. Room temperature synchrotron XRD measurements show that the phase composition varied with composition and sintering time (see Figure 4.8). The XRD patterns of the $x=0.2$ composition display no difference in peak position or intensity, only a slight narrowing of the peaks with longer treatment time. This suggests there is no difference in phase composition or lattice parameters for the two heat treatments of compositions within the YTaO$_4$ solid solution region. However, the XRD patterns of the $x=0.3$ composition, which sits just past the solubility limit, show a significant decrease in the intensity of the peaks corresponding to the T-phase for the longer heat treatment.
**Figure 4.8 – Stabilization of T-phase**
Comparison of the x-ray diffraction scans of the \(x=0.2\) (left) and the \(x=0.3\) (right) compositions, for heat treatment times of 2 hours and 40 hours, and the same cooling rate. The peaks corresponding to the T-phase are marked by yellow stars. No difference is observed in the \(x=0.2\) composition for the two treatment times, but the T-phase peaks have decreased in the \(x=0.3\) composition after the longer treatment time.

The longer sintering time most likely results in an increase in the grain size and reduces the number of small constrained grains. As a result, less of the T-phase exists in a constrained state, allowing more to transform to the M-phase as it passes through the M-T transition temperature. Additionally, in the case of the \(x=0.3\) composition, the phases have not reached their equilibrium state for the shorter heat treatment. This is further explored in the next chapter. Even though the mechanisms stabilizing the high temperature phases to low temperatures are not fully understood, it’s clear that cooling rate, duration of sintering time, and composition affect the amount of T-phase that is retained.
4.5 Summary

The YTaO$_4$ solid solution region has been established for both monoclinic phases. The solubility limit of ZrO$_2$ into YTaO$_4$ occurs at approximately $x=0.2$ for the M'-phase and close to $x=0.3$ for the M-phase. Regardless of heat treatment, the YTaO$_4$ solid solution is a line compound with little tolerance for excess Y$^{3+}$ and Ta$^{5+}$. The different secondary phases observed for the two treatment temperatures suggests the tie-lines in the YO$_{1.5}$-TaO$_{2.5}$-ZrO$_2$ phase diagram may not be correct at lower temperatures. The ability of the YTaO$_4$ structures to accommodate large amounts of ZrO$_2$ indicates that the Zr$^{4+}$ ions are equally replacing the Y$^{3+}$ and Ta$^{5+}$ ions, most likely in neighboring pairs. In addition, the alloying of YTaO$_4$ with ZrO$_2$ reduces the M-T transformation temperature from 1426°C to 498°C near the solubility limit and stabilizes the T-phase to room temperature. However, it does not change the transformation mechanism, which may be ferroelastic. Since the T-phase observed at room temperature is metastable, the treatment temperature and time, as well as the composition, affect its stabilization. Interestingly, the addition of ZrO$_2$ does not affect the M'-T transformation temperature.
CHAPTER 5

Development of the YTaO$_4$-ZrO$_2$ Phase Diagram

Previous work has explored the YTaO$_4$-rich and ZrO$_2$-rich parts of the YTaO$_4$-ZrO$_2$ compositional, resulting in the establishment of similar structures and phase transitions. However, due to the existence of two high temperature tetragonal phases (t-ZrO$_2$ and T-YTaO$_4$) that present close crystallographic parameters and that can be mutually substituted (at least at both ends of the phase diagram), there is a strong interest in investigating the phase relationships and phase stability in the median composition range. The phase evolution, microstructural behavior, and kinetics of the two-phase region are examined in this chapter, as well as the development of the YTaO$_4$-ZrO$_2$ quasi-binary phase diagram.

5.1 Establishment of the Two-Phase Region

Room temperature synchrotron x-ray diffraction measurements were performed on powders in the compositional range $x=0.2-0.6$ in order to establish the phase evolution between the YTaO$_4$(ss) and ZrO$_2$(ss) regions of the Y$_{(1-x)}$Ta$_{(1-x)}$Zr$_{2x}$O$_4$ line. The powders were treated at 1600°C for 40 hours to obtain the desired phases. The longer treatment time was chosen based on the previous studies, which indicated that shorter treatment times caused variations in the phases.

As shown by the XRD patterns in Figure 5.1a, a two-phase region (M+t) exists at room temperature in the intermediate range ($x=0.3-0.6$). Peaks corresponding to the ZrO$_2$ t-phase
appear in the \(x=0.3\) composition and grow in intensity as the \(\text{ZrO}_2\) content increases, while the intensity of the M-phase peaks decrease. There is a shift in the M-phase peak positions between the \(x=0.2\) and \(x=0.3\) patterns, as a result of the solubility limit being closer to \(x=0.3\).

A small amount of the T-phase is stabilized to room temperature for the \(x=0.2-0.4\) compositions, yet none is detectable in the \(x=0.5-0.6\) compositions. Most likely, there is some T-phase present, but the broadness and low intensity of its peaks makes it impossible to differentiate them from the background and other peaks. There is no change in the lattice parameters, and thus the volume, as a function of composition for the M-, T-, and t-phases in the \(x=0.3-0.6\) patterns. This can be seen in Figure 5.1b, which also includes the unit cell volumes obtained from previous work and literature. The M- and T-phase volumes decrease with increasing \(\text{ZrO}_2\) concentration until the \(x=0.3\) composition, and then remains constant over the \(x=0.3-0.6\) region, with the exception of the \(x=0.3\) sample that was treated for 2 hours.

Analogously, the t-phase volume increases as the \(\text{YTaO}_4\) concentration increases, but stays constant in the \(x=0.3-0.6\) range. The constant behavior of the volume coupled with the change in the relative intensities of the phases confirms that the \(x=0.3-0.6\) compositional range is a two-phase region.
Figure 5.1 – Establishment of Two-Phase Region

(a) Room temperature synchrotron scans (Wavelength = 0.459981 Å (27 keV)) of the x=0.2-0.6 compositions, treated at 1600°C for 40hrs, showing the phase evolution through the two-phase region. The peaks of the three main phases are indicated by the black triangle (M-phase), yellow circle (T-phase), and red square (t-phase). The T-phase is retained from high temperature as a metastable phase. (b) Variation in unit cell volume as a function of composition for the three phases, given different heat treatments. The volumes for the YTaO₄(ss) and ZrO₂(ss) regions were obtained from literature.⁷⁵,⁸⁹
The solubility limits for YTaO$_4$(ss) and ZrO$_2$(ss) can be determined from the intersections of the linear fits of the three phase regimes. For the YTaO$_4$(ss), the limit occurs near the composition Y$_{0.72}$Ta$_{0.72}$Zr$_{0.56}$O$_4$, which corresponds to approximately x=0.28. This is close to that predicted based on first-principles computations (x~0.25). For the ZrO$_2$(ss), the limit is Y$_{0.37}$Ta$_{0.37}$Zr$_{1.26}$O$_4$, corresponding to approximately x=0.63. No computations have been reported for the ZrO$_2$ solubility limit, but it is consistent with the limit determined by Kim$^{37,68}$ and with previous work$^{69}$ demonstrating that compositions close to Y$_{0.38}$Ta$_{0.38}$Zr$_{1.44}$O$_4$ are tetragonal but will transform to monoclinic on cooling to liquid nitrogen temperatures.

Microstructural evidence also supports the existence of a two-phase region. The grain size is smallest and fairly uniform for the x=0.4 composition, which is near the center of the region, but becomes larger and more varied in size as the solubility limits are approached in either direction (Figure 5.2). In addition, backscattered SEM images show the presence of two different phase regions. The lighter grains correspond to the YTaO$_4$ solid solutions and the darker regions are ZrO$_2$ solid solution phases. This is confirmed by the EDAX images (Figure 5.3), since the tantalum atoms have a larger scattering effect. Moreover, the chemical compositions of the two regions, as determined by EDAX, are close the solvus compositions determined by the XRD studies. Interestingly, some of the grains appear to have regions of a banded structure, which will be discussed later.
Figure 5.2 – Grain Size vs ZrO₂ Concentration
Comparison of the microstructures for $x=0.2$-0.6 compositions. The grains are largest in compositions near the solubility limits. Mag 5kx, 5kV
Figure 5.3 – EDAX Mapping of Two-Phase Region
Backscattered SEM image of the x=0.4 composition, showing the presence of two different phases: YTaO$_4$(ss) and ZrO$_2$(ss). Energy-dispersive X-ray spectroscopy mapping gives the distribution of Zirconium, Yttrium, and Tantalum in the sample. The lighter regions are YTaO$_4$(ss), and the darker regions are ZrO$_2$(ss). Mag 10kx, 5kV

5.2 High-Temperature Behavior of Two-Phase Region

The high solubility limits of the YTaO$_4$ and ZrO$_2$ regimes and the similarity of the M-, T-, and t-phases sparks an interest in the high temperature behavior of the two-phase region. In particular, there is a desire to understand the extent of the two-phase region with temperature as well as the characteristics of the phase transitions within it. To understand the phase behavior in the intermediate region (x=0.3-0.6) and possibly probe higher temperature phases,
in-situ high temperature synchrotron XRD studies were performed on powder samples up to approximately 1600°C. Prior to the measurements, the powders were treated at 1600°C for 40 hours to obtain the M- and t-phases. The lattice parameters as a function of temperature of the phases in the two-phase field are shown in Figure 5.4 for the x=0.4 and x=0.5 compositions. Using Rietveld analysis, the data was extracted from the synchrotron diffraction patterns obtained during cooling from 1552 °C and 1666°C for the two compositions, respectfully. For clarity, the lattice parameter data for the ZrO$_2$ solid solution is shown separately from that of the YTaO$_4$ solid solution. As expected, the volumes of the three phases are independent of composition, regardless of temperature, and the YTaO$_4$(ss) volume is continuous through the M-T transformation. Interestingly, there is exactly a factor of four between the volumes of the two co-existing tetragonal solid solutions. This will be discussed later.

The temperature intervals between measurements were too coarse to accurately identify the transformation temperature, but the transformation temperature could be estimated based on the behavior of the monoclinic angle. Following the same procedure as in the YTaO$_4$(ss) regime, the variation of the monoclinic angle $\beta$ with temperature was fitted with the power law given by equation 4.1 using $n=0.34$. The extrapolation of the monoclinic angles suggests that the transformation temperature is 400 ± 20 °C across the two-phase region. Attempts were made to confirm this temperature using DSC measurements (not shown). However, the transformation could not be observed, suggesting that the energy required for the M-T transformation is very small within the two-phase region.
Figure 5.4 – Two-Phase Region: In-situ Synchrotron XRD Measurements

Unit cell parameters as a function of temperature of the (a) YTaO$_4$(ss) phase for $x=0.4$, (b) ZrO$_2$(ss) phase for $x=0.4$, (c) YTaO$_4$(ss) phase for $x=0.5$, and (d) ZrO$_2$(ss) phase for $x=0.5$. Variations in unit cell volumes with temperature for the three phases are shown in (e) for the two compositions. The variation of the monoclinic angle, $\beta$, as a function of temperature is shown in (f).
Although the in-situ measurements reached temperatures as high as 1666°C, no phases other than the T- and t-phases were observed at high temperatures (see Figure 5.5). However, differences in the peak profiles of the two tetragonal phases did become noticeable at the higher temperatures where the tetragonal peaks are sharpest (see Figure 5.6). Comparing the two phases, the diffraction peaks from the t-phase are sharper and more symmetric, while the peaks from the T phase are broader and asymmetric with a tail on the higher diffraction angle side. The asymmetry of the high temperature tetragonal T diffraction peaks suggests the presence of a secondary T-phase with different lattice parameters than the main phase. There are two possible explanations for this. First, it is assumed that the simultaneous replacement of one Y$^{3+}$ and one Ta$^{5+}$ by two Zr$^{4+}$ ions in the tetragonal YTaO$_4$ phase occurs randomly throughout the material. While this may be an appropriate assumption at low concentrations, at the solubility limit 28% of the Y$^{3+}$ and Ta$^{5+}$ sites have been replaced with Zr$^{4+}$ ions, making it more likely that the substitutional ions are closer together. As a result, preferential clustering of similar ions will likely occur without changing either the net charge neutrality condition or the space group. The observation that the asymmetry is on the high-angle side of the diffraction peaks suggests that the clustering causes some unit cells to contract. Since the T-phase unit cell contracts with increasing ZrO$_2$ concentration, this suggests that the asymmetry is associated with preferential clustering of the Zr$^{4+}$ ions. The second possible explanation is that the powders have not fully reached equilibrium. Although less obvious, some of the high temperature tetragonal t diffraction peaks are asymmetric with a second peak occurring on the low-angle side of the main diffraction peak. This would suggest the presence of a secondary t-phase containing excess Y$^{3+}$ and Ta$^{5+}$ ions since the volume of the t-phase
increases with YTaO$_4$ content. Given that the asymmetries of the T- and t-phases mirror each other, the secondary T- and t-phases could be non-equilibrium transient phases, resulting from a heat treatment time that is too short. It is also possible that these secondary phases are representative of constrained regions within the samples, such as the interface between the two tetragonal phases. As will be discussed later, the interfaces between the different phases have an unusual shape, stemming from the similarity of the structures.

Figure 5.5 – High Temperature XRD Scan of x=0.5 Composition
Plot of selected XRD peaks of powders of the x=0.5 composition at 1666°C. Synchrotron data with wavelength = 0.29419355 Å (42 keV). Each peak is identified by its phase and miller indices.
Another feature of the high-temperature X-ray diffraction patterns is that there is a lattice correspondence between the two tetragonal solid solution phases. In both tetragonal phases, the large solubility limits and the equal trade-off between two Zr$^{4+}$ ions and one YTa group during alloying result in almost identical long order atomic arrangements. This is observed through the similarity of the XRD patterns and the small differences in the peak positions of the t and T-phase XRD peaks. With the exception of the T(101) peak at 2θ=3.588° (not shown), the T and t peaks appear in pairs over the entire XRD pattern, meaning the planar spacing of the cations is almost equal for the two phases. The difference in the miller indices of the two tetragonal phases is a result of the unit cell definitions, which are given in table 5.1.
By comparing the cation arrangements within the two unit cells and their lattice parameters, a transformation matrix between the two phases can be determined. The T-phase is equivalent to four unit cells of the t-phase, with two stacked on top of another two in the c-direction, and the t-phase is offset from the T-phase by a rotation of 45° about the c-axis (see Figure 5.7).

This transformation is represented by the transformation matrix

\[
\begin{pmatrix}
\frac{a_t}{a_T} \\
\frac{b_t}{b_T} \\
\frac{c_t}{c_T}
\end{pmatrix} = \frac{1}{2} \begin{pmatrix}
1 & 1 & 0 \\
-1 & 1 & 0 \\
0 & 0 & 1
\end{pmatrix}
\begin{pmatrix}
\frac{a_T}{a_t} \\
\frac{b_T}{b_t} \\
\frac{c_T}{c_t}
\end{pmatrix}
\]

which is applicable at every investigated temperature within the two-phase region. As can be seen by the overlay of the unit cells, the volume of the T-phase is almost exactly four times the volume of the t-phase. Moreover, the difference in atomic spacing between the T- and t-phases is 0.4% and 2.1% along the direction of the T-phase a-axis and c-axis, respectfully.

---

Table 5.1 – Comparison of the unit cells for the T- and t-phases extracted from the x=0.5 composition XRD scan at 1666°C

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space Group</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>I 41/a</td>
<td>5.221</td>
<td>10.980</td>
<td>299.269</td>
</tr>
<tr>
<td>t</td>
<td>P 42/nmc</td>
<td>3.678</td>
<td>5.374</td>
<td>72.686</td>
</tr>
</tbody>
</table>

---

67
Figure 5.7 – Comparison of Tetragonal Structures
Comparison of the atomic arrangements in the T and t-phases at 1666°C for the x=0.5 composition. The t-phase structure is composed of 8 unit cells, while the T-phase structure contains a single unit cell. The T-phase is offset from the t-phase by a 45 degree rotation about the c-axis. In the T-phase, yttrium and tantalum occupy 36% of the cation sites each, and zirconium occupies 28% of the sites. In the t-phase, zirconium occupies 66% of the cation sites, and yttrium and tantalum occupy 17% each. For simplicity in the illustration, zirconium atoms were placed on every cation site in the t-phase, while yttrium and tantalum atoms were placed on every site in the T-phase. The projections are aids for visualizing the relationship between the two tetragonal phases.

5.3 YTaO₄-ZrO₂ Phase Diagram
Combining the in-situ high temperature measurements of the YTaO₄(ss) and two-phase regions with results from literature, the quasi-binary phase diagram was defined for the YTaO₄-ZrO₂ system (see Figure 5.8).
Figure 5.8 – Y_{0.5}Ta_{0.5}O_2–ZrO_2 Phase Diagram

Phase diagram along the Y_{0.5}Ta_{0.5}O_2–ZrO_2 quasi-binary. The full molar scale is shown on the top axis. The filled markers correspond to this work, and the open markers are data from literature^{37,75}. The room temperature solubility limits are marked by the dashed lines. Small amounts of the T-phase are retained to room temperature, as indicated by the bracketed T.

At the ZrO_2-end of the phase diagram, ZrO_2 is monoclinic (m) at room temperature and tetragonal (t) starting around 1050°C. The addition of YTaO_4 to ZrO_2 creates a solid solution that is maintained up to x=0.66 at room temperature and lowers the m-t transition temperature until approximately x=0.72 doping is reached. At this point, the m-t transition is suppressed.
below room temperature, allowing for the persistence of the t-phase to room temperature for ZrO₂ compositions with x=0.66-0.72. On the YTaO₄ end, the addition of ZrO₂ lowers the M-T transformation temperature from 1426°C to 400°C at the solubility limit of x~0.28. The transformation temperature then remains constant around 400°C in the two-phase region. A small amount of the T-phase is retained to room temperature within the two-phase region, as noted by the bracketed T.

The solubility limits at high temperatures (>400°C) were obtained using the lattice parameters from the in-situ measurements. By fitting the lattice parameters of the tetragonal phases (T and t) as a function of temperature, an expression was obtained for each parameter (a_T, c_T, a_t, c_t) at each composition. These equations enabled the lattice parameters of the two phases to be compared across composition for a given temperature. The same method was applied to data from Shian et al⁷⁵ and Sheu⁸⁹ to obtain expressions for the lattice parameters of the two tetragonal phases as a function of temperature in the solid solution regions. Using these equations, the lattice parameters of the T and t-phases were calculated across the YTaO₄-ZrO₂ compositional range every 100°C. The same intercept method used for the room temperature solubility limits in section 5.1 was applied to the calculated data at each temperature, thus allowing the calculation of the solubility limits over the temperature range 500°C-1600°C. The solubility limit of ZrO₂ into YTaO₄ occurs at approximately x=0.28 at lower temperatures and appears to slightly shift towards YTaO₄ with increasing temperature. For ZrO₂(ss), the solubility limit starts at x~0.66 at lower temperatures and curves away from ZrO₂ with increasing temperature.
From the diagram, it’s evident that the solid solutions extending from the two terminal phases, YTaO$_4$ and ZrO$_2$, cover rather large compositional ranges, and that there exists within the intermediate region an extensive dual tetragonal (T+t) phase field above the M-T transformation line, which is exceptionally stable. However, the equilibrium phases at the very highest temperatures, above 1700°C, remain to be determined. It is known that pure ZrO$_2$ exists in a cubic form (noted as ‘c’ on the phase diagram) over the 2350-2700°C temperature range. Yet, it is unknown if a corresponding cubic form of YTaO$_4$ exists at the highest temperatures. Assuming a high-temperature YTaO$_4$ cubic phase does exist, then it could be inferred that a cubic phase would also exist above 1700°C at compositions in the intermediate range of the phase diagram. However, if pure YTaO$_4$ does not exhibit a cubic phase, then it is unlikely for a continuous solid solution to exist between YTaO$_4$ and ZrO$_2$ at the highest temperatures. Given the similarity in the crystal structures of the two solid solution tetragonal phases, it is highly likely that a eutectoid reaction (cubic → T+t) occurs at higher temperatures than can be probed by in-situ measurements.

### 5.4 Phase Banding in the Microstructure

Backscattered SEM images revealed the presence of a banding structure within the grains, which could be indicative of a eutectoid transformation. However, unlike a typical eutectoid transformation microstructure, in which the eutectoid grows into one of the phases from the grain boundaries in plate-like structures, these images suggest that the phases are growing into each other. In both phases, the shape of the banding is irregular, and the ends appear to be tapered. Moreover, the phase interfaces are sharp, meaning there is no concentration gradient
across them. Using a serial sectioning imaging technique, it was observed that the banding structure occurred throughout the sample and was not limited to only surface grains.

One possible explanation for the phase banding is the curvature of the ZrO$_2$ solvus line. As shown in Figure 5.9, a change in temperature causes a change in the composition of the equilibrium phases in the two-phase region. Since the ZrO$_2$ solvus line is curved, the compositional change of the t-phase is greater than that of the T-phase. Moreover, the initial composition of the sample, denoted $C_0$, does not change. This means the phase ratio of the T- and t-phases changes with temperature, as indicated by the lever rule$^{90}$. Following heat treatment at 1600°C, the sample is slowly cooled to room temperature. As it cools, the sample undergoes phase separation, and the amount of T-phase increases while the amount of t-phase decreases. This causes nucleation of the T-phase in the t-phase, possibly leading to the phase banding observed in the microstructure. However, this explanation is only applicable at high temperatures since the cation diffusion is very slow below 1500°C, as discussed later.
Figure 5.9 – Two-Phase Region: Lever Rule
Illustration of the change in the composition of the equilibrium T- and t-phases for a sample in the two-phase region as temperature changes. A larger compositional change is observed for the t-phase due to the curvature of the ZrO$_2$ solvus line. The solid horizontal line represents the first temperature (1), and the dashed horizontal line corresponds to the second temperature (2). The initial composition of the sample is denoted by $C_0$.

To further explore the banding structure and to understand the orientation relationship of the phases, the sample was studied using transmission electron microscopy (TEM). A dark field STEM image of the phase banding in the $x=0.4$ composition is shown in Figure 5.10. The phase regions could be identified by their contrast and their individual characteristics. The lighter regions correspond to the YTaO$_4$ phase due to the larger scattering effect of the Tantalum. These regions also contain twin domains which resulted from the M-T transformation. The darker regions belong to the ZrO$_2$(ss) phase. There is an interesting
mottled effect seen in this phase, most likely representing YTaO$_4$ precipitates within the phase. The formation of YTaO$_4$ precipitates has been observed in compositions near the ZrO$_2$ solvus line when the material was sintered above the solvus line, thus resulting in YTaO$_4$ precipitating out of the ZrO$_2$ phase during cooling$^{91}$. Since the composition imaged here falls in the middle of the two-phase region, it’s not certain that the ZrO$_2$(ss) phase crossed the ZrO$_2$ solvus line during heat treatment.

Figure 5.10 – Microstructural Phase Banding
High resolution dark field image of the banding structure for the $x=0.4$ composition. The lighter regions correspond to YTaO$_4$(ss), and the darker regions to ZrO$_2$(ss). Twin domains are observed in the YTaO$_4$ phase. Taken at 200kV.
As a second check, phase identification was confirmed by EDAX mapping. Interestingly, the phase interfaces are preserved even in the smallest bands, which are only ~20nm in size. The EDAX mapping shows unequivocally that the small dark bands contain more Zr, while the surrounding light region is Y- and Ta-rich, and that there is no concentration gradient between the two regions, even on such a fine scale (see Figure 5.11). Examining the phase boundaries of the small bands proved difficult due to their sensitivity to tilt. Therefore, a larger band interface was selected to study the orientation relationship between the two phases.

Figure 5.11 – EDAX Mapping of Phase Banding
Energy-dispersive X-ray spectroscopy mapping of the x=0.4 composition, showing the chemical makeup of the small phase bands. The distribution of Zirconium, Yttrium, and Tantalum in the sample is shown here. The lighter regions are YTaO₄(ss), and the darker regions are ZrO₂(ss). Taken at 200kV.
Dark field STEM images of the interphase boundary are shown in Figure 5.12. At lower magnifications, the contrast between the YTaO$_4$ and ZrO$_2$ phases confirms that the images are centered on the phase interface. The Y and Ta atoms are not distinguishable at high magnifications in the YTaO$_4$ phase, which suggests the crystal orientation mostly likely contains columns of mixed cations. The lattice is continuous across the phase boundary, and the planes are spaced approximately 3Å apart. Along the planes, the distance between the individual columns of atoms is 2Å. No defects are observed at or near the interface. From the dark field STEM images it appears that a fully coherent interface exists between the M-YTaO$_4$ and t-ZrO$_2$ phases.

**Figure 5.12 – TEM Imaging of Interphase Boundary**

High resolution dark field STEM images of the interphase boundary between the YTaO$_4$ and ZrO$_2$ phases, taken at different magnifications. The red box (100nm x 100nm) marks the location on the interface where the STEM images were obtained. Taken at 200kV.
Understanding this coherency requires a return to the relationship between the two tetragonal phases and an evaluation of the twinning in the monoclinic structure. The twin planes in the M-phase of pure YTaO₄ are [209] and [902], which means the twin variants are rotated about the b-axis. Since the twin domains observed in the TEM image are perpendicular to the interphase boundary, the monoclinic bₘ-axis must be parallel to it. Subsequently, the cₜ-axis of the T-phase at high temperatures must also be parallel to the interface because the cₜ-axis is equivalent to the bₘ-axis. To simplify the analysis, the assumption is made that one twin domain of the M-phase is oriented along the (010) direction, meaning the other twin domain is also oriented along the (010) direction but rotated about the bₘ-axis. This translates to the (001) orientation in the T-phase. Given the coherency of the interphase boundary, the atomic arrangement in the t-phase must match that of the T-phase at high temperatures. Using the crystallographic relationship between the two tetragonal phases, the t-phase must then be oriented along the (001) direction and rotated by 45° about the cₜ-axis. This arrangement is illustrated in Figure 5.13. For a coherent boundary to exist between the YTaO₄ and ZrO₂ phases, the (100)/(001) orientations in the M-phase must aligned to the (110) orientation in the t-phase. Based on the mixed cations observed in the STEM image, as well as the spacing of the atoms, the structures corresponding to the STEM image are rotated such that the M phase is oriented along the [111] direction and the t-phase along the [101] direction.
5.5 Phase Separation in the Two-Phase Region

It is known that the heat treatment time does not have a large effect on the phases in the YTaO$_4$ solid solution region. However, a pronounced difference in the phases is observed in the two-phase region (see Section 4.5) due to the rearrangement of the atoms into the two solubility limit compositions. To study the phase separation effects in the two-phase region, in-situ high temperature synchrotron measurements were conducted at a set temperature for the x=0.5 composition, which had been first treated at 1600°C for 40 hours. The powder was heated to 1120°C and held for approximately 4 hours, with XRD scans obtained continuously during that time. The time length was chosen based on the limitations of the halogen bulbs used in the furnace. The XRD scans obtained at 1120°C are plotted as a function of time in
Figure 5.14. It is immediately obvious that there is no change in the XRD patterns with time. The peak positions and shapes remain constant for both tetragonal phases, meaning there is no change in their crystal structures. The amount of each phase is also constant, given the preservation of the relative intensities of the two phases.

There are two possible explanations for the time-independent behavior of the phases at 1120°C. First, the diffusion rate in these materials is so slow that four hours is not a long enough time to observe a change in the T- and t-phases. Given that the exchange of two Zr$^{4+}$ ions for one Y$^{3+}$ ion and one Ta$^{5+}$ ion results in no stoichiometric vacancies in either structure, the free volume within the phases is minimal, which limits the lattice diffusion. This means mass transport will most likely occur along the grain boundaries. However, the similarity between the structures results in coherency at the interphase boundaries, thus reducing the
free volume of the grain boundaries. The lack of free volume both within the grains and at the grain boundaries suggests qualitatively that the diffusion rates are slow within this system. This is further supported by the behavior of the microstructures during sintering (see Figure 5.15). A comparison of the microstructures of samples treated at 1600°C for different time lengths shows limited grain growth in the two-phase region. Even after 100 hours, the average grain size is only 1.8 microns, with very little difference observed between the grain sizes of the 40 hour and 100 hour treatments.

Figure 5.15 – Microstructure vs Sintering Time
Comparison of the microstructures for the x=0.4 and x=0.5 compositions given different heat treatments. Little grain growth is observed in the samples. Mag 5kx, 5kV
The second possible explanation for the time-independent behavior of the phases is that the YTaO₄ and ZrO₂ solubility limits are independent of temperature. Although the phase diagram in section 5.3 shows a slight bend for both solvus lines, the argument could be made that the lines are actually constant. In that case, the XRD patterns of the equilibrium phases would be independent of time at any temperature in the two-phase region. To further explore this, a series of interval heat treatments were conducted for the x=0.3-0.6 compositions. The powders were first treated at 1600°C for 2 hours to obtain the M- and t-phases. The treatment temperature then decreased by 100°C increments from 1600°C to 1500°C, and the hold time was increased to 100 hours at each temperature. The powders were cooled to room temperature between each temperature step, and a small amount was set aside for XRD measurements. The first three temperature steps are shown in Figure 5.16a, and the room temperature synchrotron XRD measurements were conducted following each of these temperature steps, as marked by the circles. As expected, there is a noticeable difference between the 1600°C and 1500°C treatments (see Figure 5.16b) since two hours at 1600°C is not enough time for the phases to reach their equilibrium state. The broadness of the peaks in the 1500°C scan indicate that the phases have not fully reached equilibrium, but the shift in peak positions means a portion of the phases are in their equilibrium state.
Figure 5.16 – Phase Separation: XRD Measurements
(a) Heat treatment profile used for the powders in the phase separation experiments. A small amount of powder was set aside after each temperature step, as indicated by the circles. (b) XRD scans of the $x=0.4$ composition after the first three temperature steps and (c) plot of the refined phase volumes as a function of treatment temperature. Synchrotron data with wavelength = 0.414166 Å (30 keV).

From the XRD studies of the 1600°C-40hrs samples, it is known that the equilibrium M-, T-, and t-phases have volumes of 284.7Å$^3$, 284 Å$^3$, and 68.9Å$^3$, respectfully. The phase volumes in the $x=0.4$ composition at 1500°C differ from those equilibrium volumes by only 0.2-0.4%, meaning that the structures observed after 100 hours at 1500°C are almost identical to those seen after 40 hours at 1600°C. This supports the hypothesis that the solvus lines are independent of temperature. Additionally, there is almost no change in the phase volumes
between 1500°C and 1400°C, nor is there a change in the peak shapes. This is another confirmation that the diffusion rates in this system are very slow.

5.6 Summary

The YTaO$_4$-ZrO$_2$ quasi-binary phase diagram has been established for temperatures up to 1600°C. Three regimes exist along the quasi-binary: YTaO$_4$ solid solution (x=0-0.28), two-phase region (x=0.28-0.65), and ZrO$_2$ solid solution (x=0.65-1). The solvus lines appear independent of temperature. The M-T transformation is constant in the two-phase region, occurring at ~400°C. This creates an extensive tetragonal (T+t) phase field over the temperature range 400-1600°C, which is promising for TBC applications. The similarities in the T and t structures suggests the possibility of a euctectoid reaction (cubic $\rightarrow$ T+t) at higher temperatures (>1700°C). This is also supported by phase banding observed in the microstructure. Analysis of the phase banding reveals a fully coherent interface between the M-YTaO$_4$ and t-ZrO$_2$ phases, which is consistent with the orientation relationship observed between the T-phase and t-phase unit cells. Furthermore, the kinetics of this system are very slow, as indicated by the small grain size and limited grain growth observed in the two-phase region.
CHAPTER 6

Properties along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ Quasi-Binary

The potential use of compositions in the ZrO$_2$-YO$_{1.5}$-TaO$_{2.5}$ system for TBCs raises an interest in the methods of heat transport (conduction and radiation) through the materials. This, in turn, requires an understanding of their thermal and optical properties. In this chapter, the thermal conductivity and the diffuse reflectance are explored along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ quasi-binary.

6.1 Thermal Conductivity

To study the thermal conductivity, thermal diffusivity measurements were performed on dense pellets using the laser flash method$^{92}$. The pellets were treated at 1600°C for 40 hours to achieve the desired M- and t-phases. The pellet parameters are given in Table 6.1.

<table>
<thead>
<tr>
<th>ZrO$_2$ Concentration (x)</th>
<th>Diameter (mm)</th>
<th>Thickness (mm)</th>
<th>Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>7.94</td>
<td>0.9452</td>
<td>96.77</td>
</tr>
<tr>
<td>0.2</td>
<td>7.79</td>
<td>1.0592</td>
<td>96.62</td>
</tr>
<tr>
<td>0.3</td>
<td>7.67</td>
<td>0.9900</td>
<td>97.47</td>
</tr>
<tr>
<td>0.4</td>
<td>7.89</td>
<td>1.1304</td>
<td>99.12</td>
</tr>
<tr>
<td>0.5</td>
<td>7.74</td>
<td>1.0456</td>
<td>97.78</td>
</tr>
<tr>
<td>0.6</td>
<td>7.71</td>
<td>1.0634</td>
<td>96.51</td>
</tr>
<tr>
<td>0.7</td>
<td>7.96</td>
<td>1.2900</td>
<td>85.76</td>
</tr>
</tbody>
</table>
The samples were coated with Au-Pd and carbon to prevent direct radiative transfer. Measurements were conducted under flowing Argon, with titanium powder serving as an oxygen getter to preserve the carbon coating against oxidation at high temperatures. The thermal diffusivity results are shown in Figure 6.1. With the exception of the x=0.4 composition, all of the samples display a slight decrease in their thermal diffusivity with increasing temperature. The decrease is most pronounced in the x=0.1 composition.

Figure 6.1 – Temperature Dependence of the Thermal Diffusivity
Temperature dependence of the thermal diffusivity for the Y(1-x)Ta(x)Zr2xO4 quasi-binary.
From the thermal conductivity data, the thermal conductivity was calculated from the relationship

\[ k = \alpha \cdot \rho \cdot C_p \quad \text{(Equation 6.1)} \]

Where \( \alpha \) is the thermal diffusivity, \( \rho \) is the sample density measured using the Archimedes method, and \( C_p \) is the heat capacity calculated from the Kopp-Neumann rule\textsuperscript{93} using data of pure \( \text{ZrO}_2 \), \( \text{Y}_2\text{O}_3 \), and \( \text{Ta}_2\text{O}_5 \) from literature\textsuperscript{93,94}. The calculated heat capacities (not shown) increased monotonically with increasing temperature. Moreover, the heat capacity appears to increase with increasing \( \text{ZrO}_2 \) concentration. The thermal conductivity was also corrected for any residual porosity (\( \varphi \)) using Maxwell’s relation

\[ k_{\text{dense}} = k_{\text{measured}} \frac{1}{(1 - 1.5\varphi)} \quad \text{(Equation 6.2)} \]

The conductivity corrected for density is shown in Figure 6.2, along with the conductivity of 7YSZ and YTaO\textsubscript{4} from the literature\textsuperscript{95}. All of the compositions have thermal conductivities which are lower than that of 7YSZ, indicating they are better thermal insulators. Additionally, the conductivities of all the compositions, except \( x=0.1 \), are independent of temperature above room temperature, which suggests that point-defect scattering caused by the mass difference of the cations dominates the thermal conductivity. This is different from 7YSZ, where the low thermal conductivity is caused by scattering from the oxygen vacancies\textsuperscript{74}. 
Figure 6.2 – Temperature Dependence of the Thermal Conductivity
Temperature dependence of the thermal conductivity for the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ quasi-binary. The thermal conductivity of dense 7YSZ and YTaO$_4$ are superimposed$^{95}$.

The thermal conductivity of a material is determined by the scattering of phonons through intrinsic processes (Umklapp scattering) and lattice defects, such as grain boundaries and point defects. At temperatures greater than the Debye temperature, size effects can be ignored, which means defect scattering is primarily a result of point defects. Additionally, the phonon-phonon scattering becomes inversely proportional to temperature.$^{96}$ According to the Klemens-Callaway phonon scattering model$^{96,97}$, the thermal conductivity can be treated as
the sum of the thermal conductivity due to intrinsic processes and the thermal conductivity
due to lattice defects, expressed as

$$\kappa_i = \kappa_{min} + \frac{k_B \sqrt{v_s}}{\sqrt{\pi} \sqrt{\Omega_0 \Gamma}} \frac{1}{\sqrt{\Omega_0 \Gamma}} \tan^{-1} \left( \frac{k_B T_D}{\hbar} \frac{\sqrt{\Omega_0 \Gamma}}{4 \pi v_s^2 C T} \right)$$  
(Equation 6.3)

where $C$ represents the anharmonic phonon-phonon scattering in the pure, defect-free
compound, $T$ is temperature, $\Gamma$ is the phonon scattering term, $v_s$ is the acoustic velocity, $T_D$ is
the Debye temperature, $\Omega_0$ is the unit cell volume, $k_B$ is Boltzmann’s constant, and $\hbar$ is
Planck’s constant. Equation 6.3 can be simplified to the form

$$\kappa_i = \kappa_{min} + \frac{k_B^2 T_D}{2 \pi^2 v_s \hbar C T} \frac{1}{\tan^{-1}(u)}$$  
(Equation 6.4)

Where the parameter $u$ has the form

$$u = \frac{k_B T_D}{\hbar} \frac{\sqrt{\Omega_0 \Gamma}}{4 \pi v_s^2 C T}$$  
(Equation 6.5)

The term $\kappa_{min}$ represents the minimum value of the thermal conductivity at high temperatures.
As temperature increases, the phonon mean free path approaches a lower limit that is
comparable with the dimensions of the unit cell of the crystal. Therefore, the thermal
conductivity must also approach a lower limit since the heat capacity is independent of
temperature at high temperatures. At these length scales, the inter-atomic distances and the
mass of the compound determine the thermal conductivity, thus $\kappa_{min}$ is independent of
temperature.
The second term provides the effect of lattice defects on the thermal conductivity. This term is inversely related to the phonon scattering coefficient, which explicitly depends on the defect concentration. The phonon scattering coefficient is proportional to the variance of the mass, and for a given cation lattice site (j), it can be expressed as

$$\Gamma_{j-site} = \sum_i x_i \left[ \frac{M_i - M_j}{M_j} \right]^2$$  \hspace{1cm} (Equation 6.6)

where \(x_i\) is the concentration of the dopant i, \(M_i\) is the dopant’s atomic mass, and \(M_j\) is the atomic mass of the j-site ion.

There are two extremes to consider: \(\Gamma \to 0\), which represents a perfect, defect-free crystal, and \(\Gamma \to \infty\), which represents a crystal with the maximum number of defects. For the case of \(\Gamma \to 0\), \(\arctan(u)/u \to 1\) and equation 6.4 reduces to

$$\kappa_i = \kappa_{min} + \frac{k_B T_D}{2\pi^2 v_s hCT}$$  \hspace{1cm} (Equation 6.7)

and the thermal conductivity becomes inversely dependent on temperature. Alternatively, if \(\Gamma \to \infty\), then \(\arctan(u)/u \to 0\) and the second term of equation 6.4 becomes increasingly smaller. Thus, the thermal conductivity approaches \(\kappa_{min}\).

For compositions along the \(Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4\) quasi-binary, the mass of \(Y^{3+}\) and \(Zr^{4+}\) are almost identical, while that of \(Ta^{5+}\) is about twice the mass of \(Y^{3+}\) (see Table 6.2). The replacement of \(Ta^{5+}\) with \(Zr^{4+}\) increases the mass disorder within the system and thus increases the phonon scattering coefficient. The temperature independent behavior of the
thermal conductivity suggests that the mass disorder in the x=0.2-0.7 compositions is large enough for $\Gamma \to \infty$, causing the thermal conductivities to approach their intrinsic thermal conductivities $\kappa_{\text{min}}$. In the case of the x=0.1 composition, the concentration of dopants is not large enough for the mass disorder to completely dominate the thermal conductivity, which means that $\Gamma$ is fairly small. This results in a $1/T$ behavior at lower temperatures.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Atomic Mass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$^{5+}$</td>
<td>181</td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>91</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>89</td>
</tr>
</tbody>
</table>

The behavior of the thermal conductivity as a function of composition differs at high and low temperatures. At 1000°C, there is a linear trend observed between the thermal conductivity and the ZrO$_2$ concentration, while at 200°C, the thermal conductivity first decreases with ZrO$_2$ content and then increases (see Figure 6.3). The parabola-like behavior observed at 200°C is related to the lattice defects, which dominate the thermal conductivity at low temperatures. Compositions closer to the end compounds (YTaO$_4$ and ZrO$_2$) contain less dopants and therefore less mass disorder. This results in slight $1/T$ dependence at lower temperatures for the thermal conductivity. However, at high temperatures, the thermal conductivity is given by $\kappa_{\text{min}}$, which is inversely proportional to the mass and the density. As the ZrO$_2$ content increases, both the mass and the density decrease, causing an increase in
Thus, the thermal conductivity increases with increasing ZrO₂ content at high temperatures.

![Figure 6.3 – Thermal Conductivity vs ZrO₂ Concentration for Selected Temperatures](image)

*Figure 6.3 – Thermal Conductivity vs ZrO₂ Concentration for Selected Temperatures*

Plot of the thermal conductivity as a function of ZrO₂ content for selected temperatures. At low temperatures, parabolic behavior is observed, while high temperatures display a linear trend.

### 6.2 Optical Properties

When previously considering heat transport through TBCs, only the thermal conductivity was studied since conduction is the prevailing mechanism at lower temperatures. However, as
engines push to higher operating temperatures (~1500°C), the effects of thermal radiation become more important. The increase in temperature shifts the blackbody radiation to the 0.35-5µm wavelength range and increases its intensity as $T^4$. This wavelength range coincides with the transparent region of Zirconia-based ceramics. As a result, an understanding of the radiative scattering and absorption properties becomes necessary in order to quantify the effect of radiation on the temperature of TBCs.

6.2.1 Diffuse Reflectance Measurements

Diffuse reflection spectroscopy using an integrating sphere was used to quantify the scattering and absorption behavior in the UV-Visible range of compositions along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ quasi-binary. Because the samples were pellets, measurements could be performed in reflection or transmission mode. However, the thickness of the pellets (~1mm) made the transmission results less reliable. The diffuse reflectance results over the 250-2500nm wavelength range are shown in Figure 6.4 for all compositions except the $x=0.8$ composition. Due to the volume change during the m-t transformation, that pellet fell apart during the heat treatment. The $x=0.9$ composition also passed through the m-t transformation temperature. The pellet exhibited significant cracking following the heat treatment and fell apart after the diffuse reflectance measurements. As a result, density data does not exist for the $x=0.9$ pellet, but the presence of cracks means the density is quite low. The anomalies occurring at 900nm and 1400nm are caused by the instrument, and the dip at 1000nm in the reflectance of the $YTaO_4$ composition, marked by the dashed arrow, is due to a contaminant in the sample. The absorption bands, marked by solid arrows, were identified by comparing the reflectance and
transmittance spectra (not shown). Each composition exhibits an absorption band over the 250-500nm wavelength range, as noted by the rapid decrease in reflectance near 350nm. This band will be discussed later. For the intermediate compositions, the pellets exhibited a slight reddish color with increasing ZrO$_2$ concentration, up to $x=0.6$. This is represented by the peak occurring near 650nm since the remaining portion of the visible light is absorbed.

![Figure 6.4 – Diffuse Reflectance Spectra](image)

**Figure 6.4 – Diffuse Reflectance Spectra**
Spectral diffuse reflectance of compositions along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2}O_4$ quasi-binary. The discontinuities at 900nm, 1400nm, and 2200nm are due to the instrument. The solid arrows indicate absorption bands in the samples, and the dashed arrow denotes an absorption peak corresponding to a contaminant in the $YTaO_4$ sample. The inset graph shows the behavior of the reflectance at low wavelengths.
The reflectance data can immediately be separated into two groups based on pellet density. The x=0, x=0.7, and x=0.9 samples, which are only 85-90% dense, exhibit high reflectance over almost the entire wavelength range from 500nm to 2500nm. On the other hand, x=0.1-0.6 samples are almost fully dense, and their reflectance remains around 70%. This difference in reflectance is caused by a difference in the number of medium/pore interfaces. Within the samples, incident light can be scattered via two different interactions: (1) reflection and refraction at the surface and (2) reflection and refraction at the medium/pore interface. Denser pellets contain fewer pores, thus reducing the number of scattering events caused by the medium/pore interface. The shape of the reflectance curve also varies across the samples. The reflectance of the x=0.3-0.5 samples appears to decrease with increasing wavelength, while the other compositions remain constant. This could be a consequence of microstructural differences, such as grain size or pore shape and distribution, or it could be caused by the presence of two chemically different phases (M- & t-phases). Interestingly, the reflectance of the x=0.7 composition increases with increasing wavelength. The shape of the reflectance is not currently well understood, and it is difficult to control the microstructure of polycrystalline pellets.

6.2.2 Determination of the Scattering Coefficient

As light travels through the sample, it is subjected to multiple scattering events, which is characterized by an overall scattering coefficient dependent on wavelength. The inverse of this parameter is the mean free path for a scattered photon. It is possible to approximate the scattering coefficient from the diffuse reflectance using Kubelka–Munk theory\textsuperscript{100}, which
assumes that multiple scattering and absorption processes occur within the medium and that the thickness of the medium is much larger than the optical mean free path. This procedure was developed to analyze paper\textsuperscript{101} and has been previously applied to TBC coatings\textsuperscript{102}. The method treats the sample as a stack of thin layers and then calculates the reflectance from the integral of the scattering of the individual layers. This leads to a relationship between the average scattering coefficient and the diffuse reflectance given by

\[ s = \frac{1}{h (1 - R) (1 - R_{bg})} \quad \text{(Equation 6.8)} \]

Where \( R \) is the measured reflectance of the sample, \( R_{bg} \) is the reflectance of the background, and \( h \) is the sample thickness. Since these are freestanding pellets, \( R_{bg} \) is zero, simplifying the equation to

\[ s = \frac{1}{h (1 - R)} \quad \text{(Equation 6.9)} \]

The average scattering coefficient over the wavelength range 500-2500nm was calculated and compared with the density of the pellets for the \( x=0-0.7 \) compositions (see Figure 6.5).
It’s apparent that the scattering coefficient is greatly affected by the amount of porosity in the sample. A ten-percentage increase in density reduces the scattering coefficient sixfold. However, there is little variation in the scattering coefficient with composition for the dense pellets. This is not surprising given the similarity of the refractive indexes of YTaO$_4$ and ZrO$_2$. After microstructure, the most influential factor affecting the scattering in a material is the refractive index mismatch between the material and air, both at the surface and within the pores. The index of refraction has been well-documented for zirconia, and it has been found...
that near the infrared region, tetragonal ZrO$_2$ has a refractive index of 2.02$^{103}$. However, in the case of YTaO$_4$, the refractive index is not well studied, with the only reports conducted in the 0-3THz regime$^{104}$. To compare the two phases, the refractive index of YTaO$_4$ was approximated using the Gladstone-Dale relationship$^{105}$, which relates a substance’s refractive index to its chemical composition and density through the use of a constant (K) called the refractive energy. This relationship is primarily employed by mineralogists to approximate the refractive index of complex minerals using the known refractive indexes of its components. The Gladstone-Dale relationship is given by the equation

$$K = \frac{n - 1}{d} = \frac{k_1p_1}{100} + \frac{k_2p_2}{100} + \cdots + \frac{k_mp_m}{100}$$

(Equation 6.10)

where $K$ is the specific refractive energy of the substance, $n$ is its refractive index, $d$ is its density, $k_m$ is the specific refractive energies of its components, and $p_m$ is the weight percentages of its components. Using the $k$ values of the individual oxides (ZrO$_2$, Y$_2$O$_3$, and Ta$_2$O$_5$)$^{106}$ and the density determined from XRD measurements, the refractive index for YTaO$_4$ was determined to be approximately 2.2, which is very close to the refractive index of ZrO$_2$. Since the refractive indexes of YTaO$_4$ and ZrO$_2$ are almost identical, the refractive index mismatches between the two oxides and air are expected to be similar. Thus, the scattering at the oxide/pore interface within each material is similar and no significant difference in the reflectance would be detectable. Moreover, the refractive index mismatch between YTaO$_4$ and ZrO$_2$ is essentially zero, which means the phase banding in the two-phase region will have a minimal effect on the reflectance.
6.2.3 Determination of the Bandgap

The absorption edge observed in the UV region was first believed to represent the bandgap of the compositions. As such, analysis was carried out to calculate the bandgap as a function of ZrO$_2$ concentration. This was done using the Kubelka-Munk theory and Tauc plots.

Based on work with amorphous semiconductors, the absorption spectrum can be related to the bandgap using the equation

\[
(h\nu\alpha)^{\frac{1}{n}} = A(h\nu - E_g) \tag{Equation 6.11}
\]

where $h$ is Planck’s constant, $\nu$ is the frequency of vibration, $\alpha$ is the absorption coefficient, $n$ is an indicator of the nature of the transition, $A$ is the proportional constant, and $E_g$ is the bandgap. There are four possible values for $n$, depending on the transition.

- Direct Allowed Transition $\rightarrow n=1/2$
- Direct Forbidden Transition $\rightarrow n=3/2$
- Indirect Allowed Transition $\rightarrow n=2$
- Indirect Forbidden Transition $\rightarrow n=3$

For these materials, the bandgap is assumed to be a direct allowed transition, which means $n=1/2$.

Since the diffuse reflectance includes both scattering and absorption events, it can be related to the absorption coefficient by the Kubelka-Munk theory\textsuperscript{100}, which is expressed as

\[
F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} = \frac{K}{S} \tag{Equation 6.12}
\]
where \( R_\infty \) is the reflectance of an infinitely thick layer, \( K \) is the absorption coefficient, and \( S \) is the scattering coefficient.

Using \( F(R_\infty) \) in place of \( \alpha \), equation 6.11 becomes

\[
\left( h \nu \cdot F(R_\infty) \right)^2 = A(h \nu - E_g) \tag{Equation 6.13}
\]

Which can be plotted as \((h\nu F(R_\infty))^2 \) versus \( h \nu \), also known as a Tauc plot. The bandgap can be extracted by fitting a tangent line to the point of inflection on the curve and extrapolating the line to \( y=0 \). Using this method, the bandgap was determined for each composition (see Figure 6.6).
Figure 6.6 – UV Absorption Band vs ZrO$_2$ Concentration
(a) Tauc plot of YTaO$_4$, illustrating the calculation of the bandgap. (b) Plot of the bandgap as a function of ZrO$_2$ concentration. The theoretical values for YTaO$_4$ and ZrO$_2$ are marked on the plot$^{108,109}$. 

YTaO$_4$

Bandgap = 3.87eV
There are two striking features of the behavior of the bandgap with ZrO$_2$ concentration. First, the bandgap decreases between $x=0$ and $x=0.1$ but then remains fairly constant for the other compositions. This is unusual given that the bandgap data covers three different phase regimes. And second, the bandgaps are significantly lower than the theoretical values for YTaO$_4$ and ZrO$_2$\textsuperscript{108,109}. Based on these features and the increase of the reflectance near 250nm, the observed absorption edge does not correspond to the bandgap. Instead, it most likely corresponds to a charge-transfer within the tantalate group\textsuperscript{110,111}. However, more work is needed to decipher these results.

6.3 Summary

The thermal and optical properties have been explored along the YTaO$_4$-ZrO$_2$ quasi-binary. All of the measured compositions display thermal conductivities which are lower than that of 7YSZ, indicating they are better thermal insulators. The thermal conductivity is independent of temperature for the intermediate compositions of the quasi-binary. This is a result of the mass difference of the cations, causing point-defect scattering to dominate. For compositions close to the endpoints, the thermal conductivity is inversely dependent on temperature at lower temperatures since the dopant concentration is not high enough for the mass disorder to completely dominate the thermal conductivity.

Diffuse reflectance spectroscopy was used to quantify the scattering and absorption behavior along the YTaO$_4$-ZrO$_2$ since thermal radiation becomes important at higher temperatures. The diffuse reflectance, and thus the scattering coefficient, was dependent on pellet density and
not chemical composition. This is due to the refractive index mismatch between the oxide material and air, both at the surface and within the pores. Moreover, the refractive indexes for YTaO$_4$ and ZrO$_2$ are almost identical, which means that the scattering at the oxide/air interface will be similar for all the compositions along the quasi-binary. The energy of the absorption edge observed at low wavelengths (~300nm) was calculated for each composition using the Kubelka-Munk theory and Tauc plots. The transition occurred at approximately 3.4eV for every composition except YTaO$_4$, which had an energy of 3.9eV. Since these values are much lower than the theoretical bandgaps of YTaO$_4$ and ZrO$_2$, the absorption edge most likely corresponds to a charge-transfer within the tantalate group.
CHAPTER 7

Compatibility with Alumina

As explained in Chapter 1, the multilayer design of TBCs provides both thermal and chemical protection at higher temperatures. However, it also makes thermochemical and thermomechanical compatibility critical to the long term stability of the system, particularly at the topcoat and bond-coat interface, where the thermally grown oxide (TGO) forms. The current high-temperature bond-coat alloys used in gas engines oxidize to form alpha-alumina oxide ($\alpha$-$\text{Al}_2\text{O}_3$) at high temperatures. This means any candidate oxide material must be compatible with $\alpha$-$\text{Al}_2\text{O}_3$ or an intermediate layer is necessary. In this chapter, the phase compatibility between alumina and compositions along the $Y_{(1-x)}\text{Ta}_{(1-x)}\text{Zr}_{2x}\text{O}_4$ quasi-binary is explored.

7.1 Background

The thermochemical compatibility of ZrO$_2$ and Al$_2$O$_3$ has been greatly explored over the years. As discussed in Chapter 2, ZrO$_2$ is polymorphic, existing as monoclinic, tetragonal, and cubic. On the other hand, Al$_2$O$_3$ only has one stable crystalline form, known as $\alpha$-$\text{Al}_2\text{O}_3$. Al$_2$O$_3$ can exist in other forms depending on the processing technique, but all of these transition forms transform to $\alpha$-$\text{Al}_2\text{O}_3$ upon heating. The mutual solubility of ZrO$_2$ and Al$_2$O$_3$ is very limited for every ZrO$_2$ phase and no interphases form between the two materials, although a noticeable solid solution region exists for the tetragonal ZrO$_2$ phase near 1800°C. This thermochemical compatibility has enabled ZrO$_2$ to be used in TBCs.
In contrast, $Y_2O_3$ reacts with $Al_2O_3$ to form multiple aluminate compounds: yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$), yttrium aluminum monoclinic (YAM, $Y_4Al_2O_9$), and yttrium aluminium perovskite (YAP, YAlO$_3$). It is known that if the amount of yttrium dopants in ZrO$_2$ surpasses a critical value, then YAG will form at the YSZ-Al$_2$O$_3$ interface$^{114}$. It is currently unknown if the alloying of ZrO$_2$ with YTaO$_4$ faces a similar restriction. Since zirconia is being co-doped with yttrium and tantalum, the tantalum may stabilize the $Y^{3+}$ ion and keep it from reacting with Al$_2$O$_3$. However, an interphase (TaAlO$_4$) does exist between Ta$_2$O$_5$ and Al$_2$O$_3$$^{117}$. This raises the possibility that YTaO$_4$ will react with Al$_2$O$_3$, even when alloyed with ZrO$_2$.

### 7.2 Compatibility between $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ Compositions and Al$_2$O$_3$

The common procedure for analyzing topcoat/TGO compatibility is to oxidize a TBC-coated superalloy for long periods of time at high temperatures (~1200°C) and then examine the topcoat/TGO interface for evidence of a reaction, such as formation of a new phase or delamination. Given the tediousness of this process, a simple yet effective method for investigating phase compatibility between alumina and candidate oxide compositions is to mix and sinter bulk powders of the materials and look for evidence of chemical reactivity. In this work, compositions along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ quasi-binary were mixed in a 50/50 weight ratio with commercial $\alpha$-Al$_2$O$_3$ and heat treated as powders at 1250°C for 6 hours. The treated powders were then pressed into pellets and sintered at 1500°C for 12 hours to increase the chance of interaction between the YTaO$_4$-ZrO$_2$ compositions and alumina. The
compositions along the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ quasi-binary were originally heat treated at 1600°C for 2 hours to achieve the desired phases. X-ray diffraction and photoluminescence measurements were performed on the initial mixed powders and following each temperature treatment to test for reactions between the materials. The experiments were repeated using $\gamma$-Al$_2$O$_3$, which is a more reactive form of alumina due to the present of hydroxyl ions and thus cation vacancies.

Results from XRD studies indicate that no reactions occurred between the YTaO$_4$-ZrO$_2$ compositions and either alumina form (Figures 7.1-7.3). Mixtures of $\alpha$-Al$_2$O$_3$ and YTaO$_4$ solid solution compositions contain the YTaO$_4$ M-phase and $\alpha$-Al$_2$O$_3$ phase when initially prepared. No change is observed in the XRD patterns following the two heat treatments, indicating no reaction between the two materials. In the case of $\gamma$-Al$_2$O$_3$, the as prepared mixtures contain the M-phase and the $\gamma$-Al$_2$O$_3$ phase. Upon heating, the $\gamma$-Al$_2$O$_3$ phase transforms to the $\alpha$-Al$_2$O$_3$ phase, but the M-phase is preserved. This also indicates no reaction between the two materials, even when a more reactive form of alumina is used. The same behavior is observed for compositions in the two-phase and ZrO$_2$ solid solution regimes of the YTaO$_4$-ZrO$_2$ quasi-binary. The variation in the peak intensities of the $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ phases and the alumina phases represents variations in the amount of each phase present in the probing volume.

The preservation of all the peaks indicates that no new phases formed during heating, with the exception of $\gamma$-Al$_2$O$_3$ converting to $\alpha$-Al$_2$O$_3$. If the compositions had reacted with alumina,
then peaks corresponding to Al-based phases, such as YAG and TaAlO$_4$, would have appeared. Moreover, the loss of yttrium or tantalum from the YTaO$_4$-ZrO$_2$ compositions would have resulted in secondary Y-rich or Ta-rich phases since YTaO$_4$ and ZrO$_2$ form a line compound. There are also no shifts in the peak positions or changes in the peak shapes. This suggests that the Al$^{3+}$ ions are not entering the M-phase or t-phase structures. If the Al$^{3+}$ ion was substituting on any of the Y$^{3+}$, Zr$^{4+}$, or Ta$^{5+}$ sites, then there would be a change in the unit cell due to the large differences between the ionic radii (0.04-0.054nm for Al$_2$O$_3$). This would cause the diffraction peaks to shift and broaden.

In addition, the symmetries of the Y$^{3+}$, Zr$^{4+}$, or Ta$^{5+}$ sites in the M- and t-phases are different than the symmetry of the Al$^{3+}$ site in alumina. If the Al$^{3+}$ ions were substituting into the M-phase and t-phase structures, then the change in site symmetry would have affected the R-line luminescence of α-Al$_2$O$_3$, either shifting the peaks or altering the number of peaks$^{118}$.

As seen in Figure 7.4, the characteristic R-line doublet is visible in every measurement except the 'As prepared Gamma' since γ-Al$_2$O$_3$ does not exhibit any sharp line luminescence. However, the γ-Al$_2$O$_3$ transforms to α-Al$_2$O$_3$ upon heating rather than reacting with the Y$_{(1-x)}$Ta$_{(1-x)}$Zr$_{2x}$O$_4$ phases, resulting in the observation of the R-line doublet in the heat treated samples. When α-Al$_2$O$_3$ is the starting alumina form, the luminescence is unchanged, even after 12 hours at 1500°C, indicating that α-Al$_2$O$_3$ does not react with the compositions along the YTaO$_4$-ZrO$_2$ quasi-binary, regardless of the phase regime. The same holds true for the γ-Al$_2$O$_3$ runs after treatment at 1250°C.
Figure 7.1 – Alumina Compatibility: YTaO₄ Solid Solution Region

XRD patterns of the x=0.1 composition mixed with α-Al₂O₃ (top) and γ-Al₂O₃ (bottom) after different temperature treatments. The x=0.1 composition resides in the YTaO₄ solid solution region, and the same behavior was observed for other compositions in this region. The YTaO₄ M-phase (black square) and α-Al₂O₃ phase (green circle) are marked. The bumps occurring at 37°, 39°, and 46° in the ‘As prepared’ pattern in the bottom graph correspond to γ-Al₂O₃ and disappear following the treatment at 1250°C.
**Figure 7.2 – Alumina Compatibility: Two-Phase Region**

XRD patterns of the $x=0.4$ composition mixed with $\alpha$-$\text{Al}_2\text{O}_3$ (top) and $\gamma$-$\text{Al}_2\text{O}_3$ (bottom) after different temperature treatments. The $x=0.4$ composition resides in the two-phase region of the YTaO$_4$-ZrO$_2$ quasi-binary phase diagram, and the same behavior was observed for other compositions in this region. The YTaO$_4$ M-phase (black square), ZrO$_2$ t-phase (purple triangle), and $\alpha$-$\text{Al}_2\text{O}_3$ phase (green circle) are marked. The bumps occurring at 32°, 37°, 39°, and 46° in the ‘As prepared’ pattern in the bottom graph correspond to $\gamma$-$\text{Al}_2\text{O}_3$ and disappear following the treatment at 1250°C.
Figure 7.3 – Alumina Compatibility: ZrO$_2$ Solid Solution Region

XRD patterns of the $x=0.7$ composition mixed with $\alpha$-Al$_2$O$_3$ (top) and $\gamma$-Al$_2$O$_3$ (bottom) after different temperature treatments. The $x=0.7$ composition resides in the ZrO$_2$ solid solution region, and the ZrO$_2$ t-phase (purple triangle) and $\alpha$-Al$_2$O$_3$ phase (green circle) are marked. The small bumps occurring at 33°, 37°, 39°, and 46° in the ‘As prepared’ pattern in the bottom graph correspond to $\gamma$-Al$_2$O$_3$ and disappear following the treatment at 1250°C.
Figure 7.4 – R-line Luminescence Measurements

Luminescence spectra from mixed powders of $Y_{(1-x)}Ta_{(1-x)}Zr_{2x}O_4$ compositions and alumina after different treatment temperatures for selected compositions. Top row, the alumina powder is $\alpha$-$Al_2O_3$ which has the characteristic R-line doublet of Cr$^{3+}$ in alumina. The luminescence is unchanged after long-term annealing, indicating that the alumina does not react with compositions along the $YTaO_4-ZrO_2$ quasi-binary. Bottom row, the alumina powder is $\gamma$-$Al_2O_3$, a more reactive alumina. In these cases, the $\gamma$-$Al_2O_3$ converts to $\alpha$-$Al_2O_3$, giving rise to the R-line luminescence, without reacting.
7.3 Summary

The thermochemical compatibility between compositions along the YTaO$_4$-ZrO$_2$ quasi-binary and alumina is important if these compositions are to be used as TBCs. XRD studies indicate no reaction between the quasi-binary compositions and $\alpha$-Al$_2$O$_3$ or $\gamma$-Al$_2$O$_3$. No new phases formed, even after exposure to 1500°C for 12 hours, and there is no indicator that the oxides are soluble in each other. In addition, the characteristic $\alpha$-Al$_2$O$_3$ R-line doublet is observed for every composition, signifying the preservation of the Al$^{3+}$ site symmetry. Thus, the XRD and luminescence studies confirm that compositions along the YTaO$_4$-ZrO$_2$ quasi-binary and alumina are compatible oxides.
CHAPTER 8

Conclusions and Future Directions

The primary objective of this investigation was to explore compositions along the YTaO$_4$-ZrO$_2$ quasi-binary which could potentially overcome the current TBC challenges and replace 7YSZ in the next generation of TBCs. Emphasis was placed on phase stability and heat transport. The following are the main results.

- A line compound exists between YTaO$_4$ and ZrO$_2$, with three distinct phase regions: YTaO$_4$ solid solution ($x$=0-0.28), two-phase region ($x$=0.28-0.65), and ZrO$_2$ solid solution ($x$=0.65-1). The ability of the YTaO$_4$ structures to accommodate large amounts of ZrO$_2$ indicates that the Zr$^{4+}$ ions are equally replacing the Y$^{3+}$ and Ta$^{5+}$ ions, most likely in neighboring pairs.

- The YTaO$_4$-ZrO$_2$ quasi-binary phase diagram has been developed up to 1600°C. The addition of ZrO$_2$ to YTaO$_4$ lowers the M/T transition temperature from 1426°C to approximately 400°C and then remains constant in the two-phase region. The solvus lines appear independent of temperature, creating an extensive tetragonal (T+t) phase field over the temperature range 400-1600°C, which is promising for TBC applications. The orientation relationship between the T-phase and t-phase unit cells suggests the possibility of a higher temperature phase (>1700°C) and offers insight into the microstructural phase banding.

- The thermal and optical properties were explored along YTaO$_4$-ZrO$_2$ quasi-binary. The thermal conductivity results indicate compositions in the intermediate region are
better thermal insulators than 7YSZ, due to their lower values and temperature independent behavior. However, there is no noticeable difference between the YTaO$_4$-ZrO$_2$ quasi-binary and 7YSZ when considering thermal radiation effects since the diffuse reflectance and scattering coefficient are dependent on pellet density and not composition.

- Thermochemical compatibility exists between compositions along the YTaO$_4$-ZrO$_2$ quasi-binary and alumina, as demonstrated by XRD and luminescence studies.

Although this work has provided considerable insight, continued efforts to understand the YTaO$_4$-ZrO$_2$ quasi-binary are necessary to transition from bulk powders to TBCs. The phase diagram remains unknown for temperatures above 1700°C, establishing the need for further phase studies. The similarities in the tetragonal phases suggest the existence of a higher temperature phase, but spinodal decomposition from the liquid region is also a possibility for this system. Additionally, the relationship between these phases merits closer attention, particularly since their similarities could provide toughening capabilities. ZrO$_2$ has demonstrated ferroelastic toughening at high temperatures, and the M-T phase transformation in YTaO$_4$ is believed to be ferroelastic. However, the mechanical properties of the two-phase region remain to be established.

The investigation of the heat transport along the YTaO$_4$-ZrO$_2$ quasi-binary in bulk form has shown promise for TBC applications. The next step is using the thermal and optical measurement results to model the temperature profile of coatings of these materials and
compare with current TBC coatings. Since the next generation of TBCs is aiming for higher operating temperatures, both thermal conduction and radiation need to be considered. Moreover, there is interest in using dopants as temperature sensors in TBCs. This would change the scattering and absorption behavior of the oxide, thus affecting the propagation of thermal radiation through the TBC. Lastly, coatings of compositions in the two-phase region need to be developed and their properties investigated.
References


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