LOST MOLD-RAPID INFILTRATION FORMING: STRENGTH CONTROL IN MESOSCALE 3Y-TZP CERAMICS

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by
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ABSTRACT

The strength of nanoparticulate enabled microdevices and components is directly related to the interfacial control between particles and the flaws introduced as these particles come together to form the device or component. One new application for micro-scale or meso-scale (10’s µm to 100’s µm) devices is surgical instruments designed to enter the body, perform a host of surgeries within the body cavity, and be extracted with no external incisions to the patient. This new concept in surgery, called natural orifice transluminal endoscopic surgery (NOTES), requires smaller and more functional surgical tools. Conventional processing routes do not exist for making these instruments with the desired size, topology, precision, and strength. A process, called lost mold-rapid infiltration forming (LM-RIF), was developed to satisfy this need. A tetragonally stabilized zirconia polycrystalline material (3Y-TZP) is a candidate material for this process and application because of its high strength, chemical stability, high elastic modulus, and reasonably high toughness for a ceramic.

Modern technical ceramics, like Y-TZP, are predicated on dense, fine grained microstructures and functional mesoscale devices must also adhere to this standard. Colloid and interfacial chemistry was used to disperse and concentrate the Y-TZP nanoparticles through a very steep, yet localized, potential energy barrier against the van der Waals attractive force. The interparticle interaction energies were modeled and compared to rheological data on the suspension. At high concentrations, the suspension was pseudoplastic, which is evidence that a structure was formed within the suspension that could be disrupted by a shearing force. The LM-RIF process exploits this
rheological behavior to fill mold cavities created by photolithography. The premise of the LM-RIF process is to process the particulate material into a dense ceramic body while the unsintered mesoscale parts are supported *en masse* by a substrate. Numerous challenges were overcome that relate to the application of photoresist on a refractory substrate capable of withstanding the high temperatures needed to sinter the ceramic parts. Strength of approximately 1 GPa was achieved for the first parts produced, which demonstrated the feasibility of the LM-RIF process.

Although respectable, a 1GPa strength is not as strong as would be predicted based on the small size (332 × 26 × 17 μm) of the parts. An effort to identify and eliminate the largest flaws in the specimen produced by the LM-RIF process was undertaken, which ultimately increased the average strength to 2.35 GPa. Geometric defects, previously unreported in ceramic microfabrication techniques, were degrading the strength of the early parts. An in-depth characterization of these defects by optical profilometry and then eliminating the underlying cause was the key to obtaining this high strength. One interesting phenomena discovered in this work was the role that the substrate plays in the sintering of the ceramic part through the enhanced diffusion pathways created by the more intimate contact of the mesoscale parts compared to macroscale analogs. Impurities of alumina and silica were found to adversely affect the sintering kinetics of mesoscale parts causing localized grain growth or exaggerated grain growth depending on the sintering conditions.

The role that the microstructure, specifically the grain size, plays in determining the strength versus the role that the surface flaw population plays, as characterized by the surface roughness, was determined through isothermal sintering experiments. It was
found that the strength of mesoscale ceramics lies in the transition region between the flaw-dominated stress intensity effect and the Hall-Petch microstructural effect. This proves that processing science and microstructural refinement about equally determine the strength of particulate based mesoscale materials.

The hierarchical approach that was used to marry the development of the LM-RIF process to the mechanical design and optimization of surgical instruments is described. This approach used nested iteration loops to refine both the design and fabrication processes to create and test surgical instrument prototypes. These prototypes as well as some of the unique shapes possible with the LM-RIF process are presented.
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as revealed by the TGA-MS data in Figure A-3. Cracking in the parts tends to occur
around the onset of shrinkage at 264°C...

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I would first like to thank my thesis advisor, Dr. James H. Adair, for the faith in allowing me to develop a way to make free-standing mesoscale ceramics and the support to see it through. Along the same line, I thank Greg Hayes for his partnership, enthusiasm, and constant consultation as we waded through the mire that is processing science. The LM-RIF process was born from his mechanical engineering and my ceramic engineering backgrounds and would not exist without his input.

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Finally I would like to thank my family for the support during the stressful times and my friends for helping me forget those stressful times. I dedicate this work to my Grandfather, Geno Antolino, who taught me the value of hard work, and to my Father who told me to try my best.
Chapter 1

Introduction

1.1 Introduction

Microfabrication has spread from integrated circuit (IC) manufacturing to micro-electro-mechanical systems (MEMS), to microfluidics and is rapidly expanding to new areas. However, the IC roots of microfabrication are impeding new applications simply because the technology of IC manufacturing with silicon is so intertwined with microfabrication that etched silicon or polymer based replicates of etched silicon are virtually the only material choices for microfabrication. By integrating the advantage of IC manufacturing to make small parts with other traditional manufacturing processes, such as ceramic powder processing, new applications can be realized that benefit from the small IC size scale but with much wider material selection and therefore, performance regimes. One of these applications is fabricating small scale surgical instruments to enable new and innovative surgical techniques that potentially decrease patient trauma, lower infection rates, and increase patient recovery time.

A new surgical method called natural orifice transluminal endoscopic surgery (NOTES) eliminates the need to make external incisions in a patient’s body.\textsuperscript{1,2} NOTES procedures use the body’s natural orifices to perform surgical procedures such as cholecystectomy (gall bladder removal)\textsuperscript{3} and nephrectomy (kidney removal).\textsuperscript{4} Smaller
multifunctional surgical instruments are required to enable these new surgical procedures. A typical surgical instrument for NOTES consists of a tool tip attached to a long (140 cm) flexible cable, which is inserted through the working channel of an endoscope as shown in Figure 1-1. In NOTES, there is a need for small (<1 mm diameter) instruments to enable more tools to fit within the endoscope thereby streamlining the surgical procedure. Because such instruments would have to fit into the 1-mm diameter of an endoscope’s working channel, there are limits to instrument size, feature size (protrusions or holes that make up the instrument), and resolution (the finest points within the instrument, e.g., edges, corners, points). One design strategy for constructing these new instruments is to rely on compliant mechanisms in order to actuate the instrument. In compliant mechanisms, the actuation mechanism depends on the elastic properties of the material rather than on rigid linkages, like hinges or ball joints. Silicon is not desirable because the toughness is only 1-2 MPa√m, which would make silicon based instruments too fragile. High toughness ceramics, like yttria stabilized tetragonal zirconia polycrystals (Y-TZP), could potentially be used since strengths in excess of 2 GPa, and a toughness as high as 20 MPa√m have been recorded. Other more traditional surgical tool materials, like stainless steel, are being considered, but the strength and elastic modulus are less desirable from a design perspective compared to Y-TZP. Unfortunately, a method has yet to be developed that fabricates free-standing mesoscale instruments from Y-TZP materials. It is advantageous from a design perspective to have the ability to change the material without significantly changing the fabrication method in case 3Y-TZP was found unsuitable.
The overarching goal of this dissertation is to develop a method for manufacturing small parts in the mesoscale regime (10’s to 1000’s \( \mu m \)) based on particulate materials processing; the specific focus is the use of ceramics to construct miniature surgical instruments that enable new types of surgery. The following criteria were established at the outset for the manufacturing process:

- High aspect ratio (>10), free-standing parts
- Edge radius of curvature less than 1\( \mu m \)
- Create large numbers of identical parts (not one off prototyping)
- Have a strength comparable to large scale materials (>1 GPa for 3Y-TZP)

An obvious place to begin in microfabrication is integrated circuit manufacturing because small parts are made on a routine basis and the size of the integrated circuit is constantly shrinking. The use of microfabrication for properties other than semiconduction has its origins in the 1960s, when silicon was used to make pressure sensors and resonating cantilever beams used for laser light modulation.\(^ {12} \) This gave birth to the field of micro electro-mechanical systems (MEMS)—a $6.9 billion market in

Figure 1-1: Images of a modern endoscope (Olympus “R” scope) taken from Reavis and Melvin.\(^ {11} \) (a) The control end of the endoscope. (b) The working end of the endoscope showing articulation. (c) The working end of the endoscope has a working channel for the surgical tool (biopsy tool shown), a cauterizing tool (white ball), lights, video camera, and air / vacuum ports. The surgical tool is separate from the endoscope and may be exchanged by sliding it out through the working channel. By shrinking the surgical tools, it may be possible to fit more tools within the endoscope to avoid tool exchange.
2008. Today, the field of engineering on the micron scale has spread to biology, power generation, chemical microreactors, optical devices, and gas sensing. Many of these new applications employ materials carried over from integrated circuit manufacturing, such as silicon, photoresist, and metallic thin films. However, for structural applications, a new strategy needs to be developed to incorporate other materials.

One strategy in micro-material fabrication is to use a powder-based approach. The particulate-based approach permits a wide variety of materials to be substituted in a manufacturing process. This is fundamentally different from the standard method of fabricating silicon microdevices from large high-purity ingots sliced into thin wafers or fabricating metallic structures by vapor deposition or sputtering. In the particulate-based approach, the material chemistry is virtually limitless and can be changed easily due to the wide variety of materials available in powder form. This bottom-up approach permits greater control of the material chemistry and microstructure, and will allow more applications to benefit from microfabrication.

Conversely, the method of patterning microdevices is best accomplished using the top-down approach of photolithography. Although lithography was invented in the late 18th century, the rapid development of photolithography since the 1950s in semiconductor manufacturing has allowed lithography to remain the preferred method for fabricating microdevices. Furthermore, the movement toward shorter wavelength photoresist continues to improve the resolution of photolithography. Bottom-up techniques, such as self-assembly, have become popular for nanofabrication, but arbitrary
designs cannot be manufactured and must rely on photolithography at some stage of the process for patterning.21

On the material side, ceramic powder processing, in the form of pottery, is the second oldest fabrication method in human history behind carving and hammering.22 Nonetheless, the challenges faced by early potters mirror those faced by modern engineers in the pursuit of micron-scale ceramic fabrication. The earliest-known pottery artifacts date to 26,000 years, and as with any new technology were highly defective.22 Among this early pottery, thousands of defective parts were discovered with only a few intact parts remaining. In some of the earliest intact pottery objects, like the Dolni Věstonice (a figurine of a woman discovered in the Czech republic), porosity, small thermal cracks, and larger drying or firing cracks are found.22 Recently, ceramic microfabrication has become possible, but the parts produced are often defective or uncharacterized to the extent that the strength limiting defects are unknown.23-26 However, unlike the earliest pottery, modern ceramic science can overcome these defects and thus hasten the development of free-standing ceramic mesoscale parts. This dissertation, therefore, focuses on identifying the defects in and quantifying the strength of small-scale (10–1000 µm) ceramic parts produced by the new manufacturing process demonstrated herein. Unlike the early ceramic figurines that were designed for aesthetics, structural ceramic applications cannot be safely realized without adequate characterization of the defects.

This dissertation is not the first effort at microfabrication in materials other than silicon; however, not only does it demonstrate a promising method for doing so, it also extends our understanding of micron-scale structural ceramics to broaden the range of
applications. There are presently three established strategies for microfabrication in materials other than silicon: direct write, self-assembly, and lithography-based. Several authors have reviewed the individual manufacturing techniques for each area.\textsuperscript{27,28,29} Table 1-1 summarizes the microfabrication techniques described in the literature. Direct writing is the serial writing of a slurry or binder, the ablation or sintering of material by a laser, or the machining of a lightly sintered body.\textsuperscript{28} The primary advantage of direct writing is that it can be used to stack 2-dimensional layers to form 3-dimensional parts; however, an important disadvantage of this technique is that the parts must be made individually, which does not readily lend itself to the manufacture of large numbers of identical parts. Self-assembly techniques such as microcontact printing\textsuperscript{30} and microtransfer molding\textsuperscript{31} use selective wetting or ligand chemistry to form patterns on a substrate to which particles may be bonded. Self-assembly techniques are well suited for thin (\textless 10 \(\mu\)m) layers, but are not well suited for thicker parts. Using lithography as a method to produce mold cavities allows many parts to be manufactured in parallel, and can potentially fabricate structures as thick as 1.2 mm.\textsuperscript{20} However, photolithography must use a layering technique to form 3-dimensional structures.\textsuperscript{32}
Table 1-1: The published methods of microfabrication have limitations in regard to smallest feature size, aspect ratio, and dimensional capability. Casting into photoresist (highlighted) has one of the finest feature resolutions, but limited aspect ratio. The challenge in this dissertation is to increase the aspect ratio and make free-standing parts, which has not previously been achieved by casting into photoresist.

<table>
<thead>
<tr>
<th>Microfabrication Method</th>
<th>Smallest Feature Resolution (µm)</th>
<th>Aspect Ratio</th>
<th>2D or 3D</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>STM-tip electrochemical etching</td>
<td>0.01</td>
<td>-</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Casting suspensions into photolithographic masks on silicon</td>
<td>1–5</td>
<td>1–2</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Soft lithography</td>
<td>1–5</td>
<td>1–3</td>
<td>2D/3 D</td>
<td>28</td>
</tr>
<tr>
<td>Microstereolithography</td>
<td>2</td>
<td>high</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Co-extrusion</td>
<td>5–16</td>
<td>high</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Maple direct write</td>
<td>10–20</td>
<td>low</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>LIGA</td>
<td>10–20</td>
<td>10</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Low-temperature co-fired ceramic multilayer</td>
<td>25–100</td>
<td>variable</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Direct ceramic machining of pre-sintered bodies</td>
<td>50</td>
<td>variable</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Screen printing</td>
<td>100</td>
<td>low</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Pulsed laser ablation</td>
<td>30–200</td>
<td>high</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Precision grinding</td>
<td>50</td>
<td>high</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Metal embossing</td>
<td>50</td>
<td>high</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Ink-jet printing of suspensions</td>
<td>70</td>
<td>low</td>
<td>2D</td>
<td>28</td>
</tr>
<tr>
<td>Freeform ink-jet printing of suspensions</td>
<td>170</td>
<td>high</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>3DP process (printing ceramic binders)</td>
<td>200</td>
<td>variable</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Micropen writing</td>
<td>250</td>
<td>1</td>
<td>3D</td>
<td>28</td>
</tr>
<tr>
<td>Selective laser sintering</td>
<td>500</td>
<td>high</td>
<td>3D</td>
<td>33</td>
</tr>
<tr>
<td>Laminated object manufacturing</td>
<td>100</td>
<td>variable</td>
<td>3D</td>
<td>27</td>
</tr>
<tr>
<td>Laser chemical vapor deposition</td>
<td>10</td>
<td>500</td>
<td>3D</td>
<td>34</td>
</tr>
<tr>
<td>Diamond machining (lathe)</td>
<td>25</td>
<td>5</td>
<td>3D</td>
<td>12</td>
</tr>
<tr>
<td>Surface micromachining</td>
<td>25</td>
<td>variable</td>
<td>2D</td>
<td>12</td>
</tr>
</tbody>
</table>
There are two primary techniques based on lithography for forming ceramic bodies: soft lithography and lost-mold processing (casting into photoresist). Although methods based on soft lithography have been somewhat successful, high-aspect ratio shapes with good registry on the substrate have proven difficult to form using flexible molds.\textsuperscript{35} Since surgical instruments using compliant mechanisms require a high aspect ratio, soft-lithography is ruled out as a possibility.\textsuperscript{10} Lost-mold processing uses a photo-curable resin to create a rigid mold on top of a substrate, which has finer dimensional tolerances and can maintain registry on the substrate. The mold is then filled with ceramic slurry, while the ultimate mold removal is achieved via chemical dissolution\textsuperscript{23,36} or thermolysis.\textsuperscript{37} This type of lost-mold technique has shown promising results; yet, many challenges remain. For example, Schonholzer \textit{et al}. comment on the challenges of mold wall blurring due to substrate reflectivity, cracking caused by mold pyrolysis, and deposition of slurry over the top of the mold.\textsuperscript{23} The process outlined in this dissertation solves many of these previously reported challenges and demonstrates the additional capability of forming free-standing parts with a high aspect ratio, which no other process has accomplished. Additionally, the processing–performance relationship is established for the strength of the 3Y-TZP micron-scale parts. This study marks the first effort to measure the strength and reliability of powder-processed micro- to meso-scale (>1 mm, <10 cm) ceramic parts from nanoparticles.

Henceforth, the term “mesoscale” will be used to refer to parts that have dimensions on the order of 10s–100s of microns. However, the term, “microfabrication” is used almost exclusively in the literature to refer to parts of a similar scale. “Mesoscale” does not refer to a rigid size range; it refers to an in-between scale. In
chemistry, mesoscale refers to the scale in-between molecular chemistry and solid state chemistry.\textsuperscript{38} The term is appropriate for the parts referenced in this dissertation, as the part size is in-between the size of particles, which function as the building blocks, and a bulk material. “Mesoscale” will be used to describe the size of the parts; “microfabrication” will be used to describe the process for making small parts.

1.2 Research Goals

The objective of this dissertation is to understand the strength limitations of particulate-based ceramic materials as the length scale approaches the scale of the microstructure. It is hypothesized that a particulate-based mesoscale material can be made stronger and more reliable compared to similarly sized materials produced using other techniques and larger sized conventional materials by reducing the flaw size relative to the microstructural dimensions. Three challenges must be met in order to prove this hypothesis: a dense, fine-grained microstructure must be achieved by controlling the colloid and interfacial chemistry (Chapter 3), dimensional accuracy must be assured (Chapter 4), and the importance of the grain size to flaw size ratio must be understood (Chapter 5). Since free-standing particulate-based ceramic materials have only recently been realized, other scientific and engineering challenges relating to the fabrication process must be overcome. These challenges are listed in Table 1-2. Engineering solutions adapted from either the photolithography or ceramic processing literature can be used whenever possible. Other challenges require in-house engineering solutions. Engineering, therefore, plays a central part in the development effort. There are
also significant scientific challenges involved in adapting nanoparticles for use in microfabrication. Colloid and interfacial chemistry is essential in this regard and ultimately enables particles to come together to form dense sintered bodies.

Table 1-2: Some scientific and engineering challenges in using nanoparticles to form mesoscale ceramic parts.

<table>
<thead>
<tr>
<th>Manufacturing Step</th>
<th>Scientific Barriers</th>
<th>Engineering Barriers</th>
</tr>
</thead>
</table>
| Nanoparticulate dispersion approaches with dimensions in the sub-100 nm regime | • Theories for attractive and repulsive energies between and among sub-100 nm particulates.  
• Phase equilibria and metastable states in nanoparticulate alloys of the system (Y₂O₃-ZrO₂) | • Processing capability to create stable nanoparticulate suspensions at solid concentrations suitable for forming operations |
| Forming operation                                       | • Theoretical particle space filling as a function of particle size                 | • Preparation of green bodies with high particle packing density                     |
|                                                         | • Intermolecular adhesion associated with green body at forming tool surfaces       | • Deformation of infiltration tool                                                  |
|                                                         | • Solubility and polymerization of monomer binders                                 | • Environmental affects that deteriorate binder                                     |
|                                                         |                                                                                     | • Drying cracks                                                                      |
| Thermal processes to achieve dense, bulk, components    | • Thermodynamics of chemical reactions for removal of processing additives          | • Processes required to remove processing additives                                 |
|                                                         | • Grain boundary diffusion and grain boundary migration thermodynamics and kinetics | • Sintering cycle to promote bulk densification with minimal grain growth            |
|                                                         | • Diffusion of ionic species between part and substrate                            |                                                                                     |
1.3 Chapter Summaries

1.3.1 Chapter 2: Characterization Techniques

The objective of this chapter is to discuss the characterization techniques used throughout this work and specifically address the principles of each technique, the limitations, and how it specifically relates to mesoscale ceramic specimen. This research used miniature bend test bars (332 × 26 × 17 µm) in order to evaluate the strength of the mesoscale materials as a function of processing changes. The characterization techniques that were used will be explained in the context of the miniature bend test specimen and other test shapes.

First, the characterization techniques used to evaluate the dispersion state of the ceramic suspension are examined. These techniques included phase analysis light scattering (PALS) for measuring ζ-potential; static and dynamic light scattering (SLS, DLS) for measuring agglomerate size in suspension; and BET surface area analysis and X-ray diffraction (XRD) for measuring particle size. A discussion regarding the different sizing techniques follows, since each technique measures a different facet of particle or agglomerate size. Second, the characterization techniques used to evaluate the ceramic green body was reviewed. These techniques included rheological measurements, thermogravimetric analysis (TGA), and differential thermal analysis (DTA). Third, the sintered parts were characterized by light microscopy, optical profilometry, confocal Raman spectroscopy, and scanning electron microscopy (SEM).
Finally, the miniature three-point bend test developed by Rebecca Kirkpatrick and Dr. Christopher Muhlstein at The Pennsylvania State University was examined in the context of instrumental and specimen errors. In the development of the three-point bend test, every effort was made to follow the current ASTM standard\textsuperscript{39} for large ceramic specimens; however, concessions had to be made to ameliorate the difficulty of testing materials barely visible to the unaided human eye. The original documentation\textsuperscript{40} used in the development of the current ASTM standards was used to evaluate the bend test since testing of free-standing ceramic bend bars at this scale had not previously been accomplished.

1.3.2 Chapter 3: Lost Mold-Rapid Infiltration Forming: Fabrication

The objective of Chapter 3 is to introduce the lost mold rapid infiltration forming process (LM-RIF) and discuss the challenges that had to be overcome to produce mesoscale parts using lithography. It was hypothesized that mold forming, casting, mold removal, and sintering could all occur on a single refractory substrate that would enable the forming of high-aspect ratio, free-standing parts \textit{en masse}, without introducing handling defects. In Chapter 3, a specific emphasis was placed on the colloid and interfacial chemistry to obtain and control the ceramic suspension and the mold-forming and mold-removal processes. In addition, the strength of the parts is measured to assess their quality.

A shear-based method called rapid infiltration forming (RIF) was used to fill the mold cavities; thus, the rheology of the suspensions influenced the part and
microstructural quality. Specifically, the Bingham yield point and high shear rate viscosity needed to be matched to the shear rate of RIF; yet, the suspension density had to be high enough to limit porosity and shrinkage during drying. The rheology of the suspension is a function of the dispersant molecular size, charge, and concentration, which provides a means to tune the rheology for RIF. In order to evaluate the state of dispersion, the average number of particles per agglomerate was calculated based on various measurements of both particle and agglomerate size.

Additionally, Chapter 3 discusses the specific adjustments to the photolithography process that were necessary to make it suitable for ceramic particulate forming. The reasons for these adjustments, the solutions, and the scientific background behind these challenges are discussed in Chapter 3.

1.3.3 Chapter 4: Lost Mold-Rapid Infiltration Forming: Geometry and Strength Improvements

Chapter 4 examines the parts produced by the LM-RIF process, as described in Chapter 3, with particular emphasis on their shortcomings in terms of their low strength and less than optimum geometry. The objective of this chapter is to increase the relatively low strength of the first generation (Chapter 3) parts by removing the largest flaws introduced by the LM-RIF process. In Chapter 4, the metrology proves to be an important area in understanding the low strength of the first generation parts. The improvements to the part geometry increase strength significantly to an average of 2.24 GPa, which is among the highest average strength recorded for polycrystalline 3Y-TZP. Specifically, the non-orthogonal cross-section and the warping of the parts is addressed.
In addition, precise measurements of the dimensional changes that occur during each stage of the LM-RIF process reveal how the geometric defects occur. The fundamental mechanisms behind these defects are discussed. The increase in strength as these defects are eliminated is also discussed relative to the strength of macroscopic 3Y-TZP.

1.3.4 Chapter 5: Grain Growth and Defect Size in Microfabricated 3Y-TZP

Chapter 5 examines the roles that grain size and surface roughness play in regard to the strength of 3Y-TZP mesoscale parts. The objective of Chapter 5 is to determine the effect of grain size on strength relative to the flaw size. It was hypothesized that a larger grained TZP would increase the Weibull modulus due to a transformation toughening effect. This hypothesis was determined to be incorrect. In fine-grained parts, strength-limiting flaws are proportional to the surface roughness. However, in coarse-grained parts the strength-limiting flaws are larger due to the additional contribution to flaw length by the grain size. The transition between surface roughness limited strength and grain size effects occurred at approximately 1 μm, and is explained by the Orowan-Petch analysis.43 The Orowan-Petch transition occurs at a finer grain size for the mesoscale specimen than for macroscale specimen. The effect of transformation toughening on strength is small relative to the grain size – flaw size correlation; therefore, the strength and Weibull modulus decreases with increasing grain size.
1.3.5 Chapter 6: Hierarchical Manufacturing of a Surgical Instrument Using the LM-RIF Process

The objective of Chapter 6 is to examine the shape forming capabilities of the LM-RIF process relative to the surgical instrument application. The processing science and strength improvements in previous chapters are used to create surgical instrument prototypes with unique functionality for the next generation of minimally invasive surgery. The surgical instrument designs are developed using mechanical engineering models\textsuperscript{5,10,44,45} that use the strength and processing data in the designs. Additionally, the design criteria shaped the LM-RIF development. Since the strength of 3Y-TZP components of this size was unknown, the design was refined according to data generated in previous chapters. Chapter 6 summarizes the ability of the LM-RIF process to manufacture surgical instruments and the interaction between design, fabrication and mechanical performance.

1.3.6 Chapter 7: Conclusions and Future Directions

This chapter summarizes the LM-RIF process and proposes continuations in the study of mesoscale ceramic strength. First, the applicability of the Weibull size effect to mesoscale ceramic strength is discussed. Preliminary data on larger scale specimen is presented to support the argument that the Weibull size effect is observed within the size range of the LM-RIF process. Additionally, other methods to decrease the flaw size of LM-RIF produced parts are presented. Finally, the question as to whether transformation toughening can occur in mesoscale specimen due to the specimen size is proposed.
1.4 References


Chapter 2

Characterization Techniques for Mesoscale Ceramics

2.1 Introduction

The chemical, microstructural, and dimensional characterization of bulk ceramic bodies is well established; however, the small size of microscale and mesoscale ceramic bodies complicates the characterization. Macroscale analogs can be made for intrinsic properties that do not scale with size, but there are significant differences between properties measured on the macroscale and mesoscale. For example, in Chapters 4 and 5 it is shown that impurities from the substrate cause grain growth in mesoscale specimen but not macroscale specimen. Density differences between mesoscale and macroscale specimen have also been observed because large pores (~100 µm) can be trapped in the macroscale analogs, but pores of this size are not possible in the mesoscale samples because of the small (30×25 µm) cross-sections. Therefore, the measured bulk density is lower for the macroscale analogs. For these reasons, characterization was done directly on the mesoscale parts rather than on macroscale analogs. In this chapter, the basic premise and limitations of each characterization technique will be examined with a particular emphasis on how the technique applies specifically to mesoscale ceramic characterization. The techniques are described in the processing order: colloidal chemistry, green body formation, sintering, sintered part evaluation, and strength measurement.
2.2 Colloid Chemistry: Dispersion, Particle Size, and Agglomeration

Dispersing agglomerates into individual particles is important in aqueous ceramic powder processing to increase density, decrease shrinkage, and achieve a fine grain size. Dispersion prevents large interagglomerate porosity from forming.\(^1\) This brings to the forefront a discussion on the methods available to evaluate the state of dispersion of the ceramic suspension. Agglomerates are composed of multiple individual particles bound by van der Waals forces, electrostatic forces, steric forces, or precipitation of material among particles (aggregate formation).\(^1\) Directly imaging particles and agglomerates can be confusing, as drying can induce agglomeration by capillary action; therefore, it becomes unclear as to whether the particles were initially disperse then agglomerated on drying, or were agglomerated in the initial suspension. This confusion can be somewhat negated by drying dilute suspensions in which the particles are separated by long distances; however, if dilute drying is done then the number of particles in the field of view is reduced, which makes gathering distribution statistics a time-consuming process. Therefore, techniques that are able to quantify particle or agglomerate size while the particles are in suspension are attractive albeit more open to interpretation since direct visible evidence is often more convincing.

Each particle/agglomerate-sizing technique measures a different size depending on the physics of the technique and the basis of the particle/agglomerate size distribution. Dynamic light scattering (DLS) is sensitive to the agglomerate size but caution has to be

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\(^1\) A note on terminology. The NIST definitions will be used for the terms “aggregate,” and “agglomerate.” An aggregate is “a cohesive mass consisting of particulate subunits,” whereas an agglomerate is “an aggregate held together by physical or electrostatic forces in a suspension.”\(^2\) The term agglomerate will be used as the default term in reference to particles in a suspension, while aggregate will be used to describe particles that are either weakly sintered or dried.
used when citing an average size when a range of sizes is detected. The technique most often used to measure the primary particle size (insensitive to agglomerates) is the Brunauer, Emmett, and Teller (BET) surface area technique, which is based on gas adsorption. Another technique used to measure the primary particle size is the Scherrer technique, which is based on X-ray diffraction from finite crystalline domains.

The average agglomeration number (AAN) is an approximation of the number of particles per agglomerate. The AAN compares the agglomerate size to the primary particle size. Since the agglomerate size and primary particle size are measured using different techniques, the AAN is a function of both the physics and distributional basis of each technique. First, the basic principles of each technique will be presented followed by a discussion on the meaning of the AAN.

2.2.1 Phase Analysis Light Scattering (PALS) ($\zeta$-potential)

Phase analysis light scattering (PALS) is a measure of the $\zeta$-potential or electrostatic potential at the shear plane of a particle in suspension. PALS does not measure particle size, but the $\zeta$-potential is used to determine whether an electrostatically or electrosterically dispersed suspension is likely to agglomerate. Additionally, the $\zeta$-potential can be used to calculate the double-layer thickness or thickness of the ionic layer surrounding the surface of a particle, which separates particles of like charge and affects the rheology and particle-packing characteristics of the suspension. The double layer is shown schematically in Figure 2-1. Finally, the double-layer thickness affects the
particle size measured by light scattering, since the hydrodynamic diameter measured by SLS or DLS includes the double-layer thickness.

![Diagram of the electric double layer](image)

A solid surface develops charge in a solvent through ionization of surface groups by the solvent, adsorbing ions dissolved within the solvent, partially dissolving the solid, or dissimilar ion exchange between the solid and solution. For metal oxides, surface charge is typically manipulated by a pH change (electrostatic dispersion) or the addition of a surfactant (electrosteric dispersion). Double layer theory treats the satisfaction of surface charge as a two-layer model consisting of an inner shell of tightly bound,
oppositely charged ions adjacent to the solid surface (Helmholtz or Stern layer) surrounded by a diffuse layer of counter-ions (Gouy-Chapman layer) of opposite sign than ions in the Helmholtz layer. The overlapping of ionic double layers of like charge provides an electrostatic repulsive force between particles. The van der Waals attractive forces (London dispersion, permanent dipole, and induced dipole) act to attract particles. DLVO (Derjaguin, Landau, Verwey and Overbeek) theory is the summation of the attractive and repulsive forces between two particles and determines the overall stability of the suspension. DLVO theory will be further discussed in chapter 3 in relation to the LM-RIF process.

The $\zeta$-potential is the charge at the shear plane, the outer portion of the Helmholtz or Stern layer (see Figure 2-1) that forms the basis of the repulsive electrostatic force. The $\zeta$-potential represents the potential at the interface between the immobile ions fixed to the surface and the mobile ions that exchange with the solvent molecules. One way to measure the $\zeta$-potential is to measure the velocity of a particle in response to an electric field (electrophoretic mobility) by laser Doppler velocimetry (LDV). Phase analysis light scattering (PALS), an extension of LDV, is able to measure smaller electrophoretic mobilities than LDV. In PALS, a laser light of frequency ($\nu_0$) is scattered off a dilute suspension of particles. The frequency is Doppler-shifted by an amount $\delta\nu_0$ according to [2.1], where $n_i$ is the refractive index of the solvent, $v_p$ is the velocity of the particle, $\lambda_0$ is the laser wavelength, $\Theta_s$ is the scattering angle, and $\phi_s$ is the angle between the electric field and the scattering vector.
\[
\delta v_0 = \frac{2n_p v_p}{\lambda_0} \sin \left( \frac{\Theta}{2} \right) \cos \phi
\]  

[2.1]

In LDV, \( \delta v_0 \) is compared to \( v_0 \) and the beat frequency is measured. In PALS, the incident beam is phase modulated to match the phase of the scattered beam in the absence of an electric field for which the phase will be constant. When there is an applied electric field, the phase changes with time, and the time-dependent phase change is then compared to the constant phase without an electric field present. The amplitude of the relative phase shift is proportional to the particle velocity (\( v_p \)). PALS is preferred to LDP for low \( \zeta \)-potentials or thick suspensions because it can measure particle velocities roughly 1,000 times smaller than LDV.\(^9\)

To calculate \( \zeta \)-potential from particle velocity, the viscous drag on the particle, ionic concentration, and electrostatic force must be considered.\(^9\) The ratio of particle radius (\( a \)) to double-layer thickness (\( \kappa^{-1} \)) determines if the particle is treated as a point charge (\( \kappa a << 1 \)) or a flat sheet (\( \kappa a > 1 \)). If (\( \kappa a << 1 \)), the Hückel equation\(^{10}\) is appropriate [2.2], and if (\( \kappa a >> 1 \)), the Smoluchowski equation\(^{11}\) [2.3] is appropriate. In [2.2] and [2.3], \( \zeta \) is the \( \zeta \)-potential, \( \eta \) is the solvent viscosity, \( E \) is the electric field, \( \varepsilon \) is the permittivity, and \( \varepsilon_0 \) is the permittivity of free space.

\[
\zeta = \frac{3v_p \eta}{2E \varepsilon \varepsilon_0} \quad \text{[2.2]}
\]

\[
\zeta = \frac{v_p \eta}{E \varepsilon \varepsilon_0} \quad \text{[2.3]}
\]

It is clear from [2.2] and [2.3] that the flat-plate or point charge assumption only changes the \( \zeta \)-potential by a factor of 3/2. The Henry equation\(^{12}\) fills in the gap between
the Hückel and Smoluchowski approximations for particles with \((\kappa a \approx 1)\), but is more
cumbersome than the simple forms of [2.2] and [2.3]. The double layer thickness for the
65 nm diameter zirconia particulate suspension described in Chapter 3 is only 1 nm due
to the high ionic strength of the solvent, which makes \(\kappa a\) equal to 34 to make the
Smoluchowski plate assumption valid.

The Stabil\textsuperscript{13} program\textsuperscript{13} was used to calculate the interaction energy between two
particles according to DLVO theory. In Chapter 3, the interaction energy as a function of
interparticle separation distance is used to calculate the maximum packing fraction and to
explain the rheology of the suspension. The double-layer thickness \((\kappa^{-1})\) is given by
[2.4], where \(I\) is the ionic strength, \(T\) is temperature, \(N_A\) is Avogadro’s number, \(e\) is the
charge of an electron, and \(k\) is Boltzmann’s constant.\textsuperscript{13}

\[
\kappa^{-1} = \sqrt{\frac{N_Ae^2\kappa T}{8\pi \varepsilon^2 I}} \tag{2.4}
\]

The attractive energy between the particles due to van der Waals forces \((V_{vdW})\) is
given by [2.5], where \(A_{131}\) is the Hamaker constant, \(a\) is the particle radius, \(\lambda_{UV}\) is the
ultraviolet absorption edge, and \(D_{sep}\) is the interparticle separation distance.\textsuperscript{13}

\[
V_{vdW} = -\frac{A_{131}a}{12\pi D_{sep}^3} \left( 1.01 - 0.56 \left( \frac{2\pi D_{sep}}{\lambda_{UV}} \right) + 0.1735 \left( \frac{2\pi D_{sep}}{\lambda_{UV}} \right)^2 - 0.028 \left( \frac{2\pi D_{sep}}{\lambda_{UV}} \right)^3 + 1.93 \times 10^{-4} \left( \frac{2\pi D_{sep}}{\lambda_{UV}} \right)^4 \right) \tag{2.5}
\]

The repulsive energy due to the electrosteric interaction is given by [2.6]; it uses the
Gregory approximation\textsuperscript{14} for polymer-layer thickness (charge on the outside of polymer
layer), and is applicable to a relatively small double-layer thickness.\textsuperscript{13}

\[
V_r = \frac{a^2}{2} \varepsilon^2 e_0 \ln(1 + \exp(-\kappa D_{sep})) \tag{2.6}
\]
The total interaction energy is the sum of the attractive \( (V_{vdW}) \) and repulsive \( (V_r) \) energies. An electrostatic barrier thickness \( (\Delta) \) corresponding to half the separation distance \( (\frac{1}{2}D_{sep}) \) at a certain interaction energy can be defined as the minimum approach distance between two particles. The particle-packing fraction \( (\phi_{eff}) \) can then be calculated using [2.7] assuming the following maximum packing fractions: 0.74 for closely packed spheres, 0.64 for random loose packed spheres.\(^3,^{15}\)

\[
\phi_{eff} = \phi_m \left(1 + \frac{\Delta}{a}\right)^3
\]

[2.7]

The \( \phi_{eff} \) can then be used to model rheological properties and green body density (see Chapter 3).

### 2.2.2 BET Surface Area

The BET (Brunauer, Emmett and Teller)\(^{16}\) technique uses gas adsorption to determine the surface area of a material of known mass (surface area per unit of mass). BET theory\(^{16}\) is a generalization of Langmuir’s earlier theory of mono-layer gas adsorption to include multi-layer adsorption.\(^{17}\) Adsorption isotherms are a measure of the volume of gas adsorbed \( (V_a) \) as a function of pressure \( (P) \) at the temperature corresponding to the boiling point of the adsorbate (77.35 K for \( N_2 \)). Brunauer, Emmett, and Teller identified five types of isotherms shown in Figure 2-2. The type-1 isotherm is the Langmuir isotherm and describes the rapid adsorption of gas molecules to monolayer saturation, which is typical of chemisorption. Type 2 is a common multilayer adsorption isotherm for non-porous materials. At high pressures, the gas undergoes bulk
condensation. The type-3 and type-5 isotherms show little adsorption at low pressures for a non-adsorbing adsorbent, whereas type 3 is for a non-porous material and type 5 is for a material with capillaries. The type-4 isotherm is similar to the type-2 isotherm with the exception that capillaries may exist that result in adsorption isotherms at two different pressures.

Figure 2-2: The five types of adsorption isotherms are shown schematically. Type 1 is characteristic of the Langmuir isotherm or monolayer adsorption. Type 2 is characteristic of a non-porous material. Type 3 and Type 5 are characteristic of a non-wetting adsorbate–adsorbent system. Type 4 is characteristic of a porous material.16,18

In deriving the BET equation [2.8], the authors16 assumed that, “the same forces that produce condensation are also responsible for multimolecular adsorption.”
The BET equation is derived by equating the rate of gas condensation to the rate of evaporation. The ratio of the gas pressure to the vapor pressure of the adsorptive gas \( P/P_0 \) can be plotted against the term on the left side of [2.8], which includes the volume of gas adsorbed \( V_a \), in order to calculate the constant \( C \) and the volume of gas adsorbed for monolayer coverage \( V_m \). The intercept is equal to the quantity \( 1/(V_mC) \), and the slope is given by \( (C-1)/(V_mC) \). The surface area \( A_{\text{BET}} \) is then calculated from \( V_m \) using [2.9], where \( a_m \) is the projected surface area of the gas molecule (16.2 Å² for N₂), \( N_A \) is Avogadro’s number, \( m \) is the sample mass, and \( V_0 \) is the molar volume of the gas.\(^{18}\)

\[
A_{\text{BET}} = \frac{V_m a_m N_A}{m V_0} \tag{[2.9]}
\]

The BET equation [2.8] is only valid for the linear portion of the adsorption isotherms in Figure 2-2. Generally, the linear portion occurs in the middle pressure ratio \( P/P_0 \). In single-point BET measurements, a single \( P/P_0 \) value is used; the linear intercept of [2.8] is assumed to be small relative to the slope, i.e., \( C>>1 \); and the slope is reduced to the quantity \( 1/V_m \). Single-point BET measurements are less expensive and quicker to perform than multi-point BET measurements, and the former are often used in the case of non-porous powders for which the equivalent spherical diameter is a suitable measurement of particle size.

This specific surface area \( A_{\text{BET}} \) is converted to primary particle size \( d_{\text{BET}} \), or equivalent spherical diameter, using the material density \( (\rho) \) and equation [2.10].\(^3\)
Equation [2.10] assumes a non-porous spherical particle; however, similar equations can be derived for non-spherical particles by dividing the volume by the surface area of the shape. The equivalent spherical diameter is an area-based measurement of particle size and does not give any information about the particle size distribution or agglomerate size.

### 2.2.3 Light Scattering

Dynamic light scattering (DLS) is sensitive to agglomerate size as well as particle size. The useful size range in DLS is between approximately 1 nm and 1 µm. There are three basic assumptions inherent in all light scattering measurements. These assumptions are that light is scattered from a single particle, that particles are spherical, and that the scattering pattern on the detector is the sum of each individual particle pattern.¹⁹

The scattered intensity can be calculated the Rayleigh approximation when the particles are much smaller than the wavelength of light \((2a<10\lambda_0)\). For commercial DLS instruments the incident wavelength is usually 633 nm, therefore, the Rayleigh limit is about 63 nm. For larger sizes, such as the particle size range of interest in ceramic processing (10 nm–10 µm), the Mie solution for electromagnetic radiation interacting with a sphere is more appropriate.

In DLS, the scattered intensity is measured as a function of time at a single scattering angle. The intensity fluctuations are proportional to the movement of the particles that undergo Brownian motion. The overall principle of DLS is that over short
time periods (on the order of microseconds) the intensity fluctuations of scattered light are correlated to each other. At a later point in time, however, the intensity fluctuations become random. Since larger particles diffuse more slowly, the scattered intensity remains correlated for a longer time. By measuring the decay rate of the scattered intensity \([G(t)]\) at a given scattering vector \((q)\), the diffusion coefficient \((D)\) of the particles in suspension can be calculated using equation \([2.11]\). The diffusion coefficient can then be used to calculate the hydrodynamic particle size \((R_H)\) using the Stokes-Einstein equation \([2.12]\), where \(k\) is Boltzmann’s constant, \(T\) is temperature, and \(\eta\) is viscosity.

\[
G(t) = \exp(-q^2Dt) \quad \text{[2.11]}
\]

\[
R_H = \frac{kT}{6\pi\eta D} \quad \text{[2.12]}
\]

The DLS instrumental calculation of the diffusion coefficient \((D)\) has more terms than given in \([2.11]\), including an additive constant for a non-zero baseline in the scattered intensity and multiple exponential terms to account for a multimodal particle size.

One potential difficulty with DLS is the convolution of scattered intensity from multiple particles of different sizes over the single fixed angle. The result of this convolution is a multimodal particle size distribution that is merely an artifact of a local minimum in the scattered intensity for a single particle size. As a real example, the scattered intensity for monochromatic, 633-nm-light at a scattering angle of 173° for spherical particles of \(\gamma\)-alumina \((n_i = 1.66+0.1i)\) in water \((n_i = 1.33)\) is shown in the upper portion of Figure 2-3. The Mie solution contains local intensity minima at various particle sizes. Since the DLS software calculates the particle size from the scattered
intensity, these minima can be convoluted into intensity peaks when in fact there are very few particles of this size. The observer would then falsely conclude that there is a large multimodal particle size distribution as shown in the lower portion of Figure 2-3.

Although there is a finite intensity signal measured between 200 nm and 900 nm, the Mie inversion algorithm has difficulty reproducing a size distribution at the local intensity minima due to the large variation in scattered intensity (note the log-scale on the vertical axis in the upper graph of Figure 2-3). As Figure 2-3 shows, the Mie inversion artifacts typically appear as a series of very sharp peaks and can be identified by calculating the Mie scattered intensity as a function of particle diameter (at constant scattering angle) using commercial Mie software, such as Scatlab®, and comparing the intensity distribution to that calculated by the DLS instrument.22
2.2.4 Scherrer Crystallite Size

The Scherrer\textsuperscript{23} crystallite size is an often-cited measurement of particle size for nanoparticles (<100 nm) for which the X-ray diffraction peak broadening is significant.
The fundamental assumption in using crystallite size by XRD is that it is equivalent to particle size, which means that there is one crystallite or grain per particle. More specifically, crystallite size refers to the size of a coherently scattering domain that is only equal to the grain size in a perfect crystal, but influenced by crystalline defects in real materials. In general, the full particle size distribution cannot be accurately determined using XRD, although an effort has been made recently to extend the Scherrer method to crystallite size distributions.

The principle that the Scherrer method uses is that of peak broadening caused by the finite size of the diffracting volume in a crystallite. In XRD, X-rays are diffracted from the crystallographic planes in the material. The constructive interference that occurs from regular atomic spacing results in peaks that are a function of the diffraction angle according to Bragg’s law [2.13].

\[ n\lambda = 2d_{hkl}\sin(\theta_B) \quad n = 1, 2, 3, \ldots \]  

[2.13]

The diffraction angle (\(\theta_B\)) is a function of the incident wavelength (\(\lambda\)), and d-spacing or distance between the (hkl) planes. For an infinite lattice, Bragg’s law results in a delta function for each set of atomic planes whose amplitude is given by the atomic scattering factor and structure factor. Peak broadening occurs because the crystallite dimensions curtail the lattice array, which means destructive interference will not occur at angles slightly off the Bragg angle (\(\theta_B\)). The peak width is given by the Scherrer equation [2.14], where \(\beta\) is the peak width at half maximum intensity, \(K\) is the shape factor for the crystallite (0.89 for spheres), and \(L_{hkl}\) is the crystallite size perpendicular to the (hkl) plane.
\[ \beta_{hkl} = \frac{K \lambda}{L_{hkl} \cos \theta_B} \]  

[2.14]

Other factors also contribute to the peak width, including the coherence of the incident beam (\( \Delta \lambda \)), instrumental broadening (\( \Delta \theta_B \)), and lattice strain (\( \Delta d_{hkl} \)). The instrumental and coherence errors are eliminated by the use of a standard calibration. The broadening due to lattice strain is proportional to \( \sin \theta_B \), which provides a means of separating the lattice strain from the crystallite size since the lattice strain increases with \( d_{hkl} \) between 0° and 180°.24

### 2.2.5 Average Agglomeration Number

The average agglomeration number (AAN) is a measurement of the average number of particles per agglomerate. However, as different techniques are used to measure agglomerate size and particle size, the AAN is a function of the techniques used to make the measurement and the underlying assumptions. The techniques that measure particle size are BET, XRD, and direct observation; SLS and DLS measure agglomerate size as well as particle size. The AAN is given in [2.15], where \( \text{D}_{\text{agg}} \) is the agglomerate diameter, \( d_p \) is the primary particle diameter, and \( \phi_p \) is the packing fraction of the particles within the agglomerate.3-5

\[ AAN = \frac{D_{agg}^3}{d_p^3} \phi_p \]  

[2.15]

However, if \( D_{agg} \) is based on the average agglomerate size by scattered intensity and \( d_p \) is based on the average particle size by area, then the AAN will include distributional
errors. Fundamentally, the BET particle size is based on area, the Scherrer size is based on volume, and the SLS/DLS sizes are based on scattered intensity. To convert particle size among the different measurement techniques and provide an accurate AAN, the distributional moment and distribution shape must be considered.

The average particle size depends on the basis of the distribution or the distributional moment. The 0th moment is the total number of particles, the 1st moment is the number average particle size, the 2nd moment is the area average particle size, the 3rd moment is the volume average particle size, and the 6th moment is the scattered intensity (volume squared for Rayleigh scattering).\(^{19}\) The average particle size increases as the moment increases because larger moments shift the distribution towards larger particle sizes. This shift is shown in Figure 2-4 for the DLS particle size distribution of gamma-alumina that has agglomerates greater than 1 \(\mu\)m and primary particles of 16 nm by BET (d\(_{\text{BET}}\) or equivalent spherical diameter). Only the higher moment intensity and volume distributions show a significant agglomerate population. As agglomerates have a large volume and scatter intensely, but are only counted as one entity, they are not a significant fraction of the number or area populations. Equations [2.16–2.19] show how the mean size for the given basis is calculated from the distribution function \(f_N(x_i)\).\(^{19}\)

\[
N = \int_{x_{\text{min}}}^{x_{\text{max}}} f_N(x_i)dx_i \quad \text{Total number of particles} \quad [2.16]
\]

\[
\bar{x}_{\text{number}} = \frac{1}{N} \int_{x_{\text{min}}}^{x_{\text{max}}} x_i f_N(x_i)dx_i \quad \text{Number} \quad [2.17]
\]
The log-normal distribution is a common particle size distribution given in [2.20], where $\sigma_g$ is the geometric standard deviation, $x_g$ is the geometric mean size, and $x_i$ is the independent size.

$$f(\ln x) = \frac{1}{2\pi \ln \sigma_g} \exp \left( -\frac{1}{2} \left( \frac{\ln x_i - \ln x_g}{\ln \sigma_g} \right)^2 \right)$$ \hspace{1cm} [2.20]

Substituting [2.20] as $f_N(x_i)$, one can convert among the average size by the number, area, and volume distributions, assuming a log-normal distribution using the equations [2.21-2.22].

$$\log \bar{x}_{area} = \log \bar{x}_{vol} - 2 \frac{\ln 10}{\ln^2 \sigma_g}$$ \hspace{1cm} [2.21]

$$\log \bar{x}_{num} = \log \bar{x}_{vol} + 3 \frac{\ln 10}{\ln^2 \sigma_g}$$ \hspace{1cm} [2.22]

The particle size distribution and analytical technique must both be considered in order to compare the relative size of agglomerates and particles on a like-for-like basis.
2.3 Green Body Evaluation

2.3.1 Rheology

In the LM-RIF process, a squeegee is used to shear the particulate suspension in order to fill the mold cavities, which will be discussed in further detail in Chapter 3. The viscoelastic response of the suspension to the shear rate determines if suspension will fill the mold cavities. Rheology is the study of how materials flow in response to a shear rate ($\dot{\gamma}$) as characterized most simply by the viscosity ($\eta$) as given in equation [2.23].

$$\tau = \eta \dot{\gamma}$$  [2.23]
In equation [2.23], the shear stress (τ) is assumed to be directly proportional to the shear rate with a constant viscosity or Newtonian behavior. The Newtonian response is only one response type for concentrated particulate suspensions. There are different types of visco-elastic responses, including shear-thinning or pseudoplastic behavior, shear-thickening behavior, or time-dependent rheopectic/thixotropic behavior. A common response for disperse, concentrated particulate suspensions is the pseudoplastic or Bingham plastic behavior. A pseudoplastic suspension is shear thinning, and has a yield point (Bingham yield point) that is defined as the shear stress at a shear rate of zero. An example of a pseudoplastic suspension (43 vol%) is shown in Figure 2-5. For comparison, a nearly perfectly Newtonian 15vol% suspension is also shown. The Bingham yield point is defined in this dissertation as the shear stress intercept for a best fit line with a range of 10–100 s⁻¹. It was found that this range provides enough data points close to a shear rate of zero to properly calculate the intercept or Bingham yield point (τ_B). Another important parameter for the pseudoplastic response is the high shear viscosity (η_High Shear). The high shear viscosity is defined as the average viscosity of between 400 s⁻¹ and 500 s⁻¹; it is nearly independent of shear rate and characterizes the flow of the suspension. The high shear viscosity is an important parameter for the LM-RIF process because it corresponds to the approximate shear rate of the squeegee action discussed in more detail in Chapter 3.
Instrumentally, the viscosity was measured by a cone-plate geometry rheometer. The cone-plate geometry is shown in Figure 2-6, where $\omega$ is the angular velocity, $T_c$ is the torque, $r_c$ is the cone radius, and $\theta_c$ is the cone angle. One advantage of the cone-plate rheometer is that the shear rate is constant at any point along the radius. The shear rate ($\dot{\gamma}$) is calculated as a function of $\omega$ and $\theta_c$ by equation [2.24].

Figure 2-5: Different particle concentrations show different viscoelastic responses. The low 15%vol concentration is Newtonian, and the high 43%vol concentration is pseudoplastic. Both suspensions are dispersed 3Y-TZP in pH 9 water. The Bingham yield point is defined as the shear stress intercept taken by linear fit between shear rates of 10–100 s$^{-1}$. A high shear viscosity ($\eta_{\text{High Shear}}$) is defined as the average viscosity of between 400 s$^{-1}$ and 500 s$^{-1}$. The Bingham yield point characterizes the plastic nature of the suspension zero shear rate; while the high shear viscosity characterizes the flow behavior of the suspension at high shear rates corresponding to the shear rate of the LM-RIF process.
\[
\dot{\gamma} = \frac{\omega}{\sin \Theta_c}
\]  \[2.24\]

The shear stress (\(\tau\)) is calculated from the measured torque (\(T_c\)) according to equation \[2.25\].

\[
\tau = \frac{T_c}{2/3 \pi c^3}
\]  \[2.25\]

Another advantage is that small volumes of liquid can be analyzed at high shear rates due to the small gap between the cone and the plate at small cone angles. A 2° cone was used in this dissertation.

Figure 2-6: The geometry of the cone-plate rheometer applies a constant shear rate to the liquid. The rheometer measures the torque as a function of angular velocity. This diagram was taken from the product literature of Brookfield Engineering Laboratories, Inc. \[2.26\]

### 2.3.2 Thermogravimetric/Differential Thermal Analysis/Mass Spectrometry

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are typically coupled together, as the analyses complement one another. Mass spectrometry
(MS) can also couple with TGA to provide a chemical fingerprint of the evolved gas based on the mass to charge ratio of the evolved species. TGA measures the weight of a sample as a function of temperature. DTA measures the difference in temperature between the sample material and a reference material as a function of temperature. TGA/DTA/MS techniques are complementary, since a thermo-chemical reaction may involve a change in mass, enthalpy, and/or reaction product. For example, the complete oxidation of carbon (graphite) to carbon dioxide results in a 100% weight loss, -394 kJ/mol enthalpy change, and a peak mass to charge ratio of 44 g/mol.  

The TGA/DTA combination is more common than TGA/MS in ceramic processing primarily due to the high cost of mass spectrometers. However, important reactions in ceramic processing can be analyzed by simply measuring the mass loss and heat change in a TGA/DTA. The TGA/DTA traces of some typical reactions are shown schematically in Figure 2-7. The temperature range of analysis can be as high as 2000ºC, but it is more typically limited to below 1500ºC and is dependent on furnace construction. The temperature measurement is accurate to a couple of degrees Celsius, and the accuracy is limited by the temperature uniformity of the furnace. The mass in TGA is typically sensitive to ±0.1 µg, whereas the temperature difference (ΔT) in DTA is typically sensitive to ±0.001°C. TGA is a quantitative technique that directly measures mass, whereas DTA is primarily a qualitative technique since an enthalpy change (ΔH) is not directly measured and must be calculated from the change in temperature (ΔT). DTA differs from differential scanning calorimetry (DSC), which measures the energy required to maintain the sample and reference at the same temperature. With calibration, DTA can
yield $\Delta H$ by integrating $\Delta T$ over a temperature range that includes the reaction, then subtracting the baseline and multiplying the result by the heat transfer coefficient ($K$) between the thermocouple and the sample that includes the sample pan. In practice, the enthalpy change is best measured using a dedicated DSC instrument rather than a calibrated DTA, whereas the DTA simply provides the reaction sign (exothermal or endothermal) and the relative magnitude. The TGA/DTA/MS analysis is used to investigate the thermolysis of the mold material and the organic binder in the LM-RIF process. The heat treatment was then tailored to the thermal analysis results in order to prevent defects such as cracking and porosity.

Figure 2-7: Temperature-dependent reactions and phase changes that result in mass and/or heat changes show characteristic signals in a TGA and DTA traces.
2.4 Sintered Part Evaluation

The microscale or mesoscale components demonstrated in the literature do not often quantify part quality that can be defined simply as the ability to accurately produce the part as designed. The driving force for quality evaluation is production, which has not yet occurred for free-standing ceramic microscale or mesoscale parts. However, part tolerance and quality are more important in microscale or mesoscale fabrication since finishing techniques, such as polishing, are not practical for parts of this size. Although the LM-RIF process was designed to manufacture parts, this dissertation does not address scale-up issues that occur as research gives way to product development and manufacturing. However, from a scientific standpoint, the reliability of mesoscale ceramics is paramount in determining the strength limitations of the LM-RIF parts since flaw size ultimately controls the strength of brittle materials.

Optical and electron microscopy are used to qualitatively evaluate part quality, while optical profilometry can be used to quantitatively evaluate mesoscale part size. As an example, Figure 2-8 compares images of ~15-µm thick bend bars using transmission optical microscopy, optical profilometry (reflection), and scanning electron microscopy. Each of these three techniques reveals a different characteristic about the bend bars. In the left image of Figure 2-8, the transmission optical micrograph shows opaque regions in an otherwise translucent specimen. These opaque regions are correlated to areas of increased grain size and/or trace amounts of porosity. In some cases, the grain size difference between the opaque regions and translucent regions is indistinguishable at first glance of a SEM micrograph. However, a simple optical microscope easily reveals the
defective bars. In the middle image of Figure 2-8, a three-dimensional measurement by optical profilometry reveals that the bend bar is not perfectly flat even though it appears to be flat on the optical and SEM images. Optical profilometry is crucial in determining the final sintered size of mesoscale parts, which is important for net-shape forming and accurate strength measurements. The right image in Figure 2-8 is a SEM image, which at first glance shows two straight bend bars. However, the defects shown in the left and center images are present in these two bend bars. Thus, high-quality parts were only produced after defects were highlighted using multiple characterization techniques.

Figure 2-8: Left: A transmission optical micrograph showing dark regions on some of the bend bars. These dark regions are correlated to regions of grain growth. Center: An optical profilometer image showing the thickness of a mesoscale bend bar. From this image, it is obvious that one end of the bend bar curves up and is concave. The blackened pixels contain no data due to scattering from the edge of the bend bar. Right: A SEM image of two bend bars. At this magnification, the defects that are present in the left and center images go unnoticed.

2.4.1 Optical Profilometry

Optical profilometry is a non-contact method that accurately measures nanometer- and micrometer-sized features and has become increasingly useful in micro-
Accurate dimensional measurements are crucial for net shape ceramic forming or producing a final part with the exact design dimensions. When the dimensionality of the mold cavity, green part, and final sintered part is evaluated, accurate shrinkage factors can be calculated and applied to the part design in order to achieve net shape forming.

Optical surface profilometers can operate in one of two modes: phase shifting interference (PSI) or vertical scanning interference (VSI). In PSI mode, monochromatic light is reflected from a surface and produces an interference pattern with the incident light. The interference pattern produces fringes at quarter wavelength intervals ($\lambda_p/4$). A piezoelectric transducer then moves the stage vertically and records another interference pattern. The step height of the sample stage must be less than $\lambda_p/4$ in order to avoid confusion between the different order interference lines. Therefore, the PSI mode is limited to relatively flat surfaces with height differences of less than $\lambda_p/4$ or 158 nm for a commercial instrument with a 632-nm wavelength incident light. The VSI mode is more appropriate for mesoscale parts because the maximum height difference that the VSI mode can analyze is 2 mm. In VSI mode, white light is used to produce an interference pattern, and a precision motor coupled with an LVDT is used to scan vertically and produce a series of interference patterns. When white light is used, the interference pattern is frequency modulated. Since the frequency modulation is inherently non-linear with respect to vertical distance, the ambiguity associated with multiple-order interference is removed. A 3-D height measurement can be calculated by demodulating the frequency signal as a function of height.
Although VSI has dramatically increased the maximum height that can be measured, the frequency demodulation and resolution of the imaging system imposes limitations. The vertical resolution of the optical profilometer can be as fine as 2 nm, but it is dependent on the angle of the feature of interest. The lateral image is captured using a CCD camera with a fixed number of pixels (512 × 512 pixels is common). Therefore, the lateral resolution ($\Delta x$ or $\Delta y$) is a function of the numerical aperture of the lens (NA) and the wavelength of light ($\lambda_p$) according to the Rayleigh criterion [2.26], where

$$\Delta x \geq \frac{0.61 \lambda_p}{NA} \tag{2.26}$$

Additionally, the pixel count and optics limit the maximum height difference that can be calculated from the frequency modulation. A maximum slope exists where the height is defined by the Nyquist limit ($\lambda_p/2$), and the horizontal distance is defined by the pixel spacing and optics (480 nm for a 20× lens) resulting in a maximum slope of about 2/3. In addition to the Nyquist limit, optical effects, such as scattering, can also limit the resolution of the technique. The result is missing data that appears as black pixels in the contour plot or non-continuous line traces shown in Figure 2-9.
2.4.2 Confocal Raman Spectroscopy

Confocal Raman spectroscopy (CRS), a valuable phase analysis tool in zirconia research, is capable of probing significantly smaller areas (1 µm) than X-ray diffraction (XRD). In addition, CRS does not require a thinning procedure for electron transparency for selected area diffraction (SAD) with transmission electron microscopy (TEM). CRS has thus become the tool of choice for evaluating the transformation toughening behavior of zirconia after fracture. In particular, measurement of the transformation zone size or area of phase transformation around a crack allows a direct quantitative measurement of the extent of transformation that is related to the material toughness. Raman microscopy is especially valuable for phase analysis of mesoscale ceramics that are both too small individually to evaluate using conventional XRD and too thick for TEM.
**Theory**

Raman spectroscopy is a vibrational technique that is more sensitive to structural differences than chemical differences; thus, it is ideal for deciphering the structurally different, chemically identical monoclinic (m-ZrO$_2$) and tetragonal phases (t-ZrO$_2$) of 3Y-TZP. The Raman spectrometer works by absorbance and emission of photons from the specimen. The monochromatic laser light in the visible region disturbs the electrons in the interatomic bonds, and this energy is reradiated at the same frequency (Rayleigh scattering) or imparted to the lattice, which vibrates at frequencies corresponding to the bonding arrangement and atomic weights of the constituent atoms at frequencies lower than that of the incident beam (Stokes-scattering). Vibrational frequencies higher than the incident beam are also possible due to the thermal energy in the material (Anti-Stokes scattering), but are not used for Raman spectroscopy due to their temperature dependence and weak signal at room temperature. The reradiated light with characteristic vibrational frequencies is collected by the optics of the microscope, and a Raman spectrum is produced on a CCD detector by a diffraction grating.

Raman spectra are complex due to the many factors that can contribute to the vibrational modes of a material. The Raman intensity as a function of frequency ($\nu$) is given by [2.27], where the variables are defined below.

\[
I(\nu_m)_R = \left( \frac{16\pi^3}{405c^4} \right) \left( \frac{hI_L N_m (\nu_0 - \nu_m)^4}{\mu \nu_m (1 - e^{-h\nu_m/kl})} \right) \left( 45(\alpha'_a)^2 + 7(\nu'_a)^2 \right)
\]

[2.27]

- $c$ \hspace{1cm} Speed of light
- $h$ \hspace{1cm} Planck’s constant
- $I_L$ \hspace{1cm} Excitation intensity
- $N_m$ \hspace{1cm} Number of scattering molecules
The complexity of equation [2.27] makes simulating the Raman spectra difficult; however, \( I(\nu_m) \) and \( I(N_m) \) are routinely exploited for phase identification and quantitative phase concentration, respectively. The concentration dependence of peak height can be used to determine the relative concentration of the monoclinic and tetragonal phases of zirconia.\textsuperscript{35} Although ideal molecules or atomic lattices vibrate at very specific frequencies, the multitude of scattering phenomena results in peak broadening. For example, fine grain size can broaden the Raman peaks of zirconia polymorphs, but this effect is only important below 80 nm.\textsuperscript{42,43}

Peak shape in Raman spectra may be Gaussian or Lorentzian or a combination of both. The population of vibrational states has a Boltzmann distribution; however, the peak shape in the Raman spectra is due to the decay time of the coherence among the vibrations.\textsuperscript{44} If the coherence decay time is long relative to the amplitude decay time, then the peak shape is Gaussian; in contrast, if the coherence time is short relative to the decay time, then the peak shape is Lorentzian.\textsuperscript{44} In solids, a Gaussian shape is more likely because vibrations remain coherent due to the highly bonded lattice. In gases and liquids, the peak shape is more likely to be Lorentzian since the molecule can dissipate vibrational energy to the surrounding molecules and is thus less coherent with a broader distribution. Deconvolution becomes more difficult than described above due to the
presence of instrumental broadening, which tends to add a Gaussian distribution. As Raman spectra are difficult to simulate because of the many variables, only the relative peak height and position are extracted for phase identification and quantification.

**Resolution**

There are three resolution limitations in confocal Raman spectroscopy: the lateral and axial resolution of the microscope, and the spectral resolution of the detector. The lateral resolution ($\Delta x$) of confocal optical microscopes can generally be described by the Raleigh criterion given in [2.26]. For 488 nm wavelength light and a 0.9 NA lens typical of a 100X lens, the lateral resolution limit is 330 nm. In confocal optical microscopes, light is captured from a point source in the focal plane by employing a pinhole at the image plane. A 3-D image can be formed by scanning in $x$, $y$, and $z$ directions. However, in the $z$-direction the resolution and penetration depth depend on the optical properties of the material due to refraction of the light within the sample. Everall discusses the depth resolution limitations in confocal Raman spectroscopy and provides a relationship [2.28] for the resolution ($\Delta z$) as a function of the focal depth ($z$), numerical aperture (NA), and material index of refraction ($n_i$).

$$\Delta z = z \left( \frac{NA^2(n_i^2 - 1)}{1 - NA^2} + n_i \right)^{1/2}$$

[2.28]

For zirconia with a refractive index of 2.19, the depth resolution ($\Delta z$) is 2.39 times the focal depth ($z$). For example, spectral information gathered at a focal depth ($F$) of 1 µm in
air will actually be gathered from a depth ranging from 2.19 µm (n_r F) to 7.42 µm (n_r F + Δz). 46

Use in Zirconia

Raman spectroscopy was first used to decipher the zirconia polymorphs by Phillippi et al. 47 The number of active modes is determined by the lattice symmetry, which corresponds to the number of spectral peaks. There are 18 expected modes for the monoclinic phase, 6 modes for the tetragonal phase, and a single mode for the cubic phase of zirconia. 48 Clarke and Adar were the first to use Raman spectroscopy to determine the amount of transformed zirconia due to fracture of the metastable tetragonal phase. 35 They calibrated Raman peak intensity ratios for m-ZrO₂ to t-ZrO₂ against the peak intensity ratios by XRD and used the calibration curve to determine the amount of the monoclinic phase. Clarke and Adar observed that Raman spectroscopy is more sensitive to small monoclinic contents than XRD. Additionally, they confirmed earlier TEM observations 49 of transformation toughening, but without thinning the sample or risking electron beam damage. The sensitivity of Raman spectroscopy to the monoclinic phase, the freedom from polishing, and the ability to scan longer distances than with TEM, all make Raman spectroscopy the preferred tool for evaluating the propensity of a material to transformation toughen. Although many researchers have chosen Raman spectroscopy to evaluate the extent of transformation toughening, 35-38 there are discrepancies between the measured toughness and the toughness calculated from transformation zone size measurements. These discrepancies are due to reversible
transformation, that is, to the tendency of a transformation toughened material to transform under stress, then revert back to the original phase post fracture.\textsuperscript{50} Transformation toughness, as measured by Raman spectroscopy, will be discussed in more detail in Chapter 5.

\underline{2.4.3 Scanning Electron Microscopy (SEM, FESEM)}

High magnification and a large depth of focus make scanning electron microscopy (SEM) the standard technique for evaluating mesoscale part quality. Magnifications as high as 500,000X, and depth of foci as large as 40 µm at 1,000X are possible.\textsuperscript{51} The combination of high magnification and large depth of focus permits observation of the three-dimensional relief of the part, the feature resolution, and the grain size with the same technique.

\textbf{Theory}

SEM impinges high-energy (1–40 keV) electrons on a bulk sample, and collects either specimen-generated secondary electrons or backscattered electrons for imaging. An image is formed by rastering the impinging beam of electrons across the sample and collecting electrons from a given location. An electromagnetic condenser lens controls the spot size or impinging electron beam diameter, while the objective lens controls the focus of the lens. The deflector coils that control the raster are located within the
objective lens. Magnification is controlled by rastering the beam across a large area for low magnification or a small area for high magnification.

As the high-energy electrons encounter the atoms of the sample material, they scatter elastically or inelastically. In elastic scattering, the electrons do not lose energy, but merely change direction. Elastic scattering forms the basis of backscatter electron imaging (BSE). In inelastic scattering, energy is lost in the scattering event, but there is no significant change in the electrons’ velocity vector. The energy lost in an inelastic scattering event can be transferred to phonon excitation (heat), plasmon generation (wave-like electron excitation in metals), secondary electron generation, Auger electron generation, broad X-ray generation, or characteristic X-ray generation. Secondary electrons are the basis for high-resolution imaging, while the other inelastic scattering events are routinely used for microanalysis.

Electron scattering can be described by the scattering cross-section ($Q_T$) or the mean free path. The scattering cross-section is the probability that an electron will be scattered by the atoms of the sample, and the mean free path is the distance between scattering events. The mean free path is the inverse of the scattering cross-section; it is sometimes used because distance is more tangible than a scattering probability. The scattering cross-section of a material is given by [2.29], where $N_A$ is Avogadro’s number, $\sigma_T$ is the scattering cross-section of an individual atom, $\rho$ is the material density, and $A$ is the atomic weight.51

$$Q_T = \frac{N_A \rho \sigma_T}{A} \quad [2.29]$$
In [2.29], the total scattering cross-section \((Q_T)\) includes all elastic and inelastic scattering events. Elastically scattered electrons have a scattering cross-section given by the Rutherford equation [2.30], which is a function of the atomic number \((Z)\), impinging electron energy \((E_0)\), and the scattering angle \((\phi_R)\).\(^{51}\)

\[
Q_{\text{elastic}} = 1.62 \times 10^{-20} \frac{Z^2}{E_0^2} \cot^2 \frac{\phi_R}{2} \quad [2.30]
\]

Equation [2.30] is derived based on the Coulombic interaction between the impinging electron and the atomic nucleus; it is valid for high scattering angles where electron/electron interactions are negligible.\(^{51}\) The elastic scattering cross-section forms the basis of BSE imaging, which shows atomic number contrast due to the dependence of \(Q_{\text{elastic}}\) on \(Z\) in [2.30]. Inelastic scattering cross-sections are generally grouped together, as the individual scattering events—phonon excitation, plasmon, secondary electron, Auger electron and X-ray generation—are more difficult to characterize for all materials. However, there are various models for determining the mean free path or the average rate of energy loss per distance that the electron travels in the material.\(^{52,53}\) The inelastic scattering models are a function of the material parameters: atomic weight, density, and atomic number. Monte Carlo simulations are used to simulate the path of an individual electron through a material from elastic and inelastic scattering.\(^{54}\) In these simulations, elastic scattering determines the angle between scattering events since equation [2.30] is a strong function of the scattering angle, while inelastic scattering determines the rate of energy dissipation. When the paths of numerous electrons are simulated, an interaction volume can be calculated that gives the total volume of material that is interrogated by the electron beam. The interaction volume is a function of beam energy, sample density,
atomic number, and atomic weight, which means that the resolution and other
information are dependent on the material being analyzed. Figure 2-10 shows Monte
Carlo simulations\(^5\) for the interaction volume for a 10 keV beam impinging on a 60–40
Au-Pd alloy, zirconia, and a 100-nm Au-Pd coating on zirconia. The backscattering
coefficient or fraction of backscattered electrons is 0.37 for zirconia, and 0.42 for both
solid Au-Pd and the 100-nm Au-Pd coating, which shows that the atomic number contrast
cannot be seen with the 100-nm Au-Pd coating at 10 keV. The resolution of the BSE is a
strong function of the material as shown by the density of red lines in the Monte Carlo
simulations in Figure 2-10. Applying a metallic coating decreases the interaction volume
and improves resolution, but as shown in Figure 2-10 will limit the atomic number
contrast. A carbon coating is preferred for BSE analysis for this reason. Secondary
electrons have an energy below 50 eV (typically 2–5 eV), and must be collected by a
positive bias on the detector.\(^5\) Secondary electrons are more easily generated from
metals due to the presence of conduction band electrons, and thus metallic coatings are
preferred for high-resolution imaging of insulators. Due to their low energy, secondary
electrons have an escape depth that is limited to approximately 1 nm for metals and 10
nm for insulators and is a function of the mean free path of the material.\(^5\) High-
resolution images can be formed from secondary electrons because the escape depth is
much shallower than for backscattered electrons; thus, the interaction volume does not
expand the spot size significantly.
Figure 2-10: The electron interaction volume is a function of the atomic number, weight, and density of the sample material. All three Monte Carlo simulations are for a 10-keV beam and 10-nm spot size and show the paths of electrons that escape the sample in red and the paths of the electrons that terminate within the sample in blue. Each simulation has a width of 824 nm and a depth of 650 nm. The left simulation is of a 60–40-Au-Pd alloy typically used as a conductive coating for SEM imaging. The center image simulation is for uncoated zirconia. The right simulation is of a 100-nm coating of Au-Pd on zirconia. Simulations were performed using the CASINO program v.2.42. These simulations show that the interaction volume is smaller for the Au-Pd alloy, which enhances resolution and prevents charging the sample.
Resolution

In addition to the resolution limitations imposed by the interaction volume, the impinging electron spot size also limits the resolution. The spot size is a function of the electron gun brightness or current density per solid angle. The source of electrons for a thermionic SEM is a bent tungsten filament that is resistively heated. The electrons overcome the work function of filament (4.5 eV for W), and a negative bias (-400 V) accelerates the electrons towards the grounded anode. Field emission scanning electron microscopes (FE-SEM) have a sharper point than the thermionic source, and the electrons are freed by tunneling through the work function barrier at higher voltages (3–5 kV). The brightness of a thermionic source is $10^5$ A/(cm$^2$sr) versus $10^8$ A/(cm$^2$sr) for field emission, which results in a spot size of about 20 nm for the thermionic source and 1.5 nm for field emission at 10 kV accelerating voltage and 0.1 nA probe current. Therefore, a FE-SEM microscope has potentially better resolution than does a SEM, but it is also more costly. The resolution is also limited by aperture diffraction and spherical and chromatic aberrations, as well as uncorrected astigmatism.

2.5 Flexure Strength

The beam-bending test has become the preferred method for evaluating the strength of ceramics in tension because ceramics’ lack of plasticity causes failure outside of the test area in a typical tensile test. However, the accuracy of the bend test is limited
by the assumptions inherent in beam theory, errors in the bend test setup, and sample irregularities. As a result, variations of characteristic strength between laboratories of more than 100 MPa for an identical material are common and accepted.\textsuperscript{56} The ASTM standard for flexure testing attempts to address the shortcomings from instrumentation and sample preparation, but the strength of ceramics remains inherently variable. There exist other difficulties with free-standing samples that have a maximum dimension of 350 \( \mu \text{m} \) that make following the ASTM protocol for flexure testing challenging. Specific standard test methods for small-scale flexure testing of free-standing ceramic parts do not exist, as these parts have only recently started to be mass produced.\textsuperscript{57} In developing a bend test for mesoscale ceramics, all attempts were made to conform to the current ASTM standard test method\textsuperscript{58} in regard to both the test method and sample dimension ratio.

The errors in the mesoscale bend test used in this dissertation are critically assessed using the same error analysis that was used in the formulation of the current ASTM standard.\textsuperscript{58} This original error analysis was published by the US Army Materials Technology Lab,\textsuperscript{59} and it addresses the errors arising from assumptions inherent in beam theory and the errors associated with the practical test itself. It is important to reconsider the errors associated with the flexure test for mesoscale ceramics, since the flexure testing of free-standing ceramic specimens on the size scale reported in chapters 3–5 has not been done before, and contains errors from the concessions that were made due to the small sample size. As the largest errors are identified, the mesoscale test can be improved.
In flexure testing, the four-point bend test is preferred over the three-point bend test because in the former the bending moment is constant between the inner span as opposed to being linearly dependent on the distance away from the loading point as in the three-point (3-pt.) test. Additionally, the three-point bend test inherently has a shear stress component between the test span, whereas the four-point (4-pt.) bend test does not. Since maximum stress occurs over a smaller area for the 3-pt. bend geometry, the three-point strengths are generally 15% higher than the strengths for 4-pt. bend testing as a rule of thumb. More accurate conversions between 4-pt. and 3-pt. bend strengths can be made using Weibull statistics, which will be discussed in later chapters. Despite having these notable advantages in regard to macroscale testing, the 4-pt. bend test geometry is difficult to reproduce at the mesoscale and is more sensitive to alignment issues than is the 3-pt. bend test. Therefore, the following discussion on errors will be limited to the 3-pt. bend test, which was used exclusively for testing as discussed in subsequent chapters.

Table 2-1 lists the types of errors considered when the current ASTM flexural test standard was established. The recommended metrics for minimizing each particular source of error and the calculated metrics for the mesoscale bend test are also given in Table 2-1. Each calculation will be described in the following sections. The equation for the maximum tensile stress at the central loading point ($\sigma_0$) in 3-pt. bending is given by [2.31], where $P_L$ is the load, $L_T$ is the span, $b$ is the width, and $d$ is the thickness.

$$\sigma_0 = \frac{3P_L L_T}{2bd^2}$$  [2.31]
Some of the errors in flexure testing come from violating the assumptions inherent to beam theory, specifically that:\(^{59}\)

1) The material is isotropic and homogenous.
2) Small deflections are relative to the beam thickness.
3) Normal bending occurs without twist or local deformation.
4) Planes normal to the longitudinal axis of the beam remain planar after deflection.
5) Stresses in the longitudinal direction are independent of lateral displacements.

The errors that occur when these assumptions are violated are represented by errors 1–4 in Table 2-1. The remaining errors in Table 2-1 are due to imprecise test geometry or errors in the specimen size and shape. Each error will now be described with more attention given to the largest errors that are calculated using the parameters from the mesoscale bend test geometry and specimen characteristics. Some of these parameters are estimated with deference toward overestimating the error. While some of these errors appear large, they tend to be small relative to the defects in the specimens themselves, and the variability inherent in brittle fracture. Additionally, if the fracture of a particular test specimen was questionable (mostly due to placement errors), it was not included.
Table 2-1: Quantification of the errors in the mesoscale beam-bending test. Eccentric load, bearing friction, load readout, and specimen dimension are the largest errors in the mesoscale bend test. The sign of the error indicates whether the presence of the particular error has the effect of decreasing the strength measurement (-) or increasing the strength measurement (+). The originality of the mesoscale three point bend test results in large errors compared to the macroscale ASTM standard three point bend test. Although these errors appear large, the error relative to the strength variability inherent to brittle materials is still small. Therefore, the mesoscale three point bend test is able to reveal strength differences between materials.

<table>
<thead>
<tr>
<th>Error</th>
<th>Recommendation</th>
<th>Metric for mesoscale test</th>
<th>Error</th>
<th>Is this a likely source of error for mesoscale parts?</th>
</tr>
</thead>
<tbody>
<tr>
<td>1  Non-homogenous material</td>
<td>New fabrication process</td>
<td>-</td>
<td>+2% for a 50 MPa stress for a 2.2 GPa strength</td>
<td>Unknown. Residual stress due to surface transformation of zirconia can be as high as 200 MPa, but is more typically &lt;50 MPa for fine-grained 3Y-TZP.</td>
</tr>
<tr>
<td>2  Beam curvature along length</td>
<td>R&lt;sub&gt;d&lt;/sub&gt;/d &gt; 100</td>
<td>R&lt;sub&gt;d&lt;/sub&gt;/d = 159</td>
<td>-0.2%</td>
<td>No</td>
</tr>
<tr>
<td>3  Anticlastic curvature</td>
<td>b/d ≤ 15</td>
<td>b/d = 1.5</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>4  Large deflection</td>
<td>L&lt;sub&gt;T&lt;/sub&gt;/d ≤ 25</td>
<td>L&lt;sub&gt;T&lt;/sub&gt;/d = 6</td>
<td>&lt;-0.1</td>
<td>No</td>
</tr>
<tr>
<td>5  Eccentric load</td>
<td>e/L&lt;sub&gt;T&lt;/sub&gt; &lt; 0.025</td>
<td>e/L&lt;sub&gt;T&lt;/sub&gt; = 0.06</td>
<td>+10%</td>
<td>Yes</td>
</tr>
<tr>
<td>6  Span error</td>
<td>e&lt;sub&gt;s&lt;/sub&gt;/L&lt;sub&gt;T&lt;/sub&gt; &lt; 0.005</td>
<td>e&lt;sub&gt;s&lt;/sub&gt;/L&lt;sub&gt;T&lt;/sub&gt; = 0.01</td>
<td>1%</td>
<td>Yes</td>
</tr>
<tr>
<td>7  Beam twist</td>
<td>θ&lt;sub&gt;f&lt;/sub&gt; &lt;&lt; 1º</td>
<td>θ&lt;sub&gt;f&lt;/sub&gt; = 2º (estimate)</td>
<td>-2%</td>
<td>Twist angle unknown</td>
</tr>
<tr>
<td>8  Bearing friction</td>
<td>Roller bearings</td>
<td>unknown μ, if μ = 0.4</td>
<td>+15%</td>
<td>Yes</td>
</tr>
<tr>
<td>9  Contact stress</td>
<td>p&lt;sub&gt;n&lt;/sub&gt;/d = 0.75</td>
<td>p&lt;sub&gt;n&lt;/sub&gt;/d = 0.007</td>
<td>-</td>
<td>Support roller will deform</td>
</tr>
<tr>
<td>10 Wedging stress</td>
<td>L&lt;sub&gt;T&lt;/sub&gt;/d ≥ 20</td>
<td>L&lt;sub&gt;T&lt;/sub&gt;/d = 6</td>
<td>-2%</td>
<td>Yes</td>
</tr>
<tr>
<td>11 Beam overhang</td>
<td>Total Length ≥ L&lt;sub&gt;T&lt;/sub&gt;+2d</td>
<td>332 μm ≥ 139 μm</td>
<td>0</td>
<td>No</td>
</tr>
<tr>
<td>12 Contact point shift</td>
<td>ρ&lt;sub&gt;n&lt;/sub&gt;/d ≤ 5</td>
<td>ρ&lt;sub&gt;n&lt;/sub&gt;/d ≤ 0.007</td>
<td>≤+0.5</td>
<td>No</td>
</tr>
<tr>
<td>13 Corner radius</td>
<td>r/d ≤ 0.06</td>
<td>r&lt;1 μm</td>
<td>≤-0.4</td>
<td>No</td>
</tr>
<tr>
<td>14 Load readout</td>
<td>error less than 0.5%</td>
<td>Voltage background to peak load voltage ~ 4%</td>
<td>±4% max</td>
<td>Yes</td>
</tr>
<tr>
<td>15 Specimen dimension</td>
<td>e&lt;sub&gt;m&lt;/sub&gt;/d &lt; 0.1%</td>
<td>e&lt;sub&gt;m&lt;/sub&gt;/d = 2%</td>
<td>±4%</td>
<td>Yes</td>
</tr>
</tbody>
</table>
2.5.1 Inhomogeneous Material

It is assumed that the elastic modulus is the same in tension as it is in compression. This assumption is inherent in the ASTM test and is generally accepted; however, any local stress distribution in the body will result in a stress distribution different than that calculated from the loading geometry. All non-cubic polycrystalline materials will have a small amount of residual stress due to anisotropy in the thermal expansion coefficient between grains, but this is generally uniform within the body. However, residual surface stress due to surface transformation of tetragonal zirconia to monoclinic zirconia can place the surface into compression. This will tend to increase the fracture strength, as the maximum tensile stress is reduced by the residual compressive stress. This residual compressive stress can be as high as 200 MPa for weathered 3Y-TZP; however, it is generally less than 50 MPa for pristine fine-grained 3Y-TZP. Since the mesoscale samples are not machined or weathered, the residual stress is likely to be less than 50 MPa. This results in a proportional error of +2% assuming strength equal to 2.2 GPa. It is unknown whether the surface residual stress is higher in mesoscale parts than in macroscale parts; however, surface residual stress is generally considered beneficial as it prevents surface cracks from forming, much like tempered glass in automobile windshields.
2.5.2 Beam Curvature Along Length

It is important to minimize the initial curvature of the flexure test specimen in mesoscale specimens because a surface-finishing technique has not been developed to ensure flatness. Chapter 4 addresses how the curvature was minimized, but not eliminated. The error \( E_c \) resulting from bend testing a beam with an initial radius of curvature \( R_c \) is given by [2.32],\(^{59}\) which is a function of the geometric parameters \( \alpha_c \) and \( \alpha_b \), where \( \alpha_c \) and \( \alpha_b \) are given by [2.33-2.34].

\[
E_c = \left( \frac{\alpha_b - \alpha_c}{\alpha_c} \right) \quad [2.32]
\]

\[
a_c = \left( \frac{d}{2R_c} \right) - \frac{1}{12} \left( \frac{d}{R_c} \right)^2 \left( 1 + \frac{1}{15} \left( \frac{d}{R_c} \right)^2 \right)
\]

\[
\left( \frac{1}{12} \left( \frac{d}{R_c} \right)^2 \left( 1 + \frac{1}{15} \left( \frac{d}{R_c} \right)^2 \right) \right) \left( 1 - \frac{d}{2R_c} \right)
\]

\[
a_b = 6 \left( \frac{R_c}{d} \right) \quad [2.34]
\]

An average radius of curvature for mesoscale bend bars is 2.8 mm, and the thickness is 17.4 µm, resulting in an \( R_c/d = 159 \) and an error of only -0.2%. This is within the acceptable limits of the ASTM standard and is considered a small amount of error.

2.5.3 Anticlastic Curvature and Large Deflection

Anticlastic curvature is curvature in the plane perpendicular to the longitudinal axis of the bend bar. This error is larger in parts that have geometry that is more similar to a plate than a beam, i.e., that have a large width/thickness ratio. Anticlastic curvature is
not expected in the mesoscale bend bars, as the specimens conform to the ASTM standard that specifies b/d ≤15. The b/d ratio for mesoscale parts is 1.5. The error resulting from anticlastic curvature is, therefore, near zero.

The small deflection assumption is also valid for the mesoscale bend bars, as the dimensional ratio conforms to the ASTM standard and the elastic modulus of zirconia is high (~200 GPa).\textsuperscript{62} The recommended L_T/d ratio is less than 25, where L_T/d = 6 for the mesoscale bend bars; therefore, the large deflection error is also near zero.

### 2.5.4 Eccentric Load

The eccentric load error is the error attributed to misalignment of the top loading point relative to the center of the span. The error (E_s) is defined as the distance along the span between the central loading point and an end loading point (e_s) compared to the total lower span length (L_T). The error is given by [2.35],\textsuperscript{59} and the recommended maximum e_s/L_T ratio of 0.005 corresponds to an error of 0.01%.

\[
E_s = 4 \left( \frac{e_s}{L_T} \right)^2 \tag{2.35}
\]

Figure 2-11 shows two mesoscale bend beams being loaded; the beam on the left has an eccentricity error of 0.1%, while the beam on the right has an eccentricity error of 6%. Figure 2-11 illustrates the difficulty of aligning the central loading point to the center of the span. The eccentricity error is expected to be significant, but <10% for the mesoscale specimen. To meet the recommended eccentricity error of 0.01%, the central loading point would have to be positioned within 0.52 µm of the span’s center.
Positioning with a resolution of 0.52 µm is difficult especially considering that the resolution of the camera used for positioning (Figure 2-11) has a resolution of only 1.4 µm per pixel. Positioning with this fine a resolution would have to be accomplished by SEM, and it would require a complete reworking of the test setup. Alternatively, a coupled upper and lower span could provide more consistent alignment.

Figure 2-11: The loading eccentricity error is large for the mesoscale specimen due to the difficulty in aligning the central loading point in the center of the loading span. The left specimen is 1.6% off center, while the right specimen is 11.8% off center. This translates to a strength error of 0.1% for the left specimen and 6% for the right specimen. The reflective material around the razor blade edges is vacuum grease used to recover the specimen after fracture.

2.5.5 Span Error

Another error similar to the eccentricity error is the uncertainty associated with the span distance measurement. This error is smaller than the eccentricity error, since the span is measured on a dedicated optical system that is precise to the order microns
(resolution limit of optical microscopy). However, even if the error is 1 μm, then the percentage error over the span length is about 1% (L_T = 104 μm), which is above the recommended limit of 0.5%.

2.5.6 Beam Twist

Beam twist is a condition whereby the beam is twisted with respect to the longitudinal axis of the beam resulting in a torque during bend testing. The additional torsional stress results in an error, since it is assumed that failure occurs from bending stress only. In the analysis of the beam twist error, it must be established if the beam makes a full line contact with the load prior to failure. This contact depends on the angle of twist in the beam. This twist angle is not precisely known for the mesoscale ceramic bend test bars; this is because the angle measurement is obscured in the roughness of the sample. However, it is thought that a 1 μm rise over the specimen width (b) is possible and would result in a twist angle of 2º. Assuming plane stress, a non-rotating support span, and the constants in Table 2-2, the estimate of beam twist error for the mesoscale bars is -2%. It is recommended the beam twist angle (ϕ_T) be limited to much less than one degree in order to avoid a significant stress error arising from the torque produced by the beam twist. Although the twist angle is not known for mesoscale bend bars, estimates suggest that it is higher than the recommended limit.
Roller bearings are suggested for the support pins in flexure testing in order to provide a low-friction surface and better satisfy the plane stress assumption inherent in the flexure test. Friction at the loading pins creates a moment opposite to that of the applied bending moment and thus the assumption of frictionless supports will tend to overestimate the strength.\(^{63}\) Newnham has found that this error can be as high as 13% for rigid supports as opposed to ball-bearing supports in a 4-pt. bend test.\(^{63}\) The bearing friction error may be large for the mesoscale bend test, since razor blades are used as the support members simply because ball bearings of a sufficiently small diameter are not available. The bearing friction error \(E_{bf}\) can be calculated for a three-point bend test.

### Table 2-2: The constants used to evaluate the beam twist error assuming a 2° angle of twist between the lower span supports of a three-point bend test specimen are given below. The unshaded parameters are measured, the lightly shaded parameters are assumed, and the darker shaded parameters are calculated using the table provided by Baratta et al.\(^{59}\) Plane stress and non-rotating supports are assumed. The contact constant \(n_c\) is less than one, which means a twist angle of 2° would not cause line contact prior to the assumed failure stress of 2 GPa.

<table>
<thead>
<tr>
<th>Constant</th>
<th>Symbol</th>
<th>Value</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Width</td>
<td>(b)</td>
<td>26</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>Thickness</td>
<td>(d)</td>
<td>17</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>b/d Ratio</td>
<td>(b/d)</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Elastic Modulus</td>
<td>(E_Y)</td>
<td>200</td>
<td>GPa</td>
</tr>
<tr>
<td>Normal Bend Strength</td>
<td>(\sigma_0)</td>
<td>2</td>
<td>GPa</td>
</tr>
<tr>
<td>Poisson's Ratio</td>
<td>(\nu)</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Span</td>
<td>(L_T)</td>
<td>104</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>Twist Angle</td>
<td>(\phi_T)</td>
<td>2°</td>
<td></td>
</tr>
<tr>
<td>Moment Arm</td>
<td>(l')</td>
<td>52</td>
<td>(\mu m)</td>
</tr>
<tr>
<td>Contact Constant</td>
<td>(n_c)</td>
<td>0.9</td>
<td></td>
</tr>
<tr>
<td>Beam Twist Error</td>
<td>(\epsilon_{BT})</td>
<td>-2%</td>
<td></td>
</tr>
</tbody>
</table>
using equation [2.36], where $\mu_f$ is the coefficient of friction, $L_T$ is the lower span, and $d$ is the thickness.\[^{59}\]

\[
E_{bf} = \frac{\mu_f}{L_T \sqrt{2d - \mu_f}}
\]

[2.36]

The coefficient of friction between the razor blades and the 3Y-TZP bend bar is not known; however, the effect on strength is potentially large. For a span of 104 $\mu$m, a thickness of 17 $\mu$m, and an assumed coefficient of friction of 0.4 (dynamic dry friction between GCr15 steel and 3Y-TZP),\[^{64}\] the bearing friction error is +15%.

### 2.5.8 Contact Stress

In the local region of the specimen contacting the supports, higher stress can result if the support diameter is not sufficiently large to distribute the load over a large area. The recommended loading point diameter on a cylindrical roller\[^{58}\] is 1.5× the beam thickness or 25.5 $\mu$m for the mesoscale specimen. Since a razor blade is used instead of a roller, the contact stress can simply be calculated using the applied load ($P_L$ for the center loading point) and a rectangular contact area with a width equal to the width of the razor blade. If the contact stress ($\sigma_{con}$) is given by the applied load ($P_L$) divided by the rectangular contact area ($b\delta_1$), where $\delta_1$ is the contact width, and the contact load is made equal to the applied load, then the ratio of contact to applied stress is given by [2.37], where $L_T$ and $d$ are given by the 3-pt. bend equation [2.31].

\[
\frac{\sigma_{con}}{\sigma_0} = \frac{2d^2}{3L_T\delta_1}
\]

[2.37]
Figure 2-12 shows the width of the razor blade (δ1) used as the loading point in the mesoscale bend test. The width of the contact point is 250 nm before testing. Therefore, the contact stress is 7.4 times the maximum applied stress to the sample or 14.8 GPa assuming that d = 17 mm, L_T = 104 mm, and σ_0 = 2 GPa. This stress is high enough to deform the stainless steel support, and possibly crush the sample. However, since the support will likely deform at stresses lower than the compressive strength of the sample, the contact stress in the sample is likely much lower.

2.5.9 Wedging Stresses

A wedging stress is created when the center loading point is too close to the lower loading points. Wedging stress increases the tensile stress through the thickness of beam, and is most detrimental on the tensile side of the beam since it adds to the tensile stress rather than reducing the compressive stress on the compression side of the neutral axis. In a three-point bend test, the center loading pin acts as a wedge that “priest apart” the beam.
The wedging stress becomes more significant as the span decreases; it can even create a tensile stress on the compression surface when the span is equal to the thickness of the beam.\(^5^9\) The error associated with the wedging stress is given in [2.38] for a three-point bend geometry, where \(\beta_T\) is the wedging parameter, \(L_T\) is the span, and \(d\) is the beam thickness.\(^5^9\)

\[
E_w = \frac{\frac{3}{4}\left(\frac{L_T}{d}\right) - \frac{3}{2}\left(\frac{x'}{d}\right) + \beta_T}{-\beta_T} \tag{2.38}
\]

The wedging parameter \((\beta_T)\) is also a function of \(x'\), which is the distance from the central loading point to the point of fracture. The maximum wedging parameter is 0.0868, if fracture occurs when \(x' = \frac{1}{4}d\).\(^5^9\) When the point of fracture is a distance equal to \(\frac{1}{4}\) of the thickness, the maximum tensile stress occurs on the tensile surface of the beam.

With a span of 104 \(\mu\)m and beam thickness of 17 \(\mu\)m, the wedging stress error \((E_w)\) is -2% if failure occurs at \(x' = \frac{1}{4}d\) or 4.25 \(\mu\)m away from the loading point. The recommended \(L_T/d\) ratio is 20 to minimize wedging stress, but the \(L_T/d\) ratio for the mesoscale bending test was 6; this means that wedging stress may have lowered the failure stress by at most 2%.

### 2.5.10 Beam Overhang

The errors due to beam overhang and corner radius are not expected to be large sources of error for the mesoscale bend test. The beam overhang must be sufficiently long to avoid any edge effects with the end of the beam. The recommended beam length
is greater than the sum of the span and twice the beam thickness\textsuperscript{59} or 138 \(\mu\)m for the mesoscale bars, which is far surpassed by the 330-\(\mu\)m length.

2.5.11 Corner Radius

Corners may be chamfered in a bend test specimen to decrease the likelihood of edge failure and the change to the failure stress due to chamfered edges is accommodated by the ASTM standard.\textsuperscript{58} The corner radius error refers to instances in which a rectangular cross-sectional area is assumed, but the actual specimen has chamfered corners. To avoid a significant error in the stress calculation, the recommended corner radius to thickness ratio is less than 6\%. This ratio corresponds to a maximum edge radius of 1 \(\mu\)m in a mesoscale bend bar and a stress error of 0.4\%. This maximum radius is generally satisfied for the mesoscale bars. However, there are significant cross-sectional geometry errors; these will be discussed in detail in Chapter 4.

2.5.12 Contact Point Tangency Shift

If the loading pin diameter is large compared to the beam depth, the loading points will shift towards each other and reduce the span. This decrease in span will decrease the measured strength proportionally according to [2.30]. Since the razor blades used as the lower support rollers have a small diameter (\(\rho_1 = 250\) nm), the contact point tangency shift error is small. If the radius of curvature on the support pin is less than the beam thickness (\(\frac{1}{2}\rho_1<d\)), then the contact point tangency shift error will be less than
The \( \frac{1}{2} \rho_1/d \) ratio for the mesoscale test is 0.007, which is much less than the recommended limit; therefore, the ratio is not a significant source of error. However, deformation of the loading point will increase the \( \rho_1/d \) ratio, but the tangency shift error is still expected to be relatively low.

### 2.5.13 Load Readout

The load readout error, which is directly proportional to the error in stress according to [2.30], is an instrumental error in the load cell that is used to measure the force. For standard testing of macroscale samples, the recommended load error is less than 0.5% of the maximum load. This low amount of error is difficult to achieve in mesoscale part testing because the failure load is very low (~0.1 N) and the background load is susceptible to small vibrations. Figure 2-13 shows that the baseline force measurement has a range of approximately 0.003 N, while the maximum force is approximately 0.13 N, resulting in an error of approximately 2%. On lower-strength samples, this error can be as high as 4%, which is a significant error. Fortunately, the load readout error is random and does not increase or decrease the strength estimate in one direction.
2.5.14 Specimen Dimensions

The error in the specimen dimensions is proportional to the error in strength through the 3-pt. bend stress equation [2.31]. The error in thickness creates a larger error \((e_d)\) than the width \((e_b)\) since it is squared in [2.31]. The total error due to specimen dimensions \((E_{\text{dim}})\) can be calculated through equation [2.39].

\[
E_{\text{dim}} = \sqrt{2\left(\frac{e_d}{d}\right)^2 + \left(\frac{e_b}{b}\right)^2}
\]  

[2.39]

Figure 2-13: A load versus time plot during the fracture of a mesoscale bend bar. The displacement is only provided as a reference and does not represent the actual displacement of the bar under load.
In this section, only measurement errors are considered. The geometric irregularities will be discussed in depth in Chapter 4. The dimensional error (95th confidence interval) in the width and thickness measurements of the mesoscale parts is 2%, which results in a 3.5% dimensional error in stress. The recommended maximum error for each dimension is 1%, but a 2% error is considered acceptable given the small-scale measurements.

2.5.15 Summary

Using the analysis template established by Baratta et al., the most significant errors in the mesoscale 3-pt. bend test are eccentric load, bearing friction, load readout, and specimen dimensions. The eccentric load and bearing friction errors are more detrimental, as they increase the strength estimate; whereas the load readout and specimen dimensional errors are random. Although the errors listed in Table 2-2 are large when referenced against the ASTM standard, it must be emphasized that testing free-standing ceramic parts at this scale is completely novel. The conclusions in this dissertation must be understood in the context that this is a first iteration in testing mesoscale parts. As a tool for evaluating the manufacturing process, the current iteration of bend testing has proved invaluable and highlighted many of the defects presented in Chapters 3 and 4. As an absolute measure of strength, the current 3-pt. bend test needs to be improved to satisfy the current ASTM flexure test standard, but in many regards already satisfies the conditions, which is remarkable given the size scale and measuring tools available. However, the variability in strength due to brittle fracture alone is larger than the combined error in the test method. For example, in the strength test of 18
samples the span of strength values was 56% of the mean strength compared to 10% for the largest testing error. The mesoscale bend test, in its current iteration, made significant contributions to LM-RIF development by identifying flaws that were simply unnoticed.

2.6 References


Chapter 3

Lost Mold Rapid Infiltration Forming: Fabrication

3.1 Introduction

Chemical inertness, high elastic modulus and a reliable failure stress are the important material parameters to consider in surgical instrument applications. Many ceramics are chemically inert and have a high elastic modulus. Zirconia, for example, is approved for use in the body as an implantable material in the load bearing artificial hip application. A reliable failure stress in a surgical instrument ensures safe operation during surgery. A reliable failure stress or high Weibull modulus in ceramics can only be achieved by removing strength-limiting processing defects. However, processing defects in microscale or mesoscale ceramic parts are typically left uncharacterized when a new fabrication technique is developed even though a micron-sized defect represents a relatively large flaw in a mesoscale part.

This study presents a manufacturing method to produce high-aspect ratio parts and provides three-point bend test data on free-standing mesoscale ceramic bend bars. Data based on mesoscale bend bars rather than macroscale analogues is critical for the design of surgical instruments based on compliant mechanisms rather than conventional rigid-link mechanisms. The discussion will be limited to the newly developed manufacturing method and the evaluation of three-point bend test bars, whereas details on our surgical instrument design can be found in another report.
Casting ceramics into molds to form micro-components has been explored by several authors for potential applications like gas sensors\textsuperscript{5}, superconducting coils,\textsuperscript{6} fuel cell electrodes,\textsuperscript{6} and microturbines\textsuperscript{7}. The lost-mold approach has been used by several groups to fabricate ceramic micro-components. Efforts by Gauckler et al. have successfully fabricated alumina and tin oxide structures on various substrates using a lost-mold approach based on chemical dissolution of the mold.\textsuperscript{6,8} Thermal pyrolysis of the mold caused cracking due to the thermal expansion of the photoresist, which prompted the adoption of chemical dissolution as a method to remove the mold.\textsuperscript{8} The cracking associated with mold thermolysis is addressed in this report. Also mentioned was the difficulty in creating sharp-edged molds on polycrystalline substrates due to reflectivity of the UV-light from the substrate.\textsuperscript{6} This problem is also addressed in the current work. After the lost mold process, Gauckler and colleagues transitioned to soft-lithography,\textsuperscript{9} a technique pioneered by the Whitesides group\textsuperscript{10} that is closer to printing or embossing than casting. A group at Sandia National Laboratories has also used a lost mold technique via chemical dissolution of a PMMA mold to make ceramic and metallic micro-components.\textsuperscript{11,12} The casting is done by capillary wetting of an epoxy based slurry that resists the chemical dissolution of the mold. The high concentration of epoxy (53\% by volume) provides strong green strength, but leaves carbon residue in the sintered body. As reported in Garino et al., some porosity remains in the ceramic parts, which results in an average MOR of only 260 MPa for alumina.\textsuperscript{12} This technique is not used in the current work since it was anticipated the combination of sub-100 nm particles in a high molecular weight epoxy will result in porosity and extensive grain growth in the final microstructure. Another lost-mold technique from the University of Birmingham
embosses a ceramic tape into a PMMA micro-mold, which is again dissolved chemically.\textsuperscript{5} This embossing technique is limited to aspect ratios less than 10. Higher embossing pressures would need to be used to increase this aspect ratio, and there exists the possibility that the molds will be destroyed since the poly[methylmethacrylate] (PMMA) molds are relatively weak. Another example of lost-mold processing by Liew et al. uses a lost mold approach via thermolysis.\textsuperscript{7,13} A polymer precursor to SiCN is cast into the photoresist mold and the polymer is cross-linked at about 400ºC. Afterward the mold is pyrolyzed and the polymer precursor is converted to SiCN.\textsuperscript{13} The primary detractor for this technique is similar to that of the Sandia technique in that a polymer suspension is used to create parts in which carbon byproducts form part of the final ceramic that promote porosity or grain growth in oxide-based ceramic bodies. The lost mold approach was favored since it does not require stripping the mold or handling the delicate green ceramic part, but issues pertaining to green strength and sintering without porosity remain for high aspect ratio mesoscale parts.

A lost-mold approach where the mold is made from patterned photoresist was chosen over the soft molding technique\textsuperscript{10} in order to prevent fracture by supporting the green parts while maintaining the as-molded geometry. Mold-forming via photolithography is one of the most cost effective and widely employed strategies in micro-manufacturing,\textsuperscript{14} but there has been difficulty in adapting ceramic powder processing to a lost-mold process where photoresist is used as the mold. This adaptation means adjusting photolithography to refractory substrates such as alpha-alumina that can withstand the high temperature required for ceramic particulate sintering. Another difficulty is removing the mold material without distorting or fracturing the un-sintered
ceramic. Mold removal can be accomplished by several methods including thermal decomposition, chemical dissolution, or reactive ion etching. Chemical dissolution has gained favor over thermal decomposition because the dimensional changes that occur over the thermal cycle can lead to cracking. In contrast, chemical dissolution requires chemically resistant binders in large concentrations which can potentially incorporate carbon or porosity into the sintered body. Additionally, many soluble photoresists cannot achieve the same high aspect ratio that the epoxy-based photoresists achieve without using an expensive X-ray source for the exposure. Reactive ion etching or dry etching is not common for thick photoresist layers due to the inefficiency of the highly cross-linked epoxy-based photoresists to decompose. However, progress has been made in this area and it is becoming more practical for layers under 100 µm. Thermal mold removal is used to produce the bend test bars described in this paper and the tendency for cracking is discussed.

We show that dense (greater than 99.5 percent theoretical density) mechanical property test specimens can be fabricated from nanoparticles of tetragonal zirconia polycrystals (TZP) by casting into a photoresist mold that is then thermally removed. The improvements that made this process viable occurred over several generations of processing iterations. Generation zero (Gen0) demonstrated that mold fabrication on alumina substrates, casting by rapid infiltration forming (RIF) and thermal mold removal were possible, although part yield and overall quality were low. The Gen0 specimens could be evaluated by three-point bend strength testing although, average strength of 670 MPa was considered relatively low. Generation one (Gen1) solved many engineering challenges that will be discussed in this report and produced mesoscale bend bars with
high part yield for which bend strength was measured on 18 specimens. Some of the challenges in the Gen1 materials included nanoparticulate de-aggregation, mold rounding from substrate reflectivity, part adhesion to the substrate, and cracking during mold thermolysis. However, geometric irregularities were noticed during the three-point bend testing of the Gen1 specimens. Therefore, second and third generations (Gen2 and Gen3) were produced to improve the geometry of the bend bars. In chapter 4, the geometric improvements from Gen1 to Gen2 and Gen3 will be quantified and evaluated by three-point bend testing to establish the link between powder processing and strength in the mesoscale TZP ceramics.

3.2 Materials and Methods

Figure 3-1 summarizes the overall fabrication process. A class 10 clean room was used for the mask and mold fabrication, whereas all other processing steps occurred in an open lab. The molds were composed of three layers; an anti-reflective coating on the substrate, an unpatterned photoresist layer, and a photoresist mold layer. An anti-reflective coating (Barli-II 90, Clariant Corp., Charlotte, NC) was applied to a polished alumina substrate (courtesy of John Rigby, Kyocera Industrial Ceramics Inc, Somerset, NJ) using the manufacturer’s recommendations. The unpatterned layer and mold layer were fabricated by spin coating SU-8-25 photoresist (Microchem Corp., Newton, MA) using the manufacturer’s recommended spin coating schedule and developer (SU-8 Developer, Microchem Corp., Newton, MA). The photoresist was exposed for 10 seconds at an intensity of 12 mW/cm².
The as-received, granulated 3 mole percent Y$_2$O$_3$ tetragonal zirconia powder (3Y-TZP, Tosoh Corp., Tokyo, Japan) was attrition milled at pH 9, the pH value of minimum yttria solubility$^{19}$ in the presence of 1.5% by mass ammonium polyacrylate (NH$_4$-PAA) (Darvan 821A, RT Vanderbuilt, Norwalk, CT) on a dry 3Y-TZP powder basis. The attrition mill (HDDM-01, Union Process, Akron, OH) was operated at 1000RPM for 60 min after a 30 min powder addition period using spherical 1 mm yttria stabilized zirconia media (High Purity Zirconium Dioxide, Union Process, Akron, OH). A 750 mL vessel filled with 1007 g of media was used to mill 200 mL of suspension at 43-45 volume % TZP powder with respect to the aqueous suspension. Primary particle size was calculated as the equivalent spherical diameter by BET surface area measurement (Gemini,
Micromeritics, Norcross, GA), while the agglomerate size was measured using dynamic light scattering (DLS) (Nano-S, Malvern Instruments, Southborough, MA). A field-emission scanning electron microscope (FE-SEM) (JSM 6700F, JEOL, Tokyo, Japan) and scanning electron microscope (SEM) (S-3000H, Hitachi, Tokyo, Japan) were used to confirm the particle size and agglomerate size measurements, respectively. All electron microscope samples were sputter coated with Au-Pd to prevent charging. ζ-potential was measured using electrophoretic light scattering (ZetaPALS, Brookhaven Instruments, Holtsville, NY). A conductivity meter and probe (Model 3200, YSI Inc., Yellow Springs, OH) calibrated against KCl solutions of known ionic strength were used to measure the ionic strength. The rheology of the suspension was measured using a parallel-plate rheometer (CSL 100, Carri-Med Ltd, United Kingdom) with a 2º cone geometry.

Methacrylamide and N,N’–methylenebisacrylamide (Sigma-Aldrich, St. Louis, MO) were used in a 6:1 mass ratio as the monomer and cross-linking agents to gelcast the suspension based on Janney et al.\textsuperscript{20} The total monomer content was 5% by mass on a dry 3Y-TZP powder basis. Ammonium peroxydisulfate (Sigma-Aldrich, St. Louis, MO) and N’,N’-tetramethylethylenediamine (Sigma-Aldrich, St. Louis, MO) were used in a 10:1 mass ratio to initiate and catalyze the polymerization reaction. The initiator and catalyst were 2.5% by mass of the total monomer content.

The suspension is cast into the molds using RIF in which a squeegee (60 Shore type E, Terra Universal, Fullerton, CA) is moved repeatedly over the mold at an angle of 45º at an approximate speed of 10 cm/s. The suspension infiltrates the mold cavities in a manner similar to that of screen printing except the mold, or screen by analogy, is fixed
to the substrate. Once cast, the molds were placed into a container with flowing nitrogen bubbled through water to prevent drying during polymerization of the gelcast agents. Nitrogen was used because oxygen can hinder the polymerization reaction on the part surface resulting in spallation.\textsuperscript{21,22} After an hour, the container was partially opened to decrease the humidity slowly and dry the parts.

Mold removal and sintering were accomplished with a single thermal treatment in air using the following cycle: 1°C/min to 400°C with a 2hr hold, and 10°C/min to 1300°C for 2hrs followed by a furnace cool. Hot stage scanning electron microscopy was performed on a Phillips FEI Quanta 200 Environmental SEM to evaluate the cracking tendency of the parts during mold thermolysis. Gelcast macroscopic specimens (0.5 x 0.5 x 2 cm) were sintered at 1200°C, 1250°C, and 1300°C for 2 hrs to determine the sintering temperature based on Archimedes density measurements and observation of the grain size. The macroscopic samples used for the density determination were screened for large, closed porosity prior to measurement that occurred in some macroscopic specimen during casting and were not included in the density measurement.

The flexural strength of the zirconia beams was tested using a three-point bend apparatus with a lower span of 227 μm. The more widely used four-point bend test was not practical due to the small sample size. Forces were applied to the beams using an electrostrictive actuator at a constant voltage rate and average displacement rate of 1.2 μm per second. The bars were placed across the testing span using a tungsten microprobe mounted in a 3-axis manipulation stage, pre-loaded to approximately 20 μN to ensure placement, and loaded until failure, which occurred when the bars were fully fractured at the centrally located point of loading. The time and applied force were recorded 10 times
per second. The mesoscale bend bars were molded with the standard ASTM dimensional ratio of 3:4:50 or nominally 25 µm x 33 µm x 417 µm. After testing, it was realized that the bars were not orthogonal, but had a trapezoidal cross-section similar to silicon beams reported in the literature. A nominal sintered thickness of 20 µm was used in the strength calculation for the specimens, but the short width and long width dimensions of the trapezoidal cross-section beams were determined from representative SEM photomicrographs, and averaged values were used to calculate bend strength (22 µm and 30 µm for the short width and long width, respectively). The short width side was always the top side as-molded. However, the bend bars were too small to optically determine if the shorter width side or longer width side of the specimen was tested in tension. Therefore, two different fracture stresses were calculated for each specimen. The strength data were evaluated using a 2-parameter Weibull distribution, which employed a maximum likelihood standard regression (calculated using Weibull++ by ReliaSoft Publishing, Tucson, Arizona).

3.3 Results and Discussion

3.3.1 Powder Preparation

In addition to forming dense, fine-grained microstructures, dispersion is critical to obtain a fine edge resolution in mesoscale parts. To achieve an edge resolution of 1 µm, the maximum agglomerate size (D) must be less than 1 µm to avoid resolution limiting
inter-agglomerate porosity. The resolution limiting number of particles per agglomerate (AAN) can be estimated for a spherical agglomerate and particle using equation [3.1],

\[
AAN = \frac{D^3}{d^3 \phi_p}
\]

where \(D\) is agglomerate diameter, \(d\) is primary particle diameter, and \(\phi_p\) is the packing efficiency of the particles within the agglomerate. The specific surface area is used to calculate the primary particle diameter \(d\) since it is assumed the nitrogen adsorbate in the BET measurement has access to the particle surface area within the agglomerates. The AAN calculation compares agglomerate volume to primary particle volume so the particle diameter \(d\) must be based on the volumetric distribution rather than the area distribution, which the BET method measures directly. The analysis by German\(^{26}\) that includes the conversion from the area distribution to the volume distribution by Allen\(^{27}\) gives,

\[
\log(d) = \log\left(\frac{6}{\rho A}\right) + \frac{4.6}{s_w^2}
\]

where \(\rho\) is the solid density (assumed theoretical density of 3Y-TZP, 6.05 g/cm\(^3\)), \(A\) is the surface area (BET measured 15.4 m\(^2\)/g), and \(s_w\) is the distribution width of the particle size. The distribution width \((s_w)\) is typically 4-5 for a commercial log-normally distributed powder,\(^{26}\) therefore, a value of \(s_w=4\) is used to estimate the maximum allowable number of particles per agglomerate. The volume-based particle diameter of the 3Y-TZP particles from equation [3.2] is 125 nm. The last assumption to calculate AAN is the packing fraction of particles within the agglomerate \((\phi_p)\), which may be as
low as 0.15 for a flocculated suspension,\textsuperscript{28} as high as 0.74 for close packed spheres, or more typically 0.6 for loose randomly-packed spheres.\textsuperscript{26} Therefore, the maximum number of particles per agglomerate (AAN) to satisfy the 1 $\mu$m resolution target is 314 particles assuming a packing fraction of 0.6. The AAN decreases to 79 for flocculated particles or increases to 388 for close packed spherical particles within the agglomerate. Consequently, the dispersion strategy must at least prevent agglomerates with more than 314 particles from forming.

Chemically-aided attrition milling is an efficient method to disperse and concentrate the suspension.\textsuperscript{29} The combination of impact, abrasion and shear from the collision, flow, and rotation of media in the attrition mill, and similar interactions among the particles results in agglomerate fracture and dispersion in much shorter times compared to ball milling or vibratory milling.\textsuperscript{30} Commercial 3Y-TZP powder has an initial granule size of 60 $\mu$m ($D_{50}$ by volume) or 36 $\mu$m by number distribution, as shown in Figure 3-2. The granules consist of particles with a diameter (d) of 125 nm by volume (46 nm by number using the conversion by Allen\textsuperscript{27} for the BET size). Observation of the granules and primary particles in Figure 3-2 confirms these size measurements. After attrition milling, the agglomerate size $D_{50}$ is 215 nm by volume or 114 nm by number. Using equation [3.1] with the agglomerate diameter (D) equal to 215 nm, a particle diameter (d) of 125 nm, and a packing fraction of 0.6, the AAN of the milled suspension is 3 particles per agglomerate. This is much lower than the 314 particles per agglomerate that would limit the resolution of the part due to inter-agglomerate porosity. Additionally, an average agglomeration number of less than 10 is generally considered a well dispersed suspension given the assumptions in equation [3.1] of spherical particles.
and atomically smooth surfaces. Both the fine edge resolution of the parts and the dense, fine microstructure described below confirm the well-dispersed state of suspension.

Figure 3-2: (a) The individual 3Y-TZP particles after attrition milling appear in white on Au-Pd coated cleaved-mica in this FE-SEM image. (b) The 3Y-TZP powder is granulated and is shown on top of carbon tape in this SEM image. (c) The particle size distributions before and after CAAM are plotted below the SEM images. The particle size of commercial 3Y-TZP powder is reduced from a $D_{50}$ of 60 μm (36 μm by number) to a $D_{50}$ of 215 nm by volume (114 nm by number) during chemically aided attrition milling.
3.3.2 Mold Forming on Ceramic Substrates

Using photolithography as a mold forming process requires modifications to the standard process used to create patterns on silicon wafers. As noted by Schonholzer et al., polycrystalline substrates, such as the alpha-alumina substrate used here, reflect UV light used to expose the photoresist. This reflection causes the bottom edge of the mold to become rounded. Light that exposes the masked regions on the alumina substrate by reflection is prevented by applying an anti-reflecting, UV-absorbing coating. In addition, the unpatterned, 25 µm SU-8 layer is applied to prevent the parts from sticking to the substrate during firing. Thicknesses of 5 µm and 10 µm were also evaluated, but did not prevent part adhesion. It is hypothesized that the sacrificial SU-8 layer prevents adhesion to the substrate by either eliminating intimate contact between the part and substrate during casting and/or by forming a thin barrier layer of carbon residue between the part and the substrate during firing.

3.3.3 Forming

The viability of the rapid infiltration forming (RIF) process lies in the pseudoplastic rheological behavior, shown in Figure 3-3, of the engineered 43 volume % 3Y-TZP suspension. The Bingham yield point of the suspension (τ_B) is 160 Pa, as shown in Figure 3-3, with the suspension relatively Newtonian above a shear rate of 200 s⁻¹. The squeegee speed for the RIF must to exceed 5 mm/s to enter the low viscosity Newtonian regime assuming simple shear over the typical 25 µm mold thickness. The
RIF process typically uses a speed of 10 cm/s, or 20 times the required shear rate to enter the Newtonian regime.

![Shear Stress and Viscosity](image)

**Figure 3-3:** The shear stress and viscosity as a function of shear rate shows shear thinning behavior for a 43 volume % solid suspension. The Bingham yield point\(^{33,34}\) is 160 Pa and the high shear viscosity (400-500 s\(^{-1}\) average) is 0.65 PAs. Each curve represents the line segments connecting 180 data points.

In addition to the well-dispersed state of the 3Y-TZP powder, the relatively low 0.65 Pa·s (650 cP) viscosity in the Newtonian regime is also a consequence of using low molecular weight monomers instead of conventional polymeric binders to form a green part. When the shearing action is stopped, the suspension behaves as an elastic solid permitting the filled mold to be handled.

Since gelcasting is used to form the green body, the wet green density is equal to the solid concentration of the suspension. To improve the dimensional tolerance of the fired part by minimizing shrinkage during sintering, the solid concentration of the suspension must be maximized without compromising the dispersion. Thus, it is critical to control the colloidal interactions among the ceramic particles. In Figure 3-4, the theoretical interaction energy as a function of interparticle separation distance is
calculated\(^{35}\) for two electrosterically stabilized 3Y-TZP particles with a D\(_{50}\) by number of 114 nm, a \(\zeta\)-potential mean of -49mV and a 0.1M ionic strength (1:1 electrolyte). The D\(_{50}\) by number is used in this calculation since it better describes the size of any given particle-particle interaction rather than the bias toward the higher volume particles in the volume distribution. A polymer layer thickness of 2 nm is used in the calculation based on previous studies with a similar molecular weight NH\(_4\)-PAA adsorbed onto a zirconia surface at pH 9.\(^{36,37}\) The Hamaker constant of 7.2x10\(^{-20}\) J is taken from Bergström with retardation effects included in the calculation.\(^{38}\) The particles can approach one another to a separation distance of 5.7 nm if 25kT is taken as the effective barrier energy. The steep energy barrier developed from 8 nm of separation to the 4 nm steric barrier is a result of the high surface charge and high ionic strength (0.1M based on a 1:1 electrolyte calibration), which screens the repulsive potential at long separation distances.

![Figure 3-4](image_url)

**Figure 3-4:** The van der Waals attraction, the electrostatic repulsion, and the total interaction energy of two spherical 3Y-TZP particles shows a steep repulsive energy that permits the particles to closely approach one another, but not agglomerate. The calculation is based on a particle diameter of 114 nm, a 2 nm layer of ionic polymer, a \(\zeta\)-potential of -49±2 mV, a Hamaker constant of 7.2x10\(^{-20}\) J and a 0.1M 1:1 electrolyte solution.

The interaction energy between two electrosterically stabilized particles provides a model for calculating the maximum solids loading in a suspension since the
electrosteric barrier prevents particles from approaching one another. Although the use of a hard sphere model is generally less accurate for polyelectrolyte dispersed ceramic suspensions at low ionic strength, the steep energy barrier at high ionic strength shown in Figure 3-4 can be thought of as an infinite potential barrier at an interparticle separation distance of 5.7 nm. Assuming the particles are spherical and pack in a loose random manner, the maximum volume fraction ($\phi_m$) of the suspension would be approximately 0.6. However, the electrosteric barrier prevents the particles from touching and decreases the effective volume fraction ($\phi_{\text{eff}}$) according to

$$\phi_{\text{eff}} = \phi_m \left(1 + \frac{\Delta}{r}\right)^{-3}$$

[3.2]

where $\Delta$ is layer thickness and $r$ is the particle radius (57 nm by number from DLS). This equation assumes an incompressible, spherical barrier layer and particle. The maximum volume fraction of zirconia decreases to 0.52 when $\Delta$ equals 2.85 nm or half the interparticle separation distance at an interaction energy of 25kT. However, the practical solid concentration limit in RIF is lower than 0.52, since drying increases the solid concentration by removing solvent. Thus, a 43-45 volume percent solid concentration is used for RIF to buffer against the loss of solvent during casting.

The maximum solids loading calculated using the interaction energy can be verified by examining the rheology as a function of solid concentration. Figure 3-5 shows the high shear viscosity and Bingham yield point as a function of solid concentration. Both the viscosity and yield point increase substantially at approximately 35 volume%. The increase in Bingham yield point at 35 volume% is the point at which
the suspension transitions from the Newtonian response to a pseudoplastic response. The pseudoplastic response is described by the modified Krieger-Dougherty relationship given in equation [3.3], where $\eta_r$ is the relative viscosity (normalized to the viscosity of the solvent), $\phi$ is the solid concentration, $\phi_m$ is the packing fraction where the viscosity is infinite, and $n$ is related to the intrinsic viscosity (Einstein viscosity).41

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-n} \quad [3.3]$$

The modified Krieger-Dougherty fit to the viscosity versus solid concentration is shown in Figure 3-5. Since $\phi_m$ is 0.68±0.04, the maximum packing fraction lies somewhere between random loose packed spheres (0.6) and close packed spheres (0.74). The maximum packing fraction by the Krieger-Dougherty fit is higher than that calculated from the interaction energy (0.68 vs. 0.52) because the Krieger-Dougherty fit is based on a suspension under a high shear stress and not an unperturbed suspension as in the interaction energy calculation. At a high shear stress, the electrosteric layer is disrupted and the hard sphere model used in the interaction energy calculation is not applicable. The exponent, $n$, in the Krieger-Dougherty fit is large compared to the Einstein viscosity constant (5/2) because the electroviscous effects are substantial in the highly charged engineered suspension, whereas Einstein only considered uncharged spherical particles in suspension.42 The electrosteric interaction between particles increases the viscosity more rapidly as the ionic layers around the particles interact.
3.3.4 Lost Mold via Thermolysis

Unlike conventional lost mold processing using a wax mold, the thermal removal of the SU-8 mold has the possibility of vastly reducing the yield by distorting and cracking high aspect ratio parts. Chemical dissolution is often preferred to thermolysis for this reason, but has other previously mentioned drawbacks. Cracks can form in the parts when the cross-linked SU-8 photoresist is rapidly heated like those shown in Figure 3-6 at a 10°C/min heating rate. The longitudinal cracks that appear at 248°C are created by parts sticking to the mold as the mold distorts. The in-plane shrinkage is both a result of a volume decrease as the photoresist further cross-links and the relief of the tensile residual stress in the photoresist. The stress relief occurs above the \( T_g \), which is roughly...
equal to the hard bake temperature of 180°C for the SU-8 photoresist. The residual stress is a function of the photoresist exposure dose, the pre-bake, and the post bake temperatures. Thus, successful thermal mold removal requires slow heating rates (1°C/min) at temperatures below 400°C. Additional TMA, TGA/MS data for the SU8 photoresist mold material can be found in Appendix A.

3.3.5 Sintered parts

An array of Gen1 mesoscale bend bars is shown in Figure 3-7(a) prior to sintering. There are 12 bend bars per square millimeter, which yields about 80,000 bend bars per 10 cm x 10 cm refractory substrate. This number increases to about 200,000 if closer packing in the array is used. The large number of parts per substrate is the major

Figure 3-6: Cracks due to mold thermolysis of the green bend bars in the SU-8 micromolds become visible in the hot stage SEM at 248°C and grow at higher temperatures when heated at a rate of 10°C/min. Slower heating rates are required to minimize this effect.
advantage of directed assembly over direct-writing. Figure 3-7(b) shows three bend bars after sintering while still on the alumina substrate. These Gen1 mesoscale bend bars were later observed to have a concave top surface, a trapezoidal cross-section and are warped. These issues were discovered during strength testing and the solutions will be addressed in Chapter 4 that addresses geometrical tolerances in mesoscale parts. The edge resolution of the mold is defined by the limits of UV-photolithography, but on a straight edge of the mold the corner sharpness approaches the grain size, or about 400 nm as shown in Figure 3-7c. The 1300ºC soak temperature was chosen based on the sintered Archimedes density for macro-scale analogue specimens. Sintered densities are 96.1%, 98.7% and 99.8% of the theoretical density as the soak temperature increases from 1200ºC, to 1250ºC and 1300ºC, respectively. The high density and minimal grain growth (300-600 nm grain size) for samples sintered at 1300ºC is apparent in Figure 3-7d. The dense, sub-micron microstructure and the fine edge resolution of the parts can be attributed to the effective suspension dispersion and rheological control of the engineered 3Y-TZP suspensions at high solids concentration.
3.3.6 Gen1 Material Strength Testing

Flexural testing is the preferred method to evaluate the strength of brittle materials and is similar to the type of loading the mesoscale surgical instrument will experience. During testing, it was observed that the cross-sectional area of the bend bars was trapezoidal and not rectangular as shown in Figure 3-8. A trapezoidal cross-sectional area has also been seen in bend test specimens of silicon, and was attributed to
anisotropic etching in the silicon after photoresist patterning.\textsuperscript{24} In the present case, the trapezoidal mold cross-section is a result of the photoresist exposure during photoresist patterning, and this shape is reproduced in the specimen also shown in Figure 3-8.

Figure 3-8: (a) The trapezoidal cross-section of a mold cavity is shown in the top layer. The unpatterned photoresist layer and alumina substrate can be seen under the mold layer. (b) The manifestation of the trapezoidal mold cross section is a mesoscale bend bar with a top width of 20 µm and a bottom width of 29 µm.

Figure 3-9 shows the probability of failure of the mesoscale beams, and the inset shows an optical image of the test apparatus. The characteristic strength ($\sigma_0$) of the beams is between 888 MPa (129 ksi) and 978 MPa (142 ksi) depending on the orientation of the specimen, which was unknown since the trapezoidal cross-section orientation could not be optically observed. The Weibull modulus (m) is 6.8 and is not dependent upon the cross-sectional geometry provided the test orientation is consistent between specimens. The Gen1 mesoscale zirconia bend bars have strengths comparable to conventionally sized specimens of TZP-zirconia,\textsuperscript{45} however given the geometrical
uncertainties (trapezoidal cross-section, concave top surface, etc.), it is likely the Weibull modulus will increase with subsequent testing of future generations with fewer geometrical irregularities. The results in Chapter 4 will compare the strength of the Gen1 bend bars, which have a concave top surface, trapezoidal cross-section, and were warped compared to Gen2 and Gen3 bend bars for which these defects are eliminated or significantly minimized.

Figure 3-9: A Weibull plot of the failure data for mesoscale beams. The stress at failure was calculated for both possible orientations of the trapezoid-shaped beam cross-sections. The inset is an optical picture of the test jig with a three-point bend specimen in place.
3.4 Summary

A new manufacturing process based on an amalgamation of thick film processing, semiconductor manufacture and ceramic powder processing produces large numbers of mesoscale ceramic parts with reasonably high strength. A lost mold process using thermal mold removal in combination with RIF and gelcasting produces dense, free-standing, high aspect ratio, ceramic mesoscale parts. Chemically-aided attrition milling efficiently disperses and concentrates the suspension allowing a fine edge resolution of 1 µm or less and a dense, fine-grained microstructure. The rheology of the suspension lends itself to RIF, a shear based casting method that reliably fills the mold cavities. The mold is removed without cracking the parts by adjusting the firing cycle to the thermal properties of the mold. A three-point bend test shows the parts have strengths similar to macroscopic 3Y-TZP bodies, but the dimensional irregularities in these Gen1 parts limit the strength and contributed to a low Weibull modulus.

3.5 References


Chapter 4

Lost Mold-Rapid Infiltration Forming: Geometry and Strength Improvements

4.1 Introduction

Microfabrication holds much promise in manufacturing for a variety of applications including microelectrical mechanical systems (MEMS), microbiology, miniature sensors and actuators, and mechatronics.\textsuperscript{1-4} In particular, free standing mesoscale components are being co-developed for the next generation of surgical instruments.\textsuperscript{5,6} Ceramics, particularly yttria tetragonal zirconia polycrystals (Y-TZP), have the high fracture strength and elastic modulus required for mesoscale surgical instruments.\textsuperscript{5} In Chapter 3, the basic lost mold-rapid infiltration forming (LM-RIF) process was introduced.\textsuperscript{7} The generation 1 (Gen1) mechanical test bend bars had relatively high aspect ratio (15:1), high resolution edges (less than 1µm) and were manufactured in large numbers on refractory substrates (up to 200,000 bend bars per 10 cm x 10 cm refractory substrate). The mesoscale (340 um x 30 um x 20 um) bend bars had reasonable bend strength with a mean strength between 829 and 913 MPa and a Weibull modulus of 6.8. The range in bend strengths reported for the Gen1 materials was created by uncertainty in the orientation of the trapezoidal cross-sections of the small bend bars. In addition to the trapezoidal cross-sections, dishing or concave upper surfaces
in cross-section and warping along the length of the bend bars are present in most of the Gen1 bend bars.

Lange\textsuperscript{8} showed that systematic processing changes to remove strength limiting flaws can lead to significant strength improvement. An average bend strength of 1340 MPa for Y-TZP was achieved with at least one specimen having a strength greater than 2210 MPa.\textsuperscript{9} In the current study, the mesoscale Y-TZP bend bars provide an excellent model for iterative process improvements to eliminate the strength limiting geometric flaws that specifically occur in mesoscale ceramics. In addition, the mechanical strength determined for the mesoscale bend bars is used in the finite element design for mesoscale applications such as surgical instruments.\textsuperscript{5} Although there are numerous forming processes for micro or mesoscale ceramics,\textsuperscript{4} the metrology of the parts produced is often left uncharacterized. The goals of this chapter are to address the processing variables that lead to the geometric defects, characterize the metrology of specimens produced with the LM-RIF process, and determine the strength distributions in the third generation (Gen3) materials in which the geometric defects have been eliminated or minimized.

LM-RIF processing is an integration between semi-conductor manufacturing based on UV-photolithography and ceramic powder processing first pioneered by Gauckler et al. who patterned ceramic colloids on substrates.\textsuperscript{10-13} Photolithography is used to produce the mold cavities and ceramic powder processing is used to fill the molds and produce a dense, submicron microstructure. Hundreds to hundreds of thousands of free standing parts are produced simultaneously on a 10 cm by 10 cm refractory substrate, which eliminates handling or manipulating the parts in the fragile green state.
The first dimensional defect that will be addressed is the trapezoidal cross-section of the first generation (Gen1) bend bars that was described in Chapter 3. Preliminary scanning electron microscopy (SEM) examination of the mold cavities revealed the photolithographic process was producing trapezoidal molds that were reproduced in the parts by the ceramic forming process. The trapezoidal side-wall profile of thick photoresists, such as SU-8, in MEMS processing based on silicon has been well documented.\textsuperscript{14-17} Non-vertical mold walls in SU-8 are caused by absorption of low wavelength light in the top portion of the photoresist creating a gradient in the photoinitiator concentration, cross-link density and chemical resistance to the developer. The solution employed by Reznikova et al. was used for the current process.\textsuperscript{15} This solution uses a 100 µm layer of SU-8 as a high pass filter for wavelengths below the absorption edge of the photoresist and the ideal 365 nm i-line. The high pass frequency is tunable by controlling the thickness of the photoresist.\textsuperscript{15} This solution has proven effective in standard photolithographic processes and works as well with the current LM-RIF process. The elimination of trapezoidal cross-sections led to generation two (Gen2) bend bar specimen with 90° sidewalls.

The dishing geometric defect was observed in the Gen2 parts during optical profilometry thickness measurements. Dishing produces a bend bar that is thinner in the center of the cross-section compared to the sides or ends. The dishing defect compromises mechanical strength as well as mechanical testing because the raised edges of the test specimen contact the testing apparatus and increase the stress intensity at these points. Preliminary analyses revealed that distortion of the polymer squeegee at the edges of the mold cavity during the RIF process causes dishing. Mannan et al. have analyzed a
similar geometric defect called scooping, in stencil printing of solder pastes that have been deposited through brass apertures or stencils. Although Mannan et al. show how scooping can be reduced, their processing solutions are not useful to the RIF process because the reduction is not great enough to limit dishing to even less than 10% of the mold thickness or less than 2.5 \( \mu \text{m} \). This is a consequence of the thin, (25 \( \mu \text{m} \)) molds being manufactured. Therefore, a different method to prevent dishing is reported in which an overcoat of ceramic suspension is deposited during RIF followed by a planarization and buffing process after drying and gelcasting.

The third geometric defect is warping along the length of the bar. Warping is a chronic problem in particulate forming processes and can manifest itself in the green state or after sintering. In the present case, two types of warping are observed, one after mold removal by reactive ion etching (RIE) and one after sintering. Curvature in the green state is often related to drying. However, warping after sintering was greater than warping in the green state and was accompanied by optically darker regions near the center of curvature. Preliminary analyses identified the warping in the Gen1 and Gen2 materials as localized transformation of tetragonal zirconia (t-\( \text{ZrO}_2 \)) to monoclinic zirconia (m-\( \text{ZrO}_2 \)) in the mesoscale bend bars. This is attributed to chemical interaction with the glass bonded 96 weight percent alumina substrate used for Gen1 and Gen2 materials. Attempts to minimize curvature in the green state are ongoing, but warping during sintering has been minimized by using higher purity alpha-alumina substrates in the Gen3 materials. This has improved the yield of straight bars from 60 percent to over 90 percent.
The metrology and processing iterations will be presented relative to the mechanical strength of each mesoscale material generation. The strength of the Gen1 material with trapezoidal cross-section, dishing and warping was reported in Chapter 3. The mechanical strengths of the Gen2 material with rectangular and not trapezoidal cross-sections but with dishing and warping present and the Gen3 material with rectangular cross-section, minimal dishing, and minimal warping are reported in this chapter.

4.2 Materials and Methods

The LM-RIF manufacturing process is described in detail in Chapter 3, but will be summarized here. A high-aspect ratio, epoxy based photoresist, SU-8, is spin coated in two layers on an alumina substrate with an antireflective coating (Barli-II 90, Clariant Corp., Charlotte, NC) to form the mold. The first layer is a 25 µm thick solid SU-8 underlayer (Microchem Corp., Newton, MA), while the second layer is a 25 µm thick patterned mold layer. Dispersion of 43-45 volume percent commercial Y-TZP (TZ-3Y, Tosoh Corp., Tokyo, Japan) is obtained by chemically aided attrition milling at pH 9 in the presence of 1.5% dry weight basis (DWB) of ammonium polyacrylate (NH₄-PAA) (Darvan 821A, RT Vanderbuilt, Norwalk, CT) to achieve a particle size D50 by dynamic light scattering of 215 nm by volume (114 nm by number). The molds are then filled by the RIF process, which uses a squeegee to shear and fluidize the pseudoplastic (Bingham yield point of 160 Pa, high shear viscosity of 0.65 Pa s), well dispersed, highly loaded (43 to 45 volume percent) ceramic suspension. Green strength is provided by
gelcasting a 5wt% (DWB) combination (6:1 mass ratio) of methacrylamide/methylene-bisacrylamide initiated (2.5% by mass of the total monomer content) with ammonium per oxydisulfate and N’N’,N’N’–tetramethylethylene diamine (Sigma-Aldrich, St. Louis, MO).\textsuperscript{23} The green parts are allowed to gel in a humid, nitrogen environment, and then slowly dried by exposure to lab air overnight. The mold is either removed thermally as described in Part 1 of the series,\textsuperscript{7} or via reactive ion etching (RIE) that will be demonstrated in the current work. The parts are sintered on the substrate, and washed off in an ethanol ultrasonic bath to be characterized by confocal optical microscopy, SEM, optical profilometry, and three point bend testing. Several improvements have been made to enhance the geometric tolerance of the parts in the current work. These improvements include adopting RIE to remove the mold, filtering the wavelength of the UV light used to expose the photoresist, modifying the RIF process to limit the effect of dishing, and employing only high purity $\alpha$-Al$_2$O$_3$ substrates.

Reactive ion etching is a common process in semiconductor manufacturing that is used to remove photoresist from the surfaces of silicon. Since oxygen is primarily used as the reactive species, the etch rate for the polymeric photoresist is much higher than that of oxide ceramics such as 3Y-TZP. The RIE (PT720, Plasma-Therm Inc., St. Petersburg, FL) settings were 350 W at 200 mTorr with 50 sccm of O$_2$ and 5 sccm of SF$_6$. These settings were modified from the work of Hong et al.,\textsuperscript{24} and found to work best on the PT720 system. An etch time of 50 min was used to remove 50 $\mu$m (underlayer and mold layer) of SU-8 for an etch rate of 1 $\mu$m per minute.
To make a high pass UV-filter, a 100 µm layer of SU-8 100 photoresist (Microchem Corp., Newton, MA) was spin coated onto a blank soda lime silicate glass mask using the manufacturers recommended spin cycle and exposure parameters. The transmittance of the filter was measured using a UV-Vis Spectrophotometer (Lambda 950, PerkinElmer, Waltham, MA). The spectral intensity of the MA6 mask aligner used to expose the photoresist was transcribed from the MA6 spectral data by Reznikova, Mohr and Hein and normalized to the 365 nm peak.\textsuperscript{15} The spectral intensity with the SU-8 100 filter and a blank glass mask was calculated by multiplying the spectral intensity of the MA6 by the percent transmittance through the filter and glass mask at each wavelength. To compensate for reduced intensity at 365 nm, the exposure time was increased from 10 s at 12 mW/cm\textsuperscript{2} to 120 s at 8 mW/cm\textsuperscript{2}.

The modification of the RIF process was slight, but significantly reduced the amount of dishing. Rather than removing the slurry deposited on top of the mold surface using a squeegee, a blanket layer of slurry is left on the entire mold surface and the monomer and crosslinker are allowed to gel. After gelling and drying the blanket layer of slurry is gently buffed away by hand using a class-10 cleanroom wipe (Polywipe C, Contec Inc., Spartanburg, SC) dampened with ethanol. Polishing cloths used in the diamond polishing of metallographic samples were also tried in an automated process, but the cloths left fibrous debris on the sample and pulled some of the bend bars out of the mold cavities.

Substrate purity was found to have an effect on warping. Two α-Al\textsubscript{2}O\textsubscript{3} substrates of different purity (Kyocera Industrial Ceramics Inc, Somerset, NJ), 96 weight % and 99 weight %, were tested. The substrate purity was verified by X-ray fluorescence (The
Mineral Lab, Lakewood, CO). The firing cycle was then changed from a soak temperature of 1300ºC for 2 hrs to 1400ºC for 1 hr because the parts became translucent signifying a microstructure with less residual porosity at a comparable grain size. However, the 96 weight % pure substrate caused the parts to warp. Confocal Raman spectroscopy (Alpha300, Witec Instruments Corp., Savoy, IL) was used to identify the amount of t-ZrO2 and m-ZrO2 at various locations on a bend bar. Spectral excitation was achieved using a 5 mW argon laser at 488 nm through a 100x objective with a spot size under 2 µm. The spectrum was collected on a 1024x127 pixel CCD camera using an 1800 line/mm grading. An integration time of 50 s was used over two hardware accumulations for the single spot spectra, while a 15 s integration time over two hardware accumulations was used for the line scan spectra. The monoclinic phase content was analyzed using the calibration curve provided by Kim, Hahn and Han25 since a calibration using X-ray diffraction could not be made due to the small sample size. Since the 180 cm\(^{-1}\) and 192 cm\(^{-1}\) monoclinic peaks could not be resolved on the spectra, a deconvolution was performed using the PeakFit\textsuperscript{®} program (PeakFit ver.4.12, SeaSolve Software Inc.). The peak intensities were found by fitting the background to a linear baseline with endpoints at 120 cm\(^{-1}\) and 205 cm\(^{-1}\) and deconvoluting the peaks with a Gaussian plus Lorentzian peak shape. Initial peaks were placed at 148, 180 and 192 cm\(^{-1}\) and refined using the software until the \(r^2\) value was at least above 0.990 or typically 0.997.

The parts were imaged using a scanning electron microscope (S-3000H, Hitachi, Tokyo, Japan). Physical dimensions were measured with an optical profilometer (Wyko NT1100, Veeco Instruments Inc., Plainview, NY). The optical profilometer was fitted with a 20X objective and a 0.5X FOV lens. At this magnification, the lateral sampling
interval is 0.82 µm. The dimensions of three-point bend test bars were measured while in the mold, after RIE, and after sintering. The in-mold thickness was calculated by subtracting the difference in height between the part and top surface of the mold from the mold thickness measured before casting. All of the other measurements were made directly.

Gen3 bend bars were tested in three-point bending with a lower span of 114 µm. Prior to testing, intact bars were selected from sintered specimen using a stainless steel microprobe and placed onto a glass slide. The dimensions of each bend test bar were measured using optical profilometry. Only the strength data for the bars lying face up as molded was included since the minimum and maximum height could be measured only for these bars. Each bar was then manipulated with tungsten microprobes onto the edge of a TEM grid, then onto the lower span of the test apparatus. Several modifications were made to the apparatus prior to testing the new generation of materials. Forces were applied to the bars using a piezoelectric actuator at a constant displacement rate of 1 µm per second and measured using a 50 g load cell. The testing span was mounted on a 3-axis manipulation stage, samples were preloaded to approximately 0.01 N to ensure placement during testing, and then loaded until failure, which occurred when the bars were fully fractured at the centrally located point of loading. The time and applied force were recorded at a rate of 100 samples per second. The force-displacement curves show linear elastic behavior followed by catastrophic, brittle failure. Because we were unable to collect the specimens after fracture, the calculation of strength was made using the average height measured by optical profilometry for each individual bar. The strength data were evaluated using a 2-parameter Weibull distribution, which employed a

### 4.3 Results and Discussion

An important modification to the photolithographic process enables vertical sidewalls in the SU-8 photoresist by filtering the sub-365 nm wavelength light during the exposure. Figure 4-1 shows a comparison between the mold walls for an unfiltered exposure (a) and a filtered exposure (b). The high aspect ratio capability of SU-8 is enabled by its high transmittance at 365 nm (i-line). The adsorption edge (50% transmittance) of a comparable 10μm thick, unexposed SU-8 layer is 350 nm.\(^{17}\) However, the emission of the mercury lamp below 350 nm can be as high as 15% of the peak value as shown in Figure 4-1(c).\(^{15}\) This shorter wavelength light is absorbed in the upper portion of the SU-8 layer resulting in a higher local concentration of photoacid and a higher crosslink density in the upper region. After development, the higher crosslink density in the upper region of the photoresist creates wider mold walls at the top of the mold. The net result of the absorption difference is the trapezoidal mold cross-section that is shown in Figure 4-1(a). A high pass filter made of SU-8 100 eliminates the sub-350 nm wavelength light shown in the inset of Figure 4-1(c) and uniformly crosslinks the photoresist creating the vertical sidewalls in Figure 4-1(b). Using the 100 μm SU-8 filter, a sidewall angle of 90.2°±0.2° (±95% confidence interval) was achieved in Gen2 molds versus 82.9°±0.9° for the unfiltered exposure in the Gen1 molds as shown in Table 4-1. By measurement of SEM images of Gen1 sintered test bars, the top width of the
trapezoidal cross-section was 20±0.3 µm and the bottom width was 28.7±0.6 µm.\textsuperscript{7}

Assuming a thickness of 20 µm, the sidewall angle is 78.2°, which is similar to the Gen1 mold wall angle of 82.9° verifying that the forming process reproduces the trapezoidal mold. A difference in the top and bottom width of Gen2 bend bars could not be distinguished in either the SEM or optical profilometer, which means any difference is less than 1 µm.

Figure 4-1: (a) The mold produced without filtering the exposure light has a trapezoidal cross-section. (b) Using an SU-8 100 filter to remove the sub-365nm light, the mold walls are vertical. (c) The emission of the MA6 aligner below 365 nm\textsuperscript{15} is substantial even through a soda lime silicate glass mask. This light is absorbed in the upper portion of the photoresist and creates a crosslink gradient, which after developing, results in the angled mold walls shown in (a). By filtering out the light below the absorption edge of the photoresist, the photoresist is uniformly cross-linked through the thickness and the vertical mold walls in (b) are achieved.
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Table 4-1: Improvements in the geometry of the bend bars were made in each successive material generation, resulting in strength improvement. In the first generation (Gen1), the largest defect was the trapezoidal cross-section, which was eliminated in the second generation (Gen2) bend bars by filtering the wavelength of the exposure light in photolithography. However, the Gen2 bars had both dishing (see Figure 4-2) and warping (see Figure 4-4). This led to Gen3 bend bars with an average strength of 2.2 GPa as warping and dishing were minimized by the use of a higher purity substrate and incorporation of the buffing planarization technique. Warping is defined as the maximum height difference along the length of the bar divided by the length (d/l). The radius of curvature is also given, which is calculated assuming the geometry shown in cartoon (a) below the warping data.

<table>
<thead>
<tr>
<th>Generation</th>
<th>Major Defects</th>
<th>Process Change</th>
<th>Trapezoidal Angle (θ)</th>
<th>±95% Conf.</th>
<th>Dishing</th>
<th>Warping</th>
<th>Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Max. Height Difference (ρ) (µm)</td>
<td>±95% Conf. (µm)</td>
<td>Deflection Over Length (d/l) (%)</td>
</tr>
<tr>
<td>Gen1</td>
<td>Trapezoidal x-section, Warping, Dishing</td>
<td>Filter UV exposure</td>
<td>mold: 82.9° part: 78.2°</td>
<td>0.9° 0.5°</td>
<td>Not measured</td>
<td>Not measured</td>
<td>821 (142) to 913 (157)</td>
</tr>
<tr>
<td>Gen2</td>
<td>Warping, Dishing</td>
<td>Substrate purity, Buffing</td>
<td>mold: 90.2° part: ~90°</td>
<td>0.2° NA</td>
<td>4 2</td>
<td>~8% R_{curv}=500 µm</td>
<td>-</td>
</tr>
<tr>
<td>Gen3</td>
<td>Warping, Grain Size</td>
<td>Heat Treatment</td>
<td>mold: 90.2° part: ~90°</td>
<td>0.2° NA</td>
<td>0.9 0.2</td>
<td>1.5% R_{curv}=2.758 µm</td>
<td>0.3%</td>
</tr>
</tbody>
</table>

The mold cavities for mesoscale bend bars have five sides, including the bottom, with the top side left open to fill the mold. An effect called dishing can occur on the top side of the bend bars, which results in a thickness gradient in the part as shown in Table 4-1. Distortion of the polymer squeegee as it passes over the mold cavity causes dishing.

Figure 4-2 shows a thickness variation of 3 µm over the 18 µm thickness of a representative Gen2 bend bar. The average amount of dishing in sintered Gen2 samples was 4±2 µm over a thickness of 15±3 µm. A stiffer squeegee would alleviate dishing, but the slight variations in mold height and the presence of an edge bead on the outer edge of the substrate cause the suspension to spread unevenly over the mold when using a
stiff squeegee. Squeegees of varying stiffness (60, 90, 100 Shore A) at different qualitative pressures were tried, but 4 μm was the minimum amount of dishing that was achieved while still maintaining uniform mold filling across the entire substrate. A mathematical model of squeegee deformation into the mold cavities from the literature, summarized in Appendix B.3, with the qualitative observations just summarized.

Dishing was minimized using a novel solution which casts a layer of suspension over the entire substrate and then buffs it away after the layer is allowed to gel and dry. The amount of dishing is decreased to an average of 0.9±0.2 μm or 5% of the thickness using this buffing process. Although the dishing is reduced, the buffing results in a higher surface roughness compared to the bend bar surfaces in contact with the mold walls and bottom. This is a result of the debris that is removed from the edges of the parts and deposited over the surface. The average root-mean squared roughness (Rₚ) on the buffed surface is 0.4±0.1 μm, whereas the Rₚ of a surface cast against the mold walls is 0.2±0.1 μm. A roughness of 0.4 μm is considered tolerable since it is not significantly larger than the grain size.
Warping is curvature along the length of the bend test bars. Two types of warping are observed: the first type is characterized by as-sintered out of plane curvature; the second type is characterized by as-molded out of plane curvature. The as-sintered out of plane curvature means the bars curve away from whichever side they are resting on as they are fired. Thus, both thickness/height curvature, and width/height curvature are possible since the bend bars can lay on either the as-molded bottom or the as-molded side. Figure 4-3(a) is an optical image in transmission of a Gen2 bend bar that was fired lying on its side with a radius of curvature of 502 µm or 8% deflection. Deflection is defined as the maximum difference in height divided by the length of the bend bar and is
diagrammed in Table 4-1. Figure 4-3(b) is an optical image in transmission of a straight Gen3 bend bar whose particular radius of curvature is 8.2 mm. Curvature at a radius of 8.2 mm over the bend bar length is negligible relative to the bend bar length of 332 µm, and results in a deflection of only 0.5%. Figure 4-3(c) is a backscattered electron image of the more opaque (darker) area in Figure 4-3(a). From Figure 4-3(a) and Figure 4-3(c), the area in contact with the 96% pure alumina substrate during firing is optically opaque and composed of larger grains. Energy dispersive spectroscopy (EDS) did not show any chemical differences between the curved and strain regions. Therefore, any difference in local chemistry was below the detection limit of EDS or a few atomic percent. While transmission electron microscopy combined with electron energy loss spectroscopy can potentially verify the elemental contamination, such a program of study is beyond the scope of the current work. Confocal Raman spectroscopy was used to compare the crystalline phase of the coarse grains (optically dark region) to the crystalline phase of the fine grains (optically light region). The spectra in Figure 4-3(d) show the coarse grains near the contact area with the substrate are primarily monoclinic, whereas the fine grains near the end of the bar are primarily tetragonal.26 SEM backscatter electron (BSE) diffraction verified the phase composition from the Raman spectra, but the Kikuchi lines were too diffuse for publication due to the unpolished nature of the sample. Figure 4-3(e) shows the intensity ratio (X_M) as a function of distance along a line extending from the coarse grain region to the fine grain region. The intensity ratio is the sum of the monoclinic 180 and 192 cm\(^{-1}\) peak intensities divided by the sum of the monoclinic peak intensities plus the 148 cm\(^{-1}\) tetragonal peak intensity.25 The fraction of monoclinic phase (f_M)\(^{25}\) is also given as a function of distance from the coarse grains (distance = 0 µm) into
the interior of the bend bar (distance = 20 µm). The \( f_M \) data appears scattered at high monoclinic concentrations since the calibration curve\(^{25}\) is non-linear and highly sensitive to \( X_M \) at high monoclinic concentrations and is an extrapolation above 30wt% monoclinic phase. The dip in intensity ratio for the 8.5 µm data point is likely due to the depression running along the middle of the bar in Figure 4-3c, which stems from a mold defect in this particular bend bar. Additionally, the number of grains sampled decreases over the line scan as the grain size increases since the spot size remains constant. This sensitizes the data to the structure of a single grain. Although the grain size changes over the course of the line scan, the spectra are not expected to change significantly due to grain size alone. Siu et al.\(^{27}\) and Fangxin et al.\(^{28}\) show grain size dependence in the Raman spectra of m-ZrO\(_2\) only below 80 nm, which is significantly below the minimum grain size in the bend bars (~200 nm). Therefore, the spectral changes are likely from phase content alone. The amount of monoclinic phase decreases rapidly at about 14 µm away from initial region of the line scan. A ten grain average of the grain diameter near the 14 µm mark reveals the decrease in monoclinic phase occurs at a grain size of 540±70 nm. A grain size of 540 nm roughly correlates to the grain size above which the tetragonal phase is no longer stable for 3mol% yttria in the zirconia alloy.\(^{29}\) Therefore, the curvature occurring during firing is likely due to localized compositional variations leading to grain coarsening and subsequent tetragonal phase destabilization producing a ~3-5 volume % expansion\(^{30}\) on the side of the bend bar in contact with the 96 weight % alumina substrate. This volume expansion on the side of the bend bar contacting the substrate causes the bars to warp with the concave side facing away from the substrate.
Figure 4-3: The source of warping in the Gen2 bend bars when fired on a 96 weight % pure alumina substrate is a result of localized destabilization of the tetragonal phase. (a) The transmitted light image of a Gen2 bend bar reveals that this bar was fired on its side and warped with the concave side facing away from the substrate. The radius of curvature is 502 µm. The more opaque or darker region in this transmitted light image corresponds to larger grain sizes shown in (d), and primarily monoclinic zirconia shown in (d) and (e). (b) This transmitted light image shows a straight Gen3 bend bar that was fired on a 99 weight % pure alumina substrate. There is no localized decrease in transmitted light in Gen3 bend bars verifying the uniform, fine grained microstructure. (c) The backscattered electron SEM images of the opaque region of the bar in part (a) reveal that the dark region is composed of coarse grains. The approximate location of the line scan in (e) is shown. The depression in the center of the bar is a mold defect in this
The cause of the localized grain growth is indicated by the composition of the 96% pure alumina substrate based on X-ray fluorescence analysis. The substrate contained 0.11% Na$_2$O, 1.24% MgO and 2.43% SiO$_2$ by mass. An Al$_2$O$_3$-SiO$_2$-Y$_2$O$_3$ eutectic occurs between 1300ºC and 1400ºC, and can cause liquid phase sintering of 3Y-TZP when Al$_2$O$_3$ and SiO$_2$ are present as impurities.$^{31}$ In the present case, localized liquid phase sintering due to contact with the impurities in the substrate likely causes grain growth at the primary point of contact between the 3Y-TZP bend bars and the alumina substrate. The decrease in translucency in the curvature region may be due to grain boundary scattering in the birefringent monoclinic phase,$^{32}$ and/or scattering due to microcracking$^{33}$ from the phase transformation. Warping during sintering was eliminated by switching to a higher purity 99 weight % $\alpha$-Al$_2$O$_3$ substrate (0.08% Na$_2$O, 0.27% MgO and 0.18% SiO$_2$), but maintaining the same 1400ºC firing temperature. Minimization of warping from a deflection of 8% to 1.5% by using the higher purity substrate is consistent with the hypothesis that the impurities in the 96 weight % substrate were responsible for this type of warping.

The second type of warping is characterized by out of plane curvature in the as-molded orientation only. This type of warping occurs in the green state and persists through sintering as shown in Figure 4-4; however, it only appears after RIE and not...
when the test bars are still in the mold. The line scan data in Figure 4-4 can be fit to a circle and the radius of curvature obtained. The radius of curvature of the green specimen is roughly twice that of the corresponding fired specimen. The most plausible explanation is that of residual drying stress. If this hypothesis is correct, then the mold constrains the dried green body and prevents warping until the mold is removed by RIE. Warping can occur by either a moisture gradient through the thickness of the green body20 or by capillary tension.34 The short transport distance in the 20.8 µm thick green bodies makes a through thickness moisture gradient less likely. As-molded warping is most likely due to the capillary tension that develops during drying as the body is constrained by the mold but released when the mold is removed by RIE. Residual warping away from the substrate has been noted by several authors in ceramic thick films dried on substrates.34-36 The small 0.6% differential strain needed to produce the 1.79 mm radius of curvature in the green bend bar in Figure 4-4 is similar to the small shrinkage strains associated with the collapse of the repulsive dispersion layer as the body moves from a saturated state to a dry state.34,37
Overall, the warping is reduced from a deflection of 8% for Gen2 specimen to 1.5% for Gen3 specimen. A deflection of 1.5% is tolerable in the mesoscale bend bars which have an aspect ratio of 19:1, meaning the bars have an average maximum height difference of 5 µm. Although the deflection is small in Gen3 bend bars, it will not be acceptable for higher aspect ratio parts for which the manufacturing process is ultimately intended. Efforts to further reduce the warping and accompanying drying cracks in the higher aspect ratio parts will be addressed in a later report.

Figure 4-4: The height profile along the length of a Gen3 bend bar shows modest warping after reactive ion etching removes the mold and after sintering. The upper chart shows warping on a magnified height axis, while the lower chart shows warping on a 1:1 height to length scale. The dotted lines represent the fitted curves used to calculate the radii of curvature. The radius of curvature after RIE is 1.7 mm, and the radius of curvature after firing was 3.6 mm for this particular bend bar.
Accurate dimensional measurements are required in most manufacturing processes to verify final part dimensions and to account for shrinkage in the design specifications for near net shape forming since machining fired ceramics is impractical especially at the mesoscale. Table 4-2 summarizes the dimensions and percent dimensional change of the Gen3 bend test bars from the mask design through firing. The mold dimensions are slightly smaller than the design dimensions, but are within 2 µm. The as-molded bend test bars are 2.5 µm thinner than the mold due to the buffing process. After reactive ion etching, the test bars appear to grow in length, and thickness, but shrink in width. The apparent growth in the thickness is due to a small amount of photoresist under the parts that is not totally removed in the RIE process. The growth in the length may be due to the RIE process itself or warping along the length. The sintering process results in the largest dimensional change. Isotropic sintering would result in a linear shrinkage of 24.5% assuming a green density of 43% of theoretical density (suspension solid concentration). If the post-RIE dimensions are used as the green size, isotropic shrinkage in sintering is verified. If the as-molded dimensions are used as the green size, the thickness shrinks less than the width or length during sintering. The likely explanation is that the body consolidated more in the thickness prior to sintering. This is expected to occur in one-sided drying during the constant rate period, which consolidates the thickness, but not the width or length.
The in-plane minimum radius of curvature is limited by the mold, which is formed by conventional UV-photolithography. Therefore, the radius of curvature is on the order of a few microns depending on the exposure parameters. However, the edge sharpness that corresponds to the interface between the suspension, mold and atmosphere on the top side of the part may be below 1 µm as was shown in Chapter 3. In order to better determine the lateral resolution of the process, triangular shapes with a 30º pointed tip were made on the mask. By measuring the tip radius, the lateral resolution limitations imposed by the LM-RIF process can be assessed. Figure 4-5 shows an image of a triangular mold tip (a) and triangular part tip (b). The tip radius of the mold is 3.3 µm whereas the radius of the part is 3.0 µm. This is the effective lateral resolution of the LM-RIF process for 24 µm thick photoresist and is consistent with the scattering limitations imposed by UV-photolithography. Finer resolution (sub-50 nm) may be achieved by using a higher resolution exposure technique such as electron beam exposure, but this more expensive technique is not required for the current work. Through the use of optical profilometry, the 3D quantification of many mesoscale parts is possible, for example, the

<table>
<thead>
<tr>
<th>Process Step</th>
<th>Width (µm)</th>
<th>±95% Conf.</th>
<th>Thickness (µm)</th>
<th>±95% Conf.</th>
<th>Length (µm)</th>
<th>±95% Conf.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design</td>
<td>33.3</td>
<td>NA</td>
<td>25.0</td>
<td>NA</td>
<td>416.7</td>
<td>NA</td>
</tr>
<tr>
<td>Mold</td>
<td>32.4 (12)</td>
<td>0.5</td>
<td>23.3 (12)</td>
<td>0.5</td>
<td>414.7 (12)</td>
<td>0.7</td>
</tr>
<tr>
<td>Green Part in Mold</td>
<td>34.8 (17)</td>
<td>0.2</td>
<td>20.8 (17)</td>
<td>0.6</td>
<td>415.6 (17)</td>
<td>0.5</td>
</tr>
<tr>
<td>Post-RIE</td>
<td>33 (17)</td>
<td>1</td>
<td>23.0 (17)</td>
<td>0.7</td>
<td>423 (17)</td>
<td>2</td>
</tr>
<tr>
<td>Sintered</td>
<td>25.8 (65)</td>
<td>0.5</td>
<td>17.4 (37)</td>
<td>0.3</td>
<td>332.1 (65)</td>
<td>0.6</td>
</tr>
</tbody>
</table>

% Change

| In mold to sintered | -26%  | 2%  | -16%  | 3%  | -20.1% | 0.2% |
| Post-RIE to sintered| -23%  | 4%  | -24%  | 3%  | -21.5% | 0.5% |
| Design to sintered  | -23.0 | 0.7%| -30.5%| 0.7%| -20.29%| 0.05%|

Table 4-2: Dimensional measurements of three-point bend test bars. The percent change between the design, as-molded, and post-RIE dimensions versus the sintered dimensions. The number of samples measured is given inside the parentheses.
bend bars shown in Figure 5(c). This has enabled geometric deviations to be identified and eliminated through process improvements. Additionally, accurate strength measurements can be made at the mesoscale since the test bar geometry can be accurately measured.

Figure 4-5: (a) The radius of curvature of a 24 µm thick triangular mold cavity is 3.3 µm and limited by the UV-photolithography. (b) The 3.0 µm tip radius of a part produced in the triangular mold cavity is nearly identical to the mold cavity radius. Therefore, the resolution of the LM-RIF process is limited by the mold forming process and not the ceramic powder processing. (c) A 3D optical profilometer image representing the height of Gen3 parts. Once the data set is collected, many different measurements can be made yielding reliable mesoscale dimensional data. The scale on the right is slightly misleading since there is a high point at the very top of the scan. For reference, the maximum height difference in the bar marked (1) is 8.5 µm, whereas the maximum height difference of the lower bar marked (2) is 2.4 µm.

With each successive generation, the elimination of geometric irregularities resulted in a strength improvement as given in Table 4-1 and graphically as the inset of Figure 4-6. The average strength increases from 829 – 913 MPa in Gen1 (range is due to
trapezoidal cross-section) to 2.24 GPa in Gen3. The Weibull modulus (m) is roughly equal for both the Gen1 (m = 6.8) and Gen3 (m = 6.3) specimen, but the characteristic strength (σ₀) increases from 888 – 978 MPa to 2.39 GPa as shown in Figure 4-6. A Weibull plot is not available for Gen2 material since only five specimen were tested. The Gen2 specimen were the first to be measured for dishing with the optical profilometer and the 4 µm average difference in height resulted in a large uncertainty in the stress calculation. An average bend strength of 2.24 GPa for the Gen3 bars is relatively high, but consistent with the expectations based on the specimen size-scale. If Lange’s average strength of 1340 MPa (σ₄-pt, Lange) for 2.3Y-TZP⁹ is used for comparison and the loading factors (four-point vs. three-point) and specimen surface areas (S) (1.5 cm² vs. 2900 µm²) are taken into account, a mesoscale bend bar with the size of a Gen3 specimen and Weibull modulus (m) of 6.3 should have a strength (σ₃-pt, meso) of 8.0 GPa according to equation [4.1].⁴¹

\[
σ_{3\text{-pt, meso}} = σ_{4\text{-pt, Lange}} \left( \frac{m + 2}{2} \right)^\frac{1}{m} \left( \frac{S_{\text{Lange}}}{S_{\text{meso}}} \right)^\frac{1}{m}
\]

[4.1]

Equation [4.1] assumes surface flaws are strength limiting. It is not likely mesoscale bend bars will reach strengths as high as 8.0 GPa due to limits imposed by surface roughness as discussed in Chapter 5. In addition, the grain size in Gen3 bend bars is approximately 300 – 600 nm, which is likely too fine for transformation toughening in the 3 mole percent Y₂O₃-TZP,⁴²,⁴³ making the specimen less resistant to defects. Strength as high as 3-4 GPa is thought possible with further surface and microstructure refinements. Chapter 5 will determine the effect of grain size on strength.
4.4 Summary

Several modifications to the original LM-RIF process have eliminated the trapezoidal cross-sections characteristic of Gen1 parts, reduced the amount of dishing in
Gen2 parts and eliminated warping that occurred during firing. The current Gen3 parts are orthogonal with uniform rectangular cross-sections and have dimensional tolerances from 1-3 µm and a tip resolution of 3 µm, which is characteristic of the UV-photolithographic process that forms the mold cavities. Reactive ion etching has replaced thermolysis as the method of mold removal, and a buffing process has been added to eliminate dishing. The warping during sintering was due to grain growth likely from liquid phase sintering enabled by contact with the impurities in a 96 weight % pure alumina substrate. The localized grain growth destabilized the tetragonal phase causing a localized volume increase that subsequently warped the bend bar. The use of a 99 weight % pure substrate eliminated this type of warping. The second type of warping occurs in the green state and is hypothesized to be drying related, but the amount of warping is small enough to neglect in the Gen3 bend bars. These process improvements have increased the average bend strength from 829 MPa to 2,236 MPa.

4.5 References


Chapter 5
Grain Growth and Defect Size in Microfabricated 3Y-TZP

5.1 Introduction

Ceramic microfabrication using a powder-based approach represents a recent marriage between ceramic powder processing and a semiconductor photolithographic manufacturing technique that is used to form free-standing mesoscale parts with dimensions ranging from 1 \( \mu \text{m} \) to 1 cm.\(^1\)\(^2\) Innovation in this area aims to capitalize on the high-strength, refractory properties, and corrosion resistance of ceramics in small-scale parts traditionally made from silicon, steel, or thin film metals.\(^3\)\(^-\)\(^5\) Recently, prototypes of 3Y-TZP micro-forceps were fabricated that capitalize on the high strength, and high elastic modulus of tetragonally stabilized zirconia polycrystals (TZP).\(^6\) Before these structural ceramic materials can be implemented in sensitive applications such as surgical instruments, their critical flaws and strengths must be assessed. As shown in Chapter 4, the strength of bulk ceramics cannot be simply scaled using Weibull statistics from the fracture of macroscale materials since the flaw populations are different.\(^2\) In mesoscale ceramics, the flaw size becomes a large fraction of the specimen dimensions and these flaws must be eliminated in order to increase the specimen strength.\(^2\) However, flaws will always limit strength in brittle materials; that is, in brittle materials, flaws will be created either through processing defects such as inclusions and porosity, or by the surface finishing technique through scratches.\(^7\) Considering this limitation, can the...
In the case of a TZP material, grain size can be optimized to improve the damage tolerance of the material through transformation toughening,\(^8\) which has been shown to increase strength up to the point of spontaneous transformation.\(^9,10\) However, strength can also decrease with increasing grain size through the Petch relationship.\(^11,12\) To examine this question in more detail, this study uses isothermal heat treatments to ascertain how the grain size and initial flaw size affect the strength of mesoscale Y-TZP parts. First, the effects of flaw size and grain size on the strength of macroscale brittle materials will be reviewed, as the critical flaws and grain size-strength relationships have not previously been explored in regard to free-standing mesoscale parts. This study serves to explore a hitherto unexamined area, that of brittle fracture in a size scale regime in which flaw size, grain size, and transformation zone size are all nearly equivalent.

5.2 Background

The Griffith-Irwin equation\(^13\) \([5.1]\) describes the failure stress \(\sigma_f\) as a function of the flaw size \(c\) where \(K_{lc}\) is the fracture toughness, and \(Y\) is a constant depending on the crack geometry.\(^14\) \(Y\) is equal to \(\pi^{1/2}\) for a perpendicular through-thickness crack or \(1.12 \pi^{1/2}\) for a perpendicular surface crack in a semi-infinite body.\(^14\)

\[
\sigma_f = \frac{K_{lc}}{Y \sqrt{c}} \quad [5.1]
\]

While equation \([5.1]\) relates the strength of a brittle material to the stress intensity from extrinsic flaws it does not include provisions for microstructural features such grain size.
However, it is well documented that the grain size affects the strength of polycrystalline materials.\textsuperscript{15,16} Whereas equation [5.1] describes the strength as a function of stress intensity due to a flaw, the grain size affects crack initiation and propagation through crack growth resistance or toughness ($K_{IC}$). It has been shown that for many ceramics two regions exist in the grain size versus strength plot: a region where the extrinsic flaw size dominates, and a region where the intrinsic grain size dominates.\textsuperscript{15} In this sense, the term “extrinsic flaws” refers to processing induced flaws and stress concentration, while the term “intrinsic grain size” refers to the grain size/boundary contribution to the crack generated at the stress concentrator. There may also be a third region at grain sizes near the single crystal size that originates from the difference between a polycrystalline $K_{IC}$ value and directionally dependent $K_{IC}$ from single crystal cleavage.\textsuperscript{16} The relative magnitude of the extrinsic flaw size compared to the intrinsic grain size determines whether strength is dominated more by the stress concentration at the flaw or by the crack growth resistance of the microstructure. The Orowan-Petch analysis has been successfully used to explain the effect of grain size on the strength of machined ceramics\textsuperscript{15,17,18} for which the flaws are well characterized.\textsuperscript{19-23} Additionally, the Orowan-Petch approach has been used to determine the effect of grain size on strength for well-defined induced porosity.\textsuperscript{24}

In general, as the grain size is reduced, the strength of polycrystalline samples increases. In ductile materials, this behavior is described by the Hall-Petch relationship, which states that strength is inversely proportional to the square root of the grain size as dislocations pile up at the grain boundaries.\textsuperscript{25} In ceramics, a similar grain size-strength relationship is observed, but, in contrast to ductile materials, this relationship is caused by
the correlation of the flaw size (c) and grain size (G) with $\sigma_f \propto G^{-1/2}$ as shown in equation [5.1].

The $\sigma_f \propto G^{-1/2}$ correlation is stronger when the flaw size is less than the grain size. Therefore, eliminating large processing flaws is required before grain size-dependent strength becomes dominant. This effect has been demonstrated in conventionally processed alumina. Zimmerman and Rödel frame the transition in terms of the flaw size to grain size (c/G) ratio. In this construction, the strength is flaw-dominated for c/G>1 or the “Petch” regime and grain size-dominated for c/G<1 or the “Orowan” regime. This does not imply that strength is independent of grain size in the extrinsic flaw-dominated regime, but the variation of strength with grain size is certainly less than that in the intrinsic grain size-dominated regime.

In TZP materials the grain size can be manipulated to increase the toughness ($K_{ic}$) to provide damage tolerance. In general, $\sigma_f$ increases with $K_{ic}$ according to equation [5.1] although the strength of the correlation depends on the characteristics of the material such as porosity, density or grain size. Munro and Freiman frame this correlation as the partial derivative, $\left( \frac{\delta \sigma_f}{\delta K_{ic}} \right)_x$, where x is the material characteristic held constant. The various material characteristics make it difficult to predict the strength or fracture toughness across different studies. Moreover, the studies themselves use different processing routes, starting materials, heat treatments, etc., for which the material variables are not constant. Fortunately, the affect of grain size on transformation toughening in TZP systems is a well-documented phenomenon, but the affect on strength is less clear. Swain and Rose show that strength increases with toughness according to equation [5.1]; this is because the rising crack growth resistance (R-curve)
behavior makes the material tolerant of flaws until the flaws reach a critical size, at which point the strength becomes flaw-size limited and decreases with further increases in toughness. The toughness of Y-TZP increases with grain size as the surface energy barrier to phase transformation (inversely proportional to grain size) is lowered until spontaneous transformation occurs. In the Y-TZP system, the strength and/or toughness of 3Y-TZP increases with increasing grain size up to approximately 1 µm. Above 1 µm, spontaneous transformation occurs, resulting in microcracking and lower strength. In contrast to these studies, Readey et al. show that Y-TZP does not show extensive R-curve effects over grain sizes from 0.4 µm to 0.8 µm; thus, $K_{IC}$ is constant. Readey et al. and Danzer et al. also show that in a toughened material, the Weibull modulus should increase and display an “S” curve shape in a Weibull plot since small cracks can extend subcritically, while large cracks will fail catastrophically according to equation [5.1]. The Y-TZP in Readey et al., however, did not show a pronounced “S” curve shape in a Weibull plot. The difference between these studies may be attributed to porosity and initial flaw size. In summary, increasing the grain size in 3Y-TZP has the potential to increase strength: however, the extrinsic flaw size can obscure this effect if the stress intensity is sufficiently high to extend the crack critically.

The current study examines the strength of mesoscale bend specimen for which the grain size is varied by isothermal heat treatment at 1400°C. The extrinsic flaw size will be evaluated first. The toughness will be then be assessed through post fracture Raman spectroscopy 3Y-TZP. Direct $K_{IC}$ measurements could not be made due to the small sample size, which cannot tolerate cracks generated by indentation without fracturing. To our knowledge, this is the first effort at determining whether fracture
toughness plays a large role in the strength of mesoscale ceramic components, which have dimensions on the order of the transformation zone size characteristic of TZP materials.

5.3 Materials and Methods

The lost-mold rapid infiltration forming (LM-RIF) process was used to fabricate bend bars of approximately 314 µm × 22 µm × 18 µm. The basic LM-RIF process will be summarized here, but details can be found in previous publications. Molds are created in a class-10 cleanroom by spincoating an antireflective coating, Barli-II 90 (Barli-II 90, Clariant Corp., Charlotte, NC), onto an alumina substrate (Kyocera Industrial Ceramics Inc, Somerset, NJ). Two 25-µm-thick layers of SU8-25 photoresist (Microchem Corp., Newton, MA) are then spincoated onto the substrate. The first layer is exposed without a mask for one minute at 8 mW/cm²; the second layer is exposed through a filter created from a 100-µm-thick layer of SU8-100 (Microchem Corp., Newton, MA) on a glass mask plate for 120 s at 8 mW/cm². All other spincoating parameters are based on the SU8 manufacturer’s recommendations.

The casting suspension was 42% by volume 3Y-TZP powder (TZ-3Y, Tosoh Corp., Tokyo, Japan) that was attrition-milled with 1.4% dry weight basis ammonium polyacrylate dispersant (Darvan 821A, RT Vanderbuilt, Norwalk, CT) at pH 9 for 1 hr. Yttria loss from particle surfaces through leaching is minimized at pH 9. The impurity content of the 3Y-TZP powder is given in Table 5-1, and is similar to that supplied by the manufacturer. The D₀ according to dynamic light scattering (Nano-S, Malvern
Instruments, Southborough, MA) was 225 nm by volume or 141 nm based on a number distribution. A 6:1 ratio of methacrylamide to methylenebisacrylamide was used to gel-cast the suspension with a total monomer content of 4.2% on a dry weight basis. Gelation was initiated and catalyzed with ammonium peroxydisulfate (Sigma-Aldrich, St. Louis, MO) and N’N’,N’N’–tetramethylethylenediamine (Sigma-Aldrich, St. Louis, MO) in a 10:1 ratio added in a 30wt% aqueous solution. The amount of dry initiator to catalyst was 4% by mass of the monomer content. The initiated suspension was cast into the mold cavities using a 60 Shore squeegee (60 Shore type E, Terra Universal, Fullerton, CA). The mold was removed by reactive ion etching (PT720, Plasma-Therm, Inc., St. Petersburg, FL) for 50 minutes using the following settings: 200W, 100 mTorr, 80 sccm oxygen, 8 sccm carbon tetrafluoride.

The parts were sintered isothermally at 1400ºC for 1 hr, 8 hrs, and 16 hrs. A bisque firing to 1200ºC was used prior to these isothermal heat treatments to give the parts strength before separating them for the various heat treatments. The heat-treated specimen came from the same mold casting. The sintering schedule was 1ºC/min to 600ºC, 10ºC/min to 1200ºC with a 1hr soak and a 10ºC/min cooling rate. The isothermal

<table>
<thead>
<tr>
<th>Impurity</th>
<th>Per Manuf.</th>
<th>XRF*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt%</td>
<td>mol%</td>
</tr>
<tr>
<td>Y₂O₃</td>
<td>5.21</td>
<td>2.91</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>&lt;0.005</td>
<td>&lt;0.006</td>
</tr>
<tr>
<td>SiO₂</td>
<td>0.005</td>
<td>0.01</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>&lt;0.002</td>
<td>&lt;0.002</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.022</td>
<td>0.04</td>
</tr>
</tbody>
</table>

* The Mineral Lab, Inc., Golden, CO

The parts were sintered isothermally at 1400ºC for 1 hr, 8 hrs, and 16 hrs. A bisque firing to 1200ºC was used prior to these isothermal heat treatments to give the parts strength before separating them for the various heat treatments. The heat-treated specimen came from the same mold casting. The sintering schedule was 1ºC/min to 600ºC, 10ºC/min to 1200ºC with a 1hr soak and a 10ºC/min cooling rate. The isothermal
heat treatments at 1400°C used a 10°C/min heating and cooling ramp. The cross-sections for grain size measurement were prepared by focused ion beam (FIB) machining. The FIB (Quanta 200, FEI Company, Hillsboro, Oregon) procedure begins with depositing a 2 µm thick Pt-layer over the width of the bend bar. The bar is then machined using a 30 kV Ga⁺ beam at 20 nA followed by polishing at 3 nA, 1 nA, and 0.3 nA. The polished surface was viewed with a 10 pA ion beam at an angle of 52°. The grain size was measured using the line intercept method on a grid pattern. The intercept distances were corrected for foreshortening in the y-direction due to the viewing angle. There was no statistical difference (95% confidence interval) between the x and y intercepts. The linear intercept data was fit to a log-normal distribution in order to calculate the average grain size and distribution width. The data was automatically binned using OriginPro8 computer software (OriginLab Corp., Northhampton, MA).

The mesoscale bend bars were tested in three-point bending using a custom apparatus in which the top loading point is fixed and the bottom loading points are raised using an electrostrictive actuator. The dimensions of each specimen were measured prior to testing using optical profilometry (Wyko NT1100, Veeco Instruments, Inc., Plainview, NY) with a 20X objective and a 0.5X field of view lens. Each bend bar was visually inspected for pores and other imperfections and the defect-free specimens were manipulated to the test span by a glass pipette pulled from a glass rod with a 1 mm diameter. The micromanipulation procedure selectively removes the largest flaws, which are either pores that span nearly the entire cross-section of the bend bar or large cracks that are also on the order of the part width and easily visible on an optical microscope. The lower span was 104 µm, measured using a binocular microscope. Forces were
applied at a constant voltage rate representing an average displacement rate of 1.2 µm per second. The force was recorded 10 times per second, and the baseline drift was corrected for each test run. The maximum force was used to calculate the failure stress for three-point bending using the individual bar dimensions. The maximum thickness in the center of the bar was used as the thickness for the stress calculation; however measuring in this way tends to underestimate the failure stress, as the thickness may vary by up to a micron across the width. Typical load-displacement curves as shown in Figure 5-1 were linear elastic until the point of failure, thus indicating brittle fracture. The probability of failure (F) for Weibull analysis is given by equation [5.2], where \( i \) is the rank and \( n \) is the total number of samples.

\[
F = \frac{i - 0.5}{n} \quad [5.2]
\]
Vickers hardness was also measured for the various isothermal sintering times of the mesoscale samples. Twelve indents per heat treatment were made using 0.25 N of force and held for 15 s on a Leco MHT 200 indenter (Leco Corp., St. Joseph, MI). Indentation was also tried at 0.10 N and 0.49 N, but the 0.10 N indents were too small to accurately measure, and the 0.49 N indents completely fractured the mesoscale bend bars. All indents were made on the bottom surface of the bend bars as molded (~350 nm Rq), which is smoother than the top surface.

Figure 5-1: The voltage of the piezoelectric actuator is recorded as a function of time in order to determine the peak voltage that corresponds to the load at fracture. The linear nature of the data shows elastic behavior with brittle failure. Three samples that failed under different loads are shown for the 1400°C-1hr heat treatment. Although the displacement can be calculated from the time using the crosshead rate, it is not an accurate measurement of the sample displacement; this is because the crosshead rate is only valid for an unloaded condition (it is provided as a reference only).
Confocal Raman spectroscopy (Alpha300, Witec Instruments Corp., Savoy, IL) was used to determine the phase adjacent to the fracture surface of the bend bars. A 5 mW, 488 nm wavelength laser illuminated through a 5.5 mm diameter aperture and a 100X, 0.9NA objective lens provided a lateral resolution of approximately 1 µm. The confocal pinhole was 100 µm in diameter. The spectra were recorded on a 1024 × 127 pixel CCD camera at 1800 lines/mm resulting in a 1.5 cm\(^{-1}\) spectral resolution. The spectra were gathered in a line-scan mode using an integration time of 5s over two hardware accumulations for each spectrum. Additionally, a spectral image was taken over a 30 × 20 µm spatial area with a spectrum taken every 0.4 µm horizontally and every 0.625 µm vertically for a total of 1200 spectra. The spectra used to make up the spectral image were gathered using an integration time of 2 s over one hardware accumulation.

The m-ZrO\(_2\) to t-ZrO\(_2\) ratio was determined by calibrating the Raman peaks against the peaks in X-Ray diffractometry (XRD) (Pad V, Scintag, Inc., Cupertino, CA) following the method of Clarke and Adar.\(^42\) The working calibration standards were mixtures of 0Y-TZP and 3Y-TZP powders (Tosoh Corp., Tokyo, Japan) that were ball milled for 16 hrs in ethanol. A lower magnification 40X, 0.6 NA aperture in the confocal Raman microscope was used for the calibration to better ensure against local variation in the powder mixture. The monoclinic fraction by XRD (\(v_m^{XRD}\)) was calculated from the monoclinic peak fraction (\(X_m^{XRD}\)) according to\(^43\)

\[
v_m^{XRD} = \frac{1.311X_m^{XRD}}{1 + 0.311X_m^{XRD}}
\]  

[5.3]

where the monoclinic fraction is a function of the peak intensities (\(I_{(hkl)}^{\text{phase}}\)).\(^43\)
The monoclinic fraction was then calculated from $v_{m}^{XRD}$ using the peak area ratio from the Raman spectra ($X_{m}^{Raman}$). The peak area was used rather than the peak intensity because the monoclinic doublet at 181 cm$^{-1}$ and 192 cm$^{-1}$ appeared as a single peak at 185 cm$^{-1}$. The peak area ratio is given by

$$X_{m}^{Raman} = \frac{A_{m}^{170\rightarrow205}}{A_{m}^{170\rightarrow205} + A_{t}^{135\rightarrow164} + A_{t}^{243\rightarrow283}}$$  [5.5]

where the superscript numbers represent the integration limits given in cm$^{-1}$, and the subscript represents the phase characteristic of the peak. A linear fit between $v_{m}^{XRD}$ and $X_{m}^{Raman}$ was then used to calculate the volume fraction of m-ZrO$_2$ from the Raman line-scans across the fracture surface. The fit equation had an $R^2 = 0.98$ and is given by equation [5.6], and is valid to $X_{m}^{Raman} = 0.6$.

$$v_{m}^{XRD} = 0.77X_{m}^{Raman} + 0.06$$  [5.6]

The intercept is non-zero because a linear baseline is used to calculate $A_{m}^{170\rightarrow205}$ and the sum of the spectral intensities within the endpoints of the baseline is negative at low monoclinic contents.
5.4 Results and Discussion

5.4.1 Grain Growth

The microstructure as a function of the isothermal sintering time is shown in the ion beam images of Figure 5-2 (a,b,c). The grain contrast is a result of Ga⁺ ion channeling from the various crystallographic orientations of the grains.⁴⁴ The grain size as a function of sintering time is plotted in Figure 5-2 (d). The inset of Figure 5-2 (d) is a logarithm plot used to determine the grain growth exponent (n) according to⁴⁵

\[
G_{avg}^n - G_0^n = kt
\]

[5.7]

where \(G_{avg}\) is the grain size at time \(t\), \(G_0\) is the initial grain size, and \(k\) is the grain growth rate constant. The grain growth exponent (n) is equal to the inverse of the slope of the double logarithm plot or 2.99±0.07 (95% CI). A grain growth exponent of three is commonly reported for 3Y-TZP and is associated with the solute drag mechanism.⁴⁶-⁵⁰
The grain size distributions for each heat treatment are plotted in Figure 5-3. A log-normal distribution was fitted to the linear intercept distance histograms according to [5.8].
\[ F = \frac{2A}{wG\sqrt{2\pi}} e^{-\left(\ln\left(\frac{G}{G_{avg}}\right)\right)^2 \frac{2w^2}{2}} \]  

A three-parameter fit was used\(^{51}\) where \( F \) is the fractional frequency, \( A \) is the area of the distribution, \( w \) is the standard deviation or a measure of the distribution width, \( G_{avg} \) is the average grain size, and \( G \) is the grain size at the center of the bin. The average grain size \((G_{avg})\) and distribution width \((w)\) are tabulated in Table 5-2. The distribution width is approximately equal for the 1 hr and 8 hr heat treatments, while the distribution width for the 16 hr heat treatment is larger. In normal grain growth, the width of the distribution should be constant; therefore this result indicates exaggerated grain growth occurred in the 16 hr specimen.\(^{52}\) Bimodal distributions are common with exaggerated grain growth.\(^{53}\) A bimodal distribution is apparent in Figure 5-3 for the 16 hr specimen. However, there are not enough observations to describe the exaggerated grain size distribution parameters because of the large grain size to cross-sectional area ratio. The large grains are centered at 1.5 \( \mu \)m, while the finer grains are centered at 0.3-0.4 \( \mu \)m.
Figure 5-3: The grain size distributions for the 1 hr, 8 hr, and 16 hr heat treatments (top to bottom) can be fitted to a three-parameter log-normal distribution. The $w$-parameter which measures the width of the distribution; it is approximately equal for the 1 hr and 8 hr heat treatments, thus signifying normal grain growth; however, the 16 hr heat treatment has a larger $w$-parameter indicating exaggerated grain growth with large grains centered at 1.5 µm.
Table 5-2: A summary of the measured (simple average), fitted, and calculated parameters for grain size, strength, and transformation behavior. The ± values given are for the 95% confidence interval of either the measured dataset or fit parameters as described in the column heading.

<table>
<thead>
<tr>
<th>Heat Treatment</th>
<th>Surface Roughness</th>
<th>Grain Size</th>
<th>Strength</th>
<th>Raman</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$R_q$ meas.</td>
<td>$R_t$ meas.</td>
<td>Arithmetic Mean Grain Size $^{52}$ (d x 1.558) measured</td>
<td>Log-Normal Average Grain Size ($G_{av}$) fit</td>
</tr>
<tr>
<td>1400°C - 1 hr</td>
<td>310±60 (nm)</td>
<td>1.3±0.3 (µm)</td>
<td>260±20 (nm)</td>
<td>167±20 (nm)</td>
</tr>
<tr>
<td>1400°C - 8 hr</td>
<td>380±130 (nm)</td>
<td>1.7±0.6 (µm)</td>
<td>500±30 (nm)</td>
<td>330±30 (nm)</td>
</tr>
<tr>
<td>1400°C - 16 hr</td>
<td>340±80 (nm)</td>
<td>1.4±0.4 (µm)</td>
<td>650±90 (nm)</td>
<td>430±100 (nm)</td>
</tr>
</tbody>
</table>
Liquid phase sintering predominates in Y-TZP materials, and the rate limiting step in the sintering kinetics is attributed to cation lattice diffusion to the grain boundary. It has been shown that cations with a lower valence and larger size than the Zr$^{4+}$ host ion diffuse more slowly than cations with a higher valence and smaller size. Thus, the grain growth kinetics for small, high-valence cations are faster. However, faster grain growth kinetics does not necessarily lead to exaggerated grain growth. Allemann et al. report that alumina and silica (1:1 ratio) additions to Y-TZP show exaggerated grain growth. Additionally, Rühle et al. report exaggerated grain growth in Y-TZP with high alumina and silica impurity contents. The authors hypothesize that the low temperature eutectic for the Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ system at (1300°C-1400°C) is responsible for the exaggerated grains that grow out of the glassy grain boundary phase, which is high in yttria content (up to 30 mol%). The same eutectic composition has also been linked to exaggerated grain growth in alumina. In Y-TZP materials, the coarse grains are typically cubic rather than tetragonal, and grow at a faster rate than the matrix tetragonal grains. These larger cubic grains generally show transgranular fracture and are detrimental to toughness. Additionally, in Chapter 4, it was shown that the silica impurity in the alumina substrate caused massive localized grain growth in the areas where the substrate was in contact with the Y-TZP parts. A higher purity alumina substrate (99%) eliminated the extensive localized grain growth; however, alumina from the substrate and silica from the starting powder and/or substrate could still be contributing to the exaggerated grain growth at the rather long (16 hr) soak time. Interestingly, the exaggerated grain growth was only limited to the mesoscale parts; it did
not occur in the macroscopic analogues with identical heat treatment. The grain growth data for macroscale analogues is given in Appendix C. This suggests that the substrate caused the exaggerated grain growth through more intimate contact. However, the grain growth was not localized to the contact region with the substrate as opposed to the grain growth observed in Chapter 4.

### 5.4.2 Three-Point Bend Strength

The average strength of the mesoscale bend bars decreased as grain size increased, as summarized in Table 5-2 and Figure 5-4. A single linear Weibull fit is shown for each data set in Figure 5-4 even though there is some grouping to the data points. At least 30 data points for each flaw population subset would have to be gathered to prove non-linearity from multiple flaw populations, which is impractical at this point for free-standing mesoscale parts. Even given the limitations in the data, the 16 hr heat treatment has a significantly lower Weibull modulus \((m = 6.4)\) than the 1 hr or 8 hr heat treatments and a lower characteristic strength \((\sigma_0 = 2.26 \text{ GPa})\). The 1hr and 8hr heat treatments show similar characteristic strengths (2.50 GPa for 1 hr and 2.38 GPa for 8 hr) and Weibull moduli (8.4 for 1 hr and 8.0 for 8 hr). The trends in strength and Weibull modulus mirror the trend in grain size. The 1 hr and 8 hr specimens have similar narrow grain size distributions and Weibull parameters \((\sigma_0, m)\), but the 16 hr specimen has a significantly wider grain size distribution and lower Weibull modulus. The low characteristic strength and Weibull modulus for the 16 hr specimen indicates that the
grain growth in these specimen is more likely increasing the flaw size and broadening the flaw distribution, rather than increasing strength and reliability by increasing $K_{Ic}$.\textsuperscript{37}

![Figure 5-4: The strength and Weibull modulus of mesoscale bend bars decreases with longer heat treatment at 1400ºC. The larger grain samples were weaker and thus support the theory that grain size is proportional to flaw size.](image)

The fracture surfaces can aid in identifying the failure mechanism that causes the difference in strength for the 16 hr specimen relative to the 8 hr and 1 hr specimens. The difficulty in recovering the fracture specimen prevents correlating the individual specimen strength to its fracture surface: however, a few fractured specimens from each heat treatment group were recovered. The fracture surfaces shown in Figure 5-5 do not
show easily discernible fracture origins, in part because the large grain texture obscures the origin and fracture mirror in these small parts. Without definitive fracture origins, a flaw size can still be estimated from the Griffith equation \[5.1\] assuming a reasonable \(K_{IC}\) of 5 MPa√m for 3Y-TZP with a similar grain size.\(^6\) Assuming failure from surface cracks \((Y = 1.12\sqrt{\pi})\) and considering the average strength for each heat treatment (Table 5-2), the average expected flaw sizes are 1.1 μm, 1.2 μm and 1.4 μm for the 1, 8, and 16 hr heat treatments, respectively.
Figure 5-5: Fracture surfaces from mesoscale bend bars broken in three-point bending. Fracture origins are not easily discernable, but should range from 1.1 µm to 1.4 µm based on a Griffith model assuming through thickness surface cracks and a toughness of 5 MPa√m.

In the absence of clearly defined fracture origins, a likely flaw source is surface roughness since the roughness is approximately equal to the flaw sizes predicted by the Griffith equation. The average root mean square surface roughness ($R_q$) over all heat treatments is 340±50 nm, whereas the average peak-to-valley roughness ($R_t$) is 1.5±0.2
µm. The $R_t$ roughness parameter is a closer approximation of the flaw size, as it emphasizes the largest stress concentration rather than the average stress concentration. The surface roughness was not significantly different (95% CI) among the heat treatments as shown in Table 5-2. Therefore, roughness is not the likely cause of the strength difference among the heat treatments. However, surface roughness is a good descriptor of the extrinsic flaw population since volumetric flaws in the cross-section have not been observed. Additionally, samples with volumetric flaws (pores, large cracks, etc.) are preferentially eliminated during micromanipulation prior to testing. The surface roughness is dictated by the LM-RIF process instead of a surface finishing technique; thus, the surface roughness cannot be changed without modifying the process. The top surface of the bend bars as molded is slightly rougher than the bottom surface ($1.7±0.3$ µm $R_t$ vs. $1.3±0.3$ µm $R_t$). In addition, bend bars tested with the top in tension tend to be slightly weaker, although the strength differences are not statistically significant ($±95\%$ CI) due to the wide scatter inherent in brittle materials. This slight trend in top versus bottom strength further supports the assertion that the initial flaw size can be characterized by the surface roughness.

In all three images in Figure 5-5 there are areas of intergranular and transgranular fracture, but even the 16hr specimen does not show extensive microcracking that is characteristic of a fully transformed TZP microstructure. A mixed mode fracture is not characteristic of a fully stabilized TZP material; instead, TZP materials show total intergranular fracture.\textsuperscript{10,33} Since the extent of the intergranular fracture remains approximately equal among the heat treatments, the toughness does not change significantly over the grain size range studied. Further evidence of this assertion will be
presented using Raman spectroscopy. Intergranular fracture is associated with the monoclinic phase and can occur if transformation takes place either after processing or ahead of the crack front. The lack of microcracking in the specimen before fracture and the Raman spectroscopy data discussed later indicates that the tetragonal phase was stable before fracture. Therefore, the intergranular regions in the fracture surfaces are likely due to fracture events (e.g. microcracking and crack deflection).

Figure 5-6 shows higher magnification images of the fracture surface texture for the 1 hr and 16 hr specimen. Transgranular fracture tends to occur primarily in the larger grains especially in the bimodal 16 hr samples. Adams et al. and Rice show bimodal particle size distributions with fully stabilized zirconia where the coarse grains show 100% transgranular fracture and the fine grains show 100% intergranular fracture.\textsuperscript{62,63} This grain size-dependent fracture mode was attributed to \{111\} cleavage in the large grains; whereas, fine grains deflect cracks to the weaker grain boundary.\textsuperscript{62,63} The smooth transgranular fracture especially seen in the 16 hr specimen (Figure 5-6(c)) may also be attributable to the presence of large cubic grains.
Figure 5-6: (a) The fracture surface of a 1 hr soak treatment shows mixed mode fracture. (b) The fracture surface of a 16 hr specimen where regions of parallel ridges exist (arrows) in some grains indicating twinning prior to fracture. (c) The fracture surface of a 16 hr specimen where smooth fracture occurred through a particularly large grain, which may indicate that this grain was cubic.33
5.4.3 Orowan-Petch Behavior

To evaluate the influence of grain size on strength, the ratio of extrinsic flaw size (c) to grain size (G) can be used to determine whether the Orowan regime (c/G<1) or Petch regime (c/G>1) is more applicable. In the Orowan regime, the slope of the $\sigma_f$ vs. $G^{-1/2}$ plot is equal to $\sqrt{2K_{IC}/Y}$ with the assumption that $c = G/2$. In this regime, failure is considered to occur through Griffith cracks with a length equal to the grain radius $(G/2)$. In the Petch regime, the slope decreases since the stress intensity due to the extrinsic flaw size overwhelms the intrinsic grain size contribution. Large flaws span many grains; thus, the crack generated between adjacent grains at the flaw tip becomes relatively insignificant compared to the stress concentration from the extrinsic flaw and the $\sigma_f$ vs. $G^{-1/2}$ slope approaches zero. Figure 5-7 shows the relationship between grain size and average strength for the three heat treatments. The maximum grain size ($G_{max}$) has been used, as is more appropriate for exaggerated grain growth. The straight lines in Figure 5-7 are the Griffith lines at various $K_{IC}$ values corresponding to the full range of $K_{IC}$ values measured for a TZP material with the assumption that $c = G/2$. It was not possible to measure $K_{IC}$ due to the small sample size, but it is clear that the data do not fit the purely Orowan behavior represented by the straight lines in Figure 5-7. The data points are non-linear and have a lower slope than the Orowan models for all reasonable toughness values of 3Y-TZP. The lower slope is more appropriate to the Petch regime where the extrinsic flaw size is dominant.
Figure 5-7: The grain size versus strength relationship for mesoscale 3Y-TZP bend bars displays an Orowan-Petch relationship at the transition region between predominantly grain size controlled strength and predominantly extrinsic flaw size controlled strength. The solid data points indicate the average strength and maximum grain size for the three heat treatments. The Orowan-Petch plot assumes that the critical flaws are through-thickness surface cracks of a length equal to the Rt roughness, and a fracture toughness of 6 MPa√m. The Orowan-Petch curve shows that the strength of mesoscale parts is primarily determined by the extrinsic process controlled flaw size (c) rather than flaws characteristic of the grain size (G/2) since the data falls above a normalized grain size of 1 (lower x-axis).

One of the difficulties in predicting the strength of mesoscale ceramic components is the roughly equivalent grain size and extrinsic defect size, which places the strength in the Orowan-Petch transition region where the ratio of extrinsic flaw size to the intrinsic grain size (c/G) is near unity. Zimmermann and Rödel treated this transition region for macroscopic alumina with a well-defined induced pore size as the defect.24,26
Without clear fracture origins in the mesoscale samples, a general approach that uses through-thickness surface flaws of length \( c \) as the extrinsic defect size and the grain size radius \( (G_{\text{max}}/2) \) as the intrinsic crack size generated from the defect\(^{15} \) can determine whether Orowan or Petch behavior is dominant. In this model, the strength is predicted in the Orowan branch \((c< G)\) by the Griffith equation with the assumption that the critical flaw size is equal to \( G_{\text{max}}/2 \). In the Petch branch \((c>G)\), the extrinsic defect size is equal to the average peak-to-valley surface roughness \( (R_t) \) plus an additional length equal to \( G_{\text{max}}/2 \) according to equation \([5.9]\).

\[
\sigma_f = \frac{K_{k}}{Y(R_t + G/2)^{1/2}} \quad [5.9]
\]

In this Orowan-Petch model, the strength can be normalized against the strength of a Griffith crack in the Orowan branch and the intrinsic grain size is normalized against the extrinsic flaw size. These normalized parameters are shown in the right y-axis and lower x-axis of Figure 5-7. The normalized size parameter \((G_{\text{max}}/2c)^{-1/2}\) is used to elucidate the normalized strength through equation \([5.10]\).

\[
\frac{\sigma_f}{\sigma_{G/2}} = \frac{1}{\left(2R_t/G_{\text{max}} + 1\right)^{1/2}} \quad [5.10]
\]

Equation \([5.10]\) assumes that the fracture toughness and crack geometry do not change with grain size. To calculate the normalized strength \((\sigma_f/\sigma_{G/2})\), a toughness value had to be assumed, which simply translates the Orowan-Petch curve vertically on the normalized strength axis. This \( K_{k\text{c}} \) value of 6 MPa\(\sqrt{m}\) was chosen to intersect the data point for the finest grain size in order to illustrate how the two data points for the larger
grain sizes lie above the curve, which would occur if the larger grained samples had a slightly higher $K_{ic}$ value. A $K_{ic}$ of 6 MPa√m is also close to the $K_{ic}$ value of 5 MPa√m previously assumed. The flaw sizes calculated above using the Griffith equation would increase if a $K_{ic}$ of 6 MPa√m were used to result in flaw sizes ranging from 1.65 µm to 2.05 µm as opposed to 1.1 µm to 1.4 µm. The experimental data will fit the Orowan-Petch model for each data point exactly, if the $K_{ic}$ values for the three grain sizes are 6.10, 6.32, 6.28 MPa√m in order of increasing grain size. Overall, these toughness values are not significantly different from the measured toughness values for similar sized 3Y-TZP material.\textsuperscript{10,31,33}

### 5.4.4 Toughness

The hypothesis that increasing the grain size would increase strength and Weibull modulus through an increase in toughness is not consistent with the strength data. However, there is substantial evidence in the literature that transformation toughness should increase with grain size over the range studied.\textsuperscript{9,10,30,35} Although the fracture surface images do not show significant intergranular fracture indicative of fully transformed zirconia, a small increase in toughness may still have occurred.

Raman spectroscopy is very sensitive to the monoclinic phase\textsuperscript{42} and can provide insight into whether the larger-grained samples transformed to a greater degree. Toughness could not be measured directly due to the large grain size to sample size ratio which makes indentation fracture toughness measurements difficult as the sample tends to fracture in half. Raman spectroscopy determines the monoclinic phase that is left in the
crack wake post-fracture. Figure 5-8 shows a series of Raman spectra over a line scan perpendicular to the fracture surface. The monoclinic peak at 185 cm$^{-1}$ increases as the scan progresses towards the fracture surface or from top to bottom, as shown in Figure 5-8. If a comparison is made between the area of the monoclinic peak at 185 cm$^{-1}$ and the total area of the tetragonal peaks at 152 cm$^{-1}$ and 234 cm$^{-1}$, the approximate monoclinic phase fraction can be calculated based on a XRD/Raman calibration. Figure 5-9 shows the amount of monoclinic phase as a function of distance across the fracture surface at each sintering condition. The overall intensity gradually decreases as scan passes over the edge of the specimen because the spot size (~1 µm) is larger than the scan increment (223 nm). The decrease in monoclinic content past the fracture edge (located at the position of the peak monoclinic content) is an artifact of the spot size and not a decrease in the monoclinic to tetragonal peak ratio. The maximum monoclinic fraction increases from 0.07 to 0.17 to 0.29 as the average grain size increases. These monoclinic fractions do not account for any reversible transformation that may have occurred post fracture, but the differences among the heat treatments reveal that the grain size increased the transformed volume fraction ($V_f$). The post-fracture transformed zone size ($h$) is approximately 1 µm for all three heat treatments (distance of increasing monoclinic fraction to the peak monoclinic fraction).
Figure 5-8: These Raman spectra were taken from a line scan perpendicular to the fractured surface of a bend test bar sintered at 1400°C for 16hrs. An example of the line scan orientation and direction is shown in the upper right inset. The uppermost spectrum in this cascade plot is taken away from the fractured edge (beginning of arrow in inset) and the line scan progresses at 223 nm intervals past the fracture surface over a distance of 3.125 µm (14 points). The overall intensity decreases over the line-scan as the laser progresses past the edge of the bend bar. The monoclinic peak increases near the fracture surface of a bend test bar, which shows the material transformed from the tetragonal phase to the monoclinic phase on fracture. The monoclinic fractions near the fracture edge are calculated and shown in Figure 5-9.
The fraction of the monoclinic phase increases at the fracture surface. The amount of the monoclinic phase increases with soak temperature, and the peak monoclinic contents are 7%, 17%, and 29% for the 1hr, 8hr, and 16hr soak durations, respectively. Each Raman line scan was taken perpendicular to the fracture surface. The edge (fracture surface) of the bend bar is approximately located at the peak monoclinic content for all three line scans as indicated by the dashed vertical line in each plot.

The Raman spectral images in Figure 5-10 indicate that the higher monoclinic phase content is only on the fracture surface and that it is not simply due to the free surface monoclinic content. Figure 5-10 (a) is a spectral image of the integrated intensity of the monoclinic peak located between 170 cm\(^{-1}\) and 205 cm\(^{-1}\). Figure 5-10 (b) is a spectral image of the tetragonal peak located between 243 cm\(^{-1}\) and 283 cm\(^{-1}\). Figure 5-10 (c) is an optical image of the region shown in Figure 5-10 (a,b). Since the lighter area in
Figure 5-10 (a) is only located on the fracture edge and not on the other free surfaces (top and sides), the phase transformation only occurred on the fracture surface.

Figure 5-10: Confocal Raman spectroscopy of a fractured 8hr specimen using a 2D scan shows the fracture surface (top edge) of an 8hr specimen. (a) A spectral image using the integration of the monoclinic peak located in the range of 170-205 cm⁻¹. The edge of the fractured surface appears bright indicating a higher amount of monoclinic phase. (b) A spectral image using the integration of the tetragonal peak located in the range of 243-283 cm⁻¹. The entire area is relatively bright indicating a large amount of tetragonal phase. The bright area in the lower left corner is likely due to a higher overall signal in this area possibly due to focal plane differences. (c) An optical image of the region where the spectral images were taken. The bright dots in (c) are due to the laser used for the Raman spectra. The spectral images prove that the increase in the monoclinic phase at the fracture surface is due to fracture and not to an edge effect, as the two other edges do not show a significant contrast difference in (a) compared to the surface.

Despite the variation in the monoclinic fraction on the fracture surface between heat treatments, the effect of toughness on strength is likely minimal. In order for toughness or R-curve behavior to have an effect on strength the crack must grow subcritically and will approach the incremental limit of toughness ($\Delta K_c$) given by$^{29}$
\[ \Delta K_t = \frac{\eta e_T V_f h^{1/2}}{1 - \nu} \]  

where \( \eta \) is a constant depending on the transformation zone shape and zone stress state (pure dilational \( \eta = 0.214 \)), \( e_T \) is the dilatational strain, \( V_f \) is the transformed volume fraction, and \( \nu \) is the Poisson’s ratio. The toughness increment \( (\Delta K_t) \) can be calculated for the different heat treatments using existing data for 3Y-TZP \( (E=210 \text{ GPa}, e_T=0.05, \nu=0.3) \) and the \( V_f \) and \( h \) values from Figure 5-9. The incremental toughness values \( (\Delta K_t) \) for the 1 hr, 8 hr and 16 hr specimens are 0.22 MPa\( \sqrt{\text{m}} \), 0.55 MPa\( \sqrt{\text{m}} \), and 0.93 MPa\( \sqrt{\text{m}} \), respectively. These \( \Delta K_t \) values are small, indicating that toughness was not an important factor in strength. However, it is possible that these lower \( \Delta K_t \) values are a result of subcritical transformation that has been shown to occur in TZP materials. Subcritical transformation refers to cases in which the transformed volume \( (V_f) \) during fracture is higher than that measured post fracture by Raman microscopy. However, the mixed mode fracture observed in the fracture surface images supports the hypothesis that toughness was not significantly changed by grain growth at least in regard to the grain sizes studied. Additionally, the small \( \Delta K_t \) values are supportive of the Orowan-Petch analysis given that a large increase in toughness with increasing grain size results in an inconsistently large slope \( (K_{1c}/Y) \). Although \( K_{1c} \) measurements were not possible through microindentation, it was possible to generate Vickers hardness values at an indentation load of 0.25N. There was no significant hardness difference between the heat treatments (1hr: 12.9±0.6 GPa, 8hr: 12.7±0.5 GPa, 16hr: 12.8±0.6 GPa), and all values are consistent with the previously reported hardness values of tetragonal zirconia. This
further supports the assertion that there were no significant changes in plastic deformation or toughness among the samples. The Raman spectra, fracture surface examination, and hardness all indicate that the toughness did not change significantly among the heat treatments.

Although TZP materials have been shown to undergo transformation toughening over the grain size range in this study, the fracture evidence indicates that is played a minor role in the strength of the mesoscale specimen. This raises the question as to whether transformation toughening by grain size optimization is a valid toughening strategy for parts where the grain size and transformation zone are a significant fraction of the part size. It is well known that transformation toughening constrains the crack through a volumetric expansion around the crack.\cite{68,69} Therefore, as the crack propagates, the crack growth resistance increases as more material is transformed through the $V_{th}^{1/2}$ relationship given in equation [5.11]. However, this relationship assumes that there is enough untransformed material around the crack to constrain the crack, which may not be the case for thin specimen like the mesoscale specimen tested herein. Evans and Cannon note that “spontaneous spreading is expected to occur when the zone size attains some fraction (< l/2) of the sample size, …”\cite{68} By this rough approximation, the transformation zone size is limited to 9 $\mu$m in mesoscale specimen considering a through thickness crack. Wang et al. document transformation zone widths in 3Y-TZP ranging from 3.8 $\mu$m for 300 nm grains to 8.91 $\mu$m for 900 nm grains in macroscale specimen.\cite{35} Therefore, it is possible that the sample size limited the transformation zone size in the mesoscale specimen since the half-thickness is 9 $\mu$m. However, this somewhat unlikely given the Raman fracture surface scans which show the measured transformation zone
only extended 1 µm away from the crack. This transformation distance is below the 9 µm limitation imposed by the specimen size. Thus, it is unlikely that the lack of toughening behavior was due to the specimen size. Additional studies examining the transformation zone as a function of specimen thickness are needed to verify that the lack transformation toughening is attributable to a loss of constraint due to the sample size.

5.5 Conclusions

This chapter discussed the relationship between grain size and strength for mesoscale 3Y-TZP bend bars. Overall, the strength differences are small relative to the strength increases previously shown for the same material as processing defects were eliminated (Chapters 3 and 4). Grain growth behavior obeys the kinetics for a solute drag mechanism as typically seen for 3Y-TZP, although exaggerated grain growth was seen after 16hrs at 1400°C. Fracture surface images do not reveal any clear fracture origins, but they do show mixed intergranular/transgranular fracture consistent with tetragonal zirconia. Raman phase analysis proves that the larger grained 3Y-TZP was more transformed although the calculated toughness increment is small. Overall, the strength is determined by the flaw population which is a function of the surface roughness and the grain size according to Orowan-Petch behavior. Toughness plays a minor role in strength at least for the grain sizes studied. To further improve the strength in polycrystalline mesoscale parts, the extrinsic flaw size should first be reduced by processing improvements as the strength is in the Petch regime. A grain size reduction will also increase the strength, but to a lesser effect than a flaw size reduction. Since the grain
size-flaw size relationship is more critical in determining the strength than the grain size-
toughness relationship, a toughening strategy that decreases the dopant concentration
rather than increasing the grain size will likely be more effective.

5.6 References


Chapter 6

Hierarchical Manufacturing of a Surgical Instrument Using the LM-RIF Process

6.1 Introduction

One could argue that nanoscale devices are useless unless they affect our macroscopic world. Just as MEMS devices were laboratory novelties until scientists and engineers learned to connect them to macroscopic systems such as airbags and portable electronic devices, nano-enabled devices will remain largely confined to the laboratory until we figure out how to integrate them with devices orders of magnitude larger. To do this, the idea of hierarchical manufacturing must be developed to efficiently mass produce hierarchical systems with nano-scale features. Hierarchical systems are really nothing new to science and engineering.\(^1\) Civil engineers have been building hierarchical structures for over one hundred years; the Eiffel Tower has three hierarchical levels. In nature, proteins have four hierarchical levels, with wood, bone, and muscle having structural levels at each length scale down to 1 nm. As scientists have looked to nature for inspiration, they have realized the importance that hierarchy has in the remarkable properties of natural and new materials systems. The rationale for hierarchical nanomanufacturing is the creation of some fascinating opportunities in design and optimization. The farther we can break down the raw materials, the more possible ways we can reassemble them. This opens up the design space tremendously; engineers can begin to consider integrating material design into the design process. Instead of being
constrained by the property limitations of traditional materials, material properties can be tailored for the specific application. The ability to design from the nanoscale up removes fundamental constraints that engineers have taken for granted for hundreds of years. The possibilities of this exploded design space are as endless as our imaginations.

In this report, a manufacturing hierarchy was used to develop the next generation of surgical instruments. In considering surgical instrument manufacture there is a hierarchy of scale that begins with the atomic scale increasing to the nano-particulate scale, then to the microcomponent scale to form the mesoscale surgical tool, and finally to the macroscale surgical instrument that interfaces with the surgeon. The yttria stabilized zirconia polycrystals used in this work, use atomic defect chemistry (oxygen vacancies and substitutional Y$^{3+}$ ions) to stabilize the high temperature tetragonal phase at room temperature. Upon fracture the tetragonal phase transforms to limit the crack propagation on the micron scale. This hierarchy employs atomic scale defects to affect microscale cracking. On the nano-particulate scale, the colloid and interfacial chemistry are tailored to permit the particles to assemble into a dense microstructure. On the microcomponent scale, the flaws are the controlling mechanism that affects the strength performance of the mesoscale surgical tool. Finally, the mesoscale tool design determines how the surgeon’s inputs are translated into precise movements. With this hierarchical approach the limitations of traditional manufacturing are removed and the instrument is designed from the atoms up.

This report demonstrates the use of the novel combination of the lost-mold rapid infiltration forming (LM-RIF) process with elegant design optimization based on the fundamental mechanical properties of the mesoscale components. We demonstrate the
hierarchical nanomanufacturing of novel surgical instruments composed of novel ceramic
components interfaced with flexible endoscopes in the surgical instrument system. We
further show a variety of dense ceramic components that can lead to mesoscale
components in a diverse range of applications from micro-electro-mechanical systems to
microfluidics.

6.2 Materials and Methods

The LM-RIF process used to form 3Y-TZP and stainless steel parts is a merger
of photolithography and powder processing. The process development is covered in
Chapters 3 and 4, and by Antolino et al. and Hayes et al. Improvements to the LM-
RIF process to increase the yield of high aspect ratio surgical instruments using a novel
design of experiments methodology can be found in Yuangyai et al. The surgical
instrument design methodology using a size optimization algorithm for minimally
invasive surgical tools based on compliant mechanisms is found in Frecker et al. The
interface between the capabilities of the LM-RIF process and the design requirements for
the surgical instruments as well as the mechanical behavior of a surgical instrument
prototype can be found in Aguirre et al.
Hierarchical manufacturing is divided into three stages shown in Figure 6-1. These stages can be thought of as loops that are iterated, which form the hierarchy. In the inner fabrication loop (shown in red), the nanoparticulate materials, shown in (a), are functionalized to efficiently pack together to form high quality and high strength materials. Additionally, the microfabrication strategy, LM-RIF, is adjusted to increase part yield, strength and dimensional accuracy. The strength is then measured using the three-point bend geometry, novel at this size scale, shown in (b). In the design loop, shown in blue, the instrument size is optimized for grasping force and opening displacement, subject to the strength and dimensional limitations from the fabrication loop. The instruments are then fabricated and the strength is verified. In the green evaluation loop, the prototypes are incorporated into a working surgical instrument that is evaluated by surgeons. Any adjustments to the design, which also may require fabrication adjustments, are fed back into this novel, smart process.
Figure 6-1: The design, fabrication and evaluation relationships are shown for manufacturing surgical instrument prototypes. The development strategy employed three iteration loops. The inner fabrication loop in red uses colloid and interfacial chemistry to optimize the strength of bend test bars. The blue design loop uses the bend strength to optimize the instrument design. The green evaluation loop uses the prototype designs to optimize the functionality of the instruments. (a) The manipulation of the interactions between nanoparticles, shown here, ultimately determines the strength the surgical instruments. (b) A miniaturized version of the standardized bend test is used to evaluate effectiveness of the colloidal chemistry and provide the FEA model with a maximum allowable failure stress. (c) The FEA model is then made into a mold, shown filled here, to evaluate the accuracy of the models predictions. (d) A prototype design uses the elastic properties, strength and desired functionality to create an optimized finite element model. (e) Surgical instruments prototypes, like this forceps, are used to evaluate the design for functionality and performance. (f) This surgical instrument prototype has been interfaced with the control unit for surgeon evaluation.
6.3.1 Fabrication Loop

The basic building blocks of metals and ceramics are the grains of the material that ultimately grow from particles. Control of the particles and grains is especially crucial in mesoscale parts since grain size represents a large portion of the part size, about 1/10\textsuperscript{th} to 1/100\textsuperscript{th} of the thickness versus about 1/10,000\textsuperscript{th} to 1/100,000\textsuperscript{th} in a macroscale part. Minimization of stress concentrating flaws is also crucial in brittle materials to obtain high strength and high reliability. Particle control and flaw minimization are the focus of the inner fabrication loop shown in red in Figure 6-1. Through colloid and interfacial chemistry and microfabrication engineering, the strength and Weibull modulus, a measure of reliability, have increased over successive generations of materials as shown in Figure 6-2. In the first generation of parts (Gen1), cracking and geometrical defects such as the concave and non-orthogonal cross section shown in Figure 6-2 contributed to the poor strength. Controlling the particle-particle interactions to increase the packing efficiency of the particles eliminated much of the cracking, and ensured a dense, translucent (low porosity), ceramic body as shown in the third generation (Gen3) bend test specimen.\textsuperscript{7} High density is conducive to strong green bodies and efficient sintering, but is limited by the thickness of the adsorbed polyelectrolyte (\(\delta\)) through equation [6.1], where \(r_c\), \(r_{\text{packing}}\), \(r_s\), and \(r_o\) are the composite density, packing density (64\% for randomly packed spheres), solid density and polyelectrolyte density, respectively.\textsuperscript{12}

\[
\rho_c = \left( \frac{\rho_{\text{packing}}}{\rho_s} \right) \left( R^3 \rho_s + \frac{(R + \delta)^3 - R^3}{(R + \delta)^3} \rho_o \right) \quad [6.1]
\]
Figure 6-2: The fabrication loop shown in Figure 6-1 resulted in four generations of parts. With each successive generation the strength increased. The first generation of parts was highly defective and had concave upper surfaces (yellow arrows) and a non-orthogonal cross-section (red arrows). (Gen 1: cross-section of a part within a mold cavity) In the second generation, the largest defects were eliminated; however, the metrology of the parts did not match the design criteria. (Gen 2: optical profilometry reveals a non-orthogonal cross-section) The third generation parts were dimensionally accurate but the strength variability was high as evidenced by the low Weibull modulus (inset graph). (Gen 3: translucent bend bars due to thickness) In the fourth generation the microstructure was optimized, but the strength increased only slightly, since the strength is controlled predominantly by the surface flaws. (Gen 4: FIB cross-section of a bend specimen)
Additional considerations must be made for nanoparticles that have to be used for mesoscale parts simply to fit in the mold cavities and to provide a fine-grained microstructure. Two important considerations are the particle solubility in the case of a yttria stabilized zirconia (Y-TZP) material, and the oxidation protection of powdered metals in the case of stainless steel both of which become more significant in high surface area nanoparticles. The gross dimensional defects in Gen1 and Gen2 parts were largely eliminated by solving problems encountered in the mold making and suspension casting processes. Only when the large dimensional defects were eliminated in the Gen3 parts did the average strength increase to 2.2 GPa for the Y-TZP ceramic. In fourth generation parts, the strength was 2.35 GPa, which is not significantly higher than the Gen2 strength, but the Weibull modulus increased from 6 to 8. In the Gen4 parts, the strength limiting defect is the surface roughness of the parts that is controlled by the fabrication technique (Chapter 5). Although a range of grain sizes were studied to explore toughening affects in the TZP material, the effect on toughness was minimal. Even though the surface roughness was only 310 nm RMS, it still represents a relatively large flaw in these small parts and overshadows the Hall-Petch effect. Thus, the strength of small, brittle parts is not orders of magnitude larger than conventionally-sized parts despite predictions based on flaw population statistics for the smaller surface area and volume of mesoscale parts.
6.3.2 Design Loop

The surgical instrument prototypes are designed to operate within the next generation endoscope working channel diameters (≤ 1 mm). Therefore, these instruments must be of acceptable size to fit within the working channel of the endoscope, while maintaining functionality as a surgical tool. Secondly, the instrument dimensions are constrained due to fabrication limitations on part width, thickness, and feature size. Finally, material strength, as determined in the red processing loop in Figure 6-1, is incorporated into the design as a maximum stress constraint.

Monolithic compliant mechanisms that rely on elastic deformation during operation were preferred as the basis for all of the surgical instrument designs to eliminate the need for joints and hinges, as well as take full advantage of the LM-RIF process. Figure 6-3 (a) and (b) show a designed forceps tool that will be used to grasp tissue during surgical procedures. The tool operates through the actuation of a sheath that slides from the base of the forceps towards the tip, pushing the two arms towards each other in a grasping motion, shown in Figure 6-3(b). The forceps is designed using a predetermined topology that incorporates contact stress relief to obtain a larger predicted deflection during operation, given the maximum allowable stress. Figure 6-3(a) shows the maximum principal stress in the forceps during actuation, as a function of the distance the sheath is moved along the length of the forceps. As the sheath is moved to 30% of the length of the forceps during actuation, the two grasping arms come into contact, redistributing the stress along the arm, lowering the overall maximum stress, and allowing further deformation of the grasping arms.
A design algorithm was developed to optimize the instrument size, subject to the given topology and fabrication size constraints, as well as simultaneously optimizing the closing force, subject to a specific maximum allowed stress, as dictated by the material strength. The finite element modeling software, ANSYS®, was used to evaluate the non-linear deformation and surface contact experienced during the forceps operation using a parametric finite element model with 454 beam elements and assuming linear material behavior.

Along with surgical forceps, biopsy needles designed to entrap cells during exploratory procedures, shown in Figure 6-3(c), could also potentially be fabricated using the LM-RIF process. These future designs, due to their 3D topology, possess their own design-fabrication-testing relationship which may be different than the forceps designs; however, the hierarchical manufacturing strategy in Figure 6-1 was developed to adapt to these new requirements.
Figure 6-3: (a) The surgical forceps design (half-forceps shown) uses compliant mechanisms to eliminate the need for hinges or joints, making them easier to assemble at this size scale and avoiding gaps to make them easier to sterilize. Additionally, the design uses contact aided stress relief that permits a greater range of motion without exceeding the material strength determined by the miniature bend test results (Figure 6-2). The instruments in (a) and (b) are actuated using an outer sheath that is slid over the tool.11 (b) Finite element analysis is used to predict the functionality and stress distribution of the instrument (left: grasping tool, right: suturing tool), which is then verified in the prototype.5,18 (c) Three dimensional designs, like this biopsy needle, are the future of hierarchical manufacturing.17
6.3.3 Evaluation Loop

As shown in the green evaluation loop in Figure 6-1, the prototype instruments fabricated with the optimized designs are tested to evaluate the final design and performance of the tool. Fabrication part yield, grasping strength, and material strength of the final prototype become inputs into the instrument design, and the model is further refined. Changes to the instrument design that require changes to the fabrication process require another iteration of the design-fabrication-evaluation process depicted in Figure 6-1.

Coupling the design, fabrication, and evaluation of surgical components using the hierarchal approach outlined in Figure 6-1 removes the interfacial barriers between each step. However, this approach is not simply limited to rapid process development. A better understanding of the structural behavior of ceramics and powder metals\(^5\) at small lengths scales has also developed. With a large emphasis on “nano,” the issue of scale and how materials characteristics, such as strength, change with size has garnered much attention;\(^{19,20}\) however, much of the work is based on bulk materials whittled down to smaller dimensions or deposited in thin films. These techniques do not characterize the behavior of materials formed in arbitrary shapes from smaller, nanoscale components, like particles. In applied materials, processing science cannot be separated from the size effect since smaller specimen must be formed using different processing routes than their macroscale counterparts. The inability to separate forming technique from strength has already been discovered in the most prevalent material used in microfabrication: silicon in MEMS devices.\(^{21}\)
Figure 6-4 summarizes the development of surgical instrument tools, such as that shown in (j), using hierarchical manufacturing. In images (a-d), the capabilities of the forming technique are quantified. The strength is highly dependent on the precise dimensionality of the test specimen and the surface roughness, which controls the critical flaw size. Examples of the bend test specimen used to evaluate the strength are shown in (e): as the designs grew in size, the bend test specimen also grew. Figure 6-4(f) shows the fine-grained microstructure in a mesoscale part. Submicron grains are a prerequisite for high strength in materials with dimensions under 10 μm. Images (g-i) demonstrate the forming capabilities of the LM-RIF process, including the ability to form toroidal shapes that are difficult due to the constraint placed by the hole during molding as the part shrinks during drying and sintering. The prototype surgical forceps shown in image (j) was designed using the strength data gathered in Figure 6-2, and FEA optimal topology modeling in Figure 6-3. Image (h) is a prototype stainless steel surgical tool within a 1 mm glass tube used to evaluate the functionality and fit of the instrument. Image (l) is a rendering of a multi-component surgical instrument predicated on the reduced size of mesoscale surgical tools. Multi-component surgical tools operating interdependently would dramatically reduce switching between tools which plagues single working channel instruments.
Figure 6-4: (a) Optical profilometry allows precise determination of dimensions critical for shrinkage factors and strength determination. (b) Mesoscale bend bars are used for strength testing, triangular pieces to evaluate tip radius and gears to evaluate toroidal shapes. (c) The edge resolution of the parts is limited to that of the photomask or 2-3 µm. (d) Confocal optical microscopy helps identify cracks in the unsintered state. (e) The LM-RIF process can accommodate a wide range of part sizes, as evidenced by the test specimens shown here. (f) This color enhanced ion beam image reveals the fine grain size of sintered 3Y-TZP and the grain orientation. (g) Larger prototypes (400 µm thick) use the fine feature size capability of lithography in millimeter scale parts. (h) This gear demonstrates the ability to fabricate hollow parts. (i) Fine features of a gear tooth. (j) A surgical instrument forceps prototype made from 3Y-TZP. (k) A stainless steel surgical forceps prototype in a 1 mm channel (glass to show instrument). (l) Smaller instruments allow more tools to fit into multichannel endoscopes. Diagram (l) is taken from Reavis and Melvin.22
6.4 Conclusions

Microfabrication has spread from integrated circuit (IC) manufacturing to micro-electro-mechanical systems (MEMS), to microfluidics and is rapidly expanding to new areas, such as surgical instruments. However, the IC origins of microfabrication are inhibiting new applications simply because the technology of IC manufacturing with silicon is so intertwined with microfabrication that etched silicon or polymer based replicates of etched silicon are virtually the only materials choices for microfabrication. By using a new hierarchical approach to manufacturing, the breadth of applications that can benefit from alternative materials in microfabrication is enormous. An example of a surgical instrument prototype to enable the next generation of surgery was given to show how both the hierarchy of size and the manufacturing hierarchy can be used to fulfill the need for decreasing patient trauma, lowering infection rates, and increasing patient recovery time. This approach would benefit other applications as well, where limitations in one area, such as design, can be overcome in other areas such as materials chemistry.

6.5 References


Chapter 7
Conclusions and Suggested Work

7.1 Conclusions

Lost mold-rapid infiltration forming (LM-RIF) is a method to make large quantities of high aspect ratio, free-standing parts that have fine edges (1-3 µm) and strengths surpassing that of conventional materials at least in 3Y-TZP. Although soft lithography has become popular in the microfabrication arena, the lost mold technique can produce higher aspect ratio free-standing parts, and does not require a master mold. To capitalize on these advantages many engineering and scientific challenges had to be overcome. The strength and reliability of 3Y-TZP have also improved with refinements in LM-RIF.

Initially the photolithography process used to produce integrated circuits had to be modified to dovetail with ceramic powder processing. These modifications included filtering the UV light during exposure, using a three-layer process (UV absorbent, SU8 underlayer, SU8 mold layer), and pyrolyzing the SU8. From the outset of the LM-RIF development process, a highly loaded ceramic suspension was designed to be plastic so it could infiltrate the miniscule mold cavities but be rigid enough to prevent spilling out of the molds. Additionally, the ideal solids concentration was found, which balanced the need for a high green density with the viscosity appropriate for casting. As evidence to the quality of the particulate suspension, volumetric defects such as agglomerates, inclusions or fine porosity were not found as strength limiting defects.
One of the largest areas of research overlooked in free-form microfabrication is metrology. Since the mesoscale is too small for humans to directly interact with, the part geometry must be precisely manufactured to interface with other control systems. In the case of structural ceramics, these interfaces will be mechanical; thus the part dimensions must be precisely controlled. Additionally, high strength cannot be realized in brittle materials until the flaws are eliminated. This research showed a 3.5 fold strength improvement from Gen0 parts to Gen4 parts, which can be attributed to processing improvements. Without flaw minimization, other strategies to improve strength such as the grain size optimization demonstrated in Chapter 5 will be overshadowed. Some of these flaws such as the warping shown in Chapter 4 are unique to mesoscale parts. In the warping example, ionic diffusion caused grain growth in the parts, and ultimately a phase change. Entirely unique to the mesoscale parts, this defect illustrates how surface related phenomena such as surface contact with the substrate play a more important role in the properties of small scale ceramics.

The iterative development of the LM-RIF process was part of a larger hierarchical manufacturing process used to design surgical instrument prototypes. The design of these prototypes can be found elsewhere in related literature.\textsuperscript{1,2} The benefit of incorporating the design into the fabrication process development was the ability to steer the fabrication process towards high aspect ratio shapes and constrained shapes more suitable for the surgical instrument application. It also led to the ability to produce free-standing ceramic parts in shapes and sizes that were not previously demonstrated. Incorporating the fabrication process into the design process led to designs that were easier to manufacture and were therefore more reliable. Mechanical testing throughout
the development process highlighted the most critical defects, which were subsequently eliminated and led to higher strength. Through higher strength, the design space was broadened thereby completing the cycle. This hierarchical process has far reaching consequences for the rapid development of ideas into products that cannot be manufactured using conventional techniques.

Although the 3Y-TZP strength is among the highest recorded for zirconia ceramics, it does not scale with the effective volume or effective surface area from macroscale 3Y-TZP strengths. As miniaturization shrinks the part size, the flaw size also shrinks but to a lesser proportion to the part size. This dissertation shows that flaw size controls strength even when the grain size is only 1/10th the sample size. A toughening effect due to grain coarsening did not increase the strength of mesoscale specimen. It is hypothesized that increasing the grain size acts to increase the flaw size rather than increase the toughness. At least down to a 400 \( \mu \text{m}^2 \) cross-sectional area, conventional theories on the strength limitations of brittle materials apply, with the exception that the strength of mesoscale specimen cannot be predicted from macroscale specimen since processing differences produce different flaw populations.

7.2 Suggested Work

7.2.1 Strength of Mesoscale Parts

How high can the strength of a ceramic like 3Y-TZP be? From a Weibull perspective, the smaller the loaded volume, the higher the strength should be for a given
flaw distribution. Chapter 4 shows the error in this reasoning; the flaws do not scale with size in practice since different techniques have to be used for different size scales. The data in Chapter 4 confirms that of Namazu et al., who found that the strength of silicon scaled according to Weibull statistics only within the size range of a given fabrication method.\textsuperscript{3} However, recent progress in creating thick, high contrast photoresist\textsuperscript{4,5} means that the LM-RIF process is capable of making specimen with thicknesses between 1 µm and 1.2 mm. Assuming a constant (3×4×50) aspect ratio bend bar, the specimen volume ratio that can be tested using only the LM-RIF technique is 1,200:1 or three orders of magnitude. This wide range of tested volumes allows one to test the Weibull size effect for any powder based material. This data would serve as the foundation for reliable microfabrication outside of silicon.

### 7.2.2 Effective Volume or Surface Area Versus Strength

Figure 7-1 shows the characteristic strength versus the test volume (cross-section multiplied by the test span) for Gen3 mesoscale specimens and mm-scale specimens both tested in three-point bending. The mm-scale specimens were made from the same starting 3Y-TZP powder, but with a different binder formulation. The characteristic strength and Weibull modulus for the mm-scale specimen were 640 MPa and 4.5, respectively.\textsuperscript{ii} The lines in Figure 7-1 represent equation [7.1], where $\sigma_{0(1,2)}$ and $m_{(1,2)}$ are the characteristic strengths and Weibull moduli of the two volumes ($V_1$, $V_2$) being compared.\textsuperscript{6}

\textsuperscript{ii} The mm-scale data is courtesy of Greg Hayes and Roi Meirom.
Figure 7-1 shows that the strength of the mm-scale 3Y-TZP bars can be accurately predicted from the strength and Weibull modulus of the mesoscale specimen, but the reverse is not true since the mm-scale specimen have a lower Weibull modulus. It is possible the mm-scale specimens have an additional flaw population because of the different binder system employed in these specimens; the Weibull modulus would decrease if these flaws were larger than the surface roughness. Verifying the applicability of equation [7.1] in Figure 7-1 allows the accurate prediction of strength for differently sized specimen under different loading conditions provided the same forming technique is used. This data would aid the design of surgical instruments and any other application, where the size, shape, or functionality is expected to change.
In Chapters 4 and 5 the strength was found to be dependent on geometric irregularities and surface roughness. Additionally, Chapter 5 proved that the grain size did not affect the strength significantly despite a 2.5 fold increase in grain size. This confirms that the grain size necessary to densify the sample is fine enough such that surface flaws are strength limiting. Thus decreasing the grain size will not give as great a strength increase as improving the surface finish. One approach is to add a surface

Figure 7-1: Through the use of Weibull statistics it is possible to estimate the strength of larger mm-scale samples from the strength of the mesoscale samples provided one forming technique (LM-RIF) is used. In this plot, the lines are the Weibull calculations based on the mesoscale data (solid line) and preliminary data on mm-scale specimen (dash line) produced using the LM-RIF process. The Weibull modulus for the mm-scale specimen was only 4.5, which overestimates the strength of mesoscale specimen. From this preliminary data it seems that the strength of larger specimen can be predicted, but not vice versa.

### 7.2.3 Further Reducing the Flaw Size

In Chapters 4 and 5 the strength was found to be dependent on geometric irregularities and surface roughness. Additionally, Chapter 5 proved that the grain size did not affect the strength significantly despite a 2.5 fold increase in grain size. This confirms that the grain size necessary to densify the sample is fine enough such that surface flaws are strength limiting. Thus decreasing the grain size will not give as great a strength increase as improving the surface finish. One approach is to add a surface
finishing technique such as polishing or focused ion beam milling. However these techniques are impractical at this size scale. Another approach is to cap the mold cavities to form a six sided mold cavity rather than leave one side open. In Chapter 5, it was found that the open side of the mold cavity produces bars with a higher roughness than the bottom side ($1.7\pm0.3 \ \mu m \ R_t$ vs. $1.3\pm0.3 \ \mu m \ R_t$ or $0.34\pm0.06 \ \mu m \ R_a$ vs. $0.3\pm0.1 \ \mu m \ R_a$). Although the strength is not statistically significantly different between top and bottom, there is a trend for higher strengths when the smoother bottom surface is tested in tension as shown in Figure 7-2. Although the strength difference is modest, by making all surfaces of equal roughness, the Weibull modulus should increase, which is the more substantial barrier to mesoscale ceramic applications than high strength. An attempt was made to cap the mold cavities, but failed since the cap introduced bubbles, and the pressure gradients inherent when the cap is pressed over the mold resulted in bulk material flow. Although the solution to overfill the molds and then “buff” away the excess suspension after drying alleviated dishing, it may not have been the best solution for minimizing surface roughness. The capping experiment is summarized in Appendix B.
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7.2.4 Improving the Mesoscale Bend Test

Although improvements to the three-point bend test would improve the precision and accuracy of the strength measurement, better post-fracture specimen recovery techniques would provide more valuable information about the strength of mesoscale ceramics. In Chapter 5, fracture surfaces were examined for each of the heat treatments, but the strength of the individual bar corresponding to the fracture surface was unknown. In the Weibull plot of the fracture data in Figure 5-4, the data appears to contain multiple flaw populations. The only way to verify this hypothesis is to determine and classify the fracture origins. Alternatively, simply fracturing more specimens makes the hypothesized

Figure 7-2: There are slight differences between the strength of the bars that were tested with the top as molded in tension versus the bottom as molded in tension. Although statistically insignificant, the trend shows that the smoother bottom surface is stronger than the “buffed” top surface.
multiple flaw populations more obvious, but does not yield any information about the defect origin. Fractography can also provide an estimation of the critical stress intensity (\(K_{IC}\)) by measuring the area of the fracture mirror;\(^7\) although, Chapter 5 shows that it is difficult to identify features on a fracture surface that has such few grains. It is recommended that the primary focus of the next generation mesoscale bend test be on sample recovery followed by improvements to the test accuracy or testing efficiency (increasing the number of specimens).

### 7.2.5 Can Transformation Toughening Exist in Mesoscale Zirconia?

In Chapter 5, it was discovered that even by growing the grains substantially, there was little evidence of a substantial toughening effect. However, 3Y-TZP does not show significant toughening compared to partially stabilized zirconia (PSZ), but is regarded as the highest strength zirconia microstructure due to the fine grain size that can be achieved in the 3Y-TZP system.\(^8,9\) In PSZ systems, like MgO doped PSZ (Mg-PSZ), the tetragonal phase is precipitated within cubic grains at higher dopant concentrations (8.5 – 10 mol\%) in the cubic+tetragonal phase field.\(^9\) The PSZ microstructure is large grained (~50 \(\mu\)m), and therefore weak, but the transformable lenticular tetragonal precipitates form a tough microstructure (>15 MPa\(\sqrt{m}\)).\(^8\) High toughness in PSZ materials is developed only after significant crack propagation (~1 mm) and relies on a large transformation zone size (30 \(\mu\)m) versus the small R-curve effect (constant toughness) and small transformation zone size in Y-TZP ceramics (4 \(\mu\)m maximum according to Hannink et al., or 1 \(\mu\)m in Chapter 5). Therefore, the PSZ system is more
applicable for high reliability mesoscale ceramics compared to Y-TZP, but will suffer from low strength since the grain size will far exceed the flaw size and actual dimensions of a mesoscale specimen. Mesoscale ceramics present a unique opportunity to study transformation toughening as the transformation zone size, grain size, and sample size are all the same order of magnitude. Since these high toughness zirconia ceramics rely on a large transformation zone size, the sample dimensions may curtail the transformation zone and thus limit the maximum toughness. This toughness limit has been experimentally verified by Liu et al. in large single edge notch beam (SENB) specimens, and could potentially eliminate transformation toughening as a way to improve reliability in mesoscale ceramics if the SENB results can be experimentally verified in mesoscale samples.

7.3 Applications of LM-RIF

The LM-RIF process can potentially impact many more areas of microfabrication other than the surgical instrument application described in Chapter 6. Rather than try to predict new applications for mesoscale ceramics, the strengths of the LM-RIF process in combination with properties typical of ceramics will be summarized followed by an example of one high potential application.

The LM-RIF process is uniquely positioned to make large arrays of free-standing, high aspect ratio parts, from powder-based materials. The process does not rely on capillary filling, like the MIMIC process and other soft lithography processes; therefore, parts as long as 30 cm (substrate limited) could be fabricated from
concentrated, viscous suspensions. Although LM-RIF was not intended as a prototyping process, the low cost (< $1,000) and rapid turnaround time (~ 1 week) to make UV-photolithography masks permits rapid screening of part designs since many different mesoscale designs can fit on a single mask. Additionally, LM-RIF is suited for material composition screening through the systematic masking and filling of mold sections. Material screening through combinatorial methods has already been exploited with thin film material chemistry,¹⁴ and through LM-RIF, this concept can be extended to particulate based systems representative of bulk materials. The LM-RIF process also lends itself to layering material through the thickness by casting successively to create a layered composite or a free-standing electroded component. The unique free-standing nature of the parts produced by LM-RIF can potentially lead to difficulties in handling as evidenced by Figure 7-3, which shows the hand-drawn vacuum pipette used to position the bend bars onto the test span. However, due to the ease of making fine features in a mask, sprues could be added to connect the parts to eliminate individual handling. It could also be possible to array the sprues in such a way that the parts could be connected after casting by masking the parts and filling the sprues with a dissolvable material to release the parts at will.
Ceramics are a very diverse group of materials, but are commonly recognized for their insulating properties (both electric and thermal), chemical resistance, and hardness. Ceramics form the basis for many technical applications including thermistors, superconductors, transparent conductors, igniters, transparent armor, oxygen sensors and thermal barrier coatings. For some of these applications, miniaturization is not appropriate, such as transparent armor. However, sensing and ignitor applications may well benefit from the LM-RIF process for miniature gas sensors, or small scale engines. The lab-on-a-chip revolution,\textsuperscript{15} for example, could contain micro-igniters, and a high temperature chamber for volatilizing solid or liquid analytes.

Figure 7-3: Manipulating free-standing mesoscale parts can be challenging as this vacuum manipulation setup used to manipulate the mesoscale bend bars shows. The bend bar in the inset is about 350 µm long. The pipette was created by hand drawing a 1 mm diameter glass tube, fracturing and polishing the end for an inside diameter of about 30 µm. The pipette is then connected to a peristaltic pump for precise control of the vacuum pressure. A mask containing sprues would be a much more efficient way to handle large quantities of parts.
One particular concept suitable for the LM-RIF process is the goal of creating a microturbine or engine for small scale portable power generation for the increasing number of portable electronic devices. A microturbine has been made out of silicon and a micro-Wankel engine has been made out of SU8 photoresist. However, silicon is extremely brittle and oxidizes at typical combustion temperatures and SU8, as Chapter 3 shows, undergoes large scale thermo-mechanical changes above 250°C. These examples show how microfabrication techniques have dictated the material choice. However, the SU8 Wankel engine example proves that microfabrication can be used to form complex 3D objects. If the engine components can be made from SU8, then a negative of the mask can be used to create SU8 molds to cast either ceramic or metallic material into engine parts. This is one potential area where the LM-RIF process could have a large impact.

The LM-RIF process was developed to explore the strength of small scale particulate based ceramics for surgical instrument prototypes, but is widely adaptable to other materials and applications. However, in considering new applications, the role of processing science cannot be understated. Careful consideration of the material assembly (colloidal and interfacial chemistry in the present case) and relative size of the microstructure, defects, and metrology is necessary for high quality materials, parts, and performance.
7.4 References


Appendix A

Thermal Properties of SU8 and the Methacrylamide Gelcast System

Appendix A provides additional data on the thermal decomposition of SU8 and the methacrylamide/bisacrylamide binder system used in the 3Y-TZP suspension.

A.1 SU8 Decomposition in Air

Cracking from mold thermolysis was first alleviated by adjusting the thermal cycle to volatilize the mold more slowly (Chapter 3) and second by replacing thermolysis by reactive ion etching (RIE) (Chapter 4). Although RIE has replaced thermolysis for the 25 µm thick mold cavities, thicker (>100 µm) photoresist is difficult and time consuming to remove by RIE; thus, thermolysis remains the best option for thicker parts. The early work on mold thermolysis will be summarized here for applications requiring thicker photoresist.

Mold thermolysis was the cornerstone of the initial LM-RIF concept that allowed the entire forming process to occur on a substrate. Mold removal and sintering in single step is also an added advantage of mold thermolysis. A study by Schonholzer et al. shows that pyrolysis of a photoresist mold has led to cracking in the ceramic body.¹ This study is correct as the cracking shown in Figure A-1 demonstrates. This type of cracking is characterized by longitudinal cracks as in Figure A-1(a,b) or as an extremely rough sidewall as shown in Figure A-1(c). The rough sidewall is a result of the crack running
close to sides of the specimen. Initially it was thought an amphiphilic surfactant, like Triton X-100 (Dow Chemical, Midland, MI), would prevent the parts from sticking to the mold cavity. However, Triton X-100 produced bubbles in parts and was abandoned. In a later experiment, silicone mold release (Leco, St. Joseph, MI) was shown to decrease drying cracks in thick (100-400 µm) parts. Another approach to limit the cracking in Figure A-1 is to adjust the heating cycle to match the thermal properties of SU8.

Figure A-1: This type of longitudinal cracking is typical of the cracking seen when the mold is pyrolyzed without considering the distortion that occurs as the photoresist is heated above its glass transition temperature. (a) Bend bars are split as the photoresist adheres to the part wall and shrinks. (c) In gears this type of cracking favors the radial direction. (c) In parts that are not split, like this bend bar, rough edges result from the removal of the part surface by the shrinking photoresist.

SU8 is a common photoresist and its thermal properties are well known, yet highly variable depending on the processing conditions, such as prebake temperature and time, postbake temperature and time, hardbake temperature and time, and exposure power. Feng and Ferris have measured the thermal and elastic properties of SU8 as a function of various processing conditions. Based on their work, a hardbake at 180°C for 20 min was used to minimize the thermal expansion coefficient of SU8. Feng and Ferris only measured the thermal properties of SU8 in a nitrogen environment up to 350°C. However, an air atmosphere and a higher temperature are used for the LM-RIF process to remove the mold and sinter the oxide ceramic. Figure A-2 shows the thermal
mechanical analysis (TMA) of a 40 \( \mu \)m thick SU8 double layer (underlayer plus mold layer) analyzed through the thickness as it undergoes a hardbake at 180\(^{0}\)C for 20 min and is then pyrolyzed in air at 5\(^{0}\)C/min. Figure A-2 is somewhat misleading since a small (0.1 N) force must be applied to the pushrod in the TMA to minimize the noise. When a force is applied, the viscoelastic changes that occur at temperatures exceeding the glass transition temperature will result in a larger displacement than would occur if no force was applied. In Chapter 3, hot-stage SEM shows that cracking was first observed at 248\(^{0}\)C and the cracks visibly widen by 311\(^{0}\)C. This roughly correlates to the onset of shrinkage at 264\(^{0}\)C in Figure A-2. Figure A-2 also shows that the dimensional changes that occur in SU8 are more subtle at a slower heating rate. However, the peaks between 435\(^{0}\)C and 577\(^{0}\)C for the sample heated at 5\(^{0}\)C/min are most likely due to the entrapment and sudden release of the volatile organic compounds trapped under the pushrod assembly in the TMA. Figure A-3 shows the weight loss and evolved species of pyrolyzed SU8.\(^4\) The primary decomposition products are gaseous oxides of carbon. Additionally, the complete volatilization of SU8 in air is accomplished below 550\(^{0}\)C, whereas, Feng and Ferris\(^2\) report an ash content of 20-30\% by weight in nitrogen. The combined thermal analysis in Figures A-2 and A-3 make mold thermolysis possible provided the heating rates used during thermolysis are adjusted for the reactions and displacements occurring in these figures. The SU8 mold walls act as a solid body that becomes fluid above the glass transition temperature and then shrinks as it decomposes. Cracks tend to occur in the parts at the onset of mold shrinkage. The mold layout is important because large areas of SU8 will shrink over a larger distance than finely arrayed mold cavities and the large SU8 area will pull the cavities toward the center of
the solid SU8 area. It is therefore advantageous to keep the mold cavity spacing uniform across the substrate.

Figure A-2: TMA of SU8 processed according to the procedure in Chapter 3. The solid line shows an SU8 layer heated at 5°C/min, and the dashed line shows an SU8 layer heated at 1°C/min. The 5°C/min sample was heated to 180°C for 20 min then cooled to measure the dimensional change that occurs during the hardbake. The massive expansion in the 5°C/min curve and the flat response in the 1°C/min curve are caused by trapped volatile species being released in the confined TMA assembly as revealed by the TGA-MS data in Figure A-3. Cracking in the parts tends to occur around the onset of shrinkage at 264°C.
A.2 Thermal Decomposition of Methacrylamide Binder

The dispersant and polymerized gelcast binder must also be pyrolyzed before the sintering process can entrap the carbonaceous residue. Figure A-4 shows the TGA-DTA curve for the 3Y-TZP green body containing the gelcast binder system described in Chapter 3. The total organic content is approximately 7.5% by mass of the dry powder according to the TGA data in Figure A-4, which is equal to the total amount added. Figure A-4 shows that after dehydration, the majority of the organic content oxidizes and becomes volatile between 200°C and 600°C. However, there is an additional 0.32% mass loss up to 1100°C which may be due to residual carbon left within the green body.

Figure A-3: The TGA-MS for SU8 in 20% O₂-80% Ar shows the primary decomposition products are oxides of carbon. There is no residual carbon ash when oxygen is present above 550°C.
The porosity is still open even at 1200°C, as Figure A-5 shows; therefore, the residual carbon does not pose a problem in the densification of the 3Y-TZP parts.

Figure A-4: The pyrolysis of the dispersant (ammonium polymethacrylate) and gelcast binder [methacrylamide (MA) and bisacrylamide (BAM)] used in the 3Y-TZP green bodies shows almost complete oxidation below 600°C. There is possibly some residual carbon that does not get oxidized until 850°C -1100°C.
Figure A-5: This surface image of a LM-RIF 3Y-TZP bend bar sintered at 1200°C for one hour shows interconnected porosity. This means that the residual carbon content in Figure A-4 does not pose a problem in the densification of the 3Y-TZP parts.
Appendix B

Rapid Infiltration Forming

B.1 Introduction

Appendix B discusses the squeegee process used to infiltrate the mold cavities. A fluid flow model and squeegee deformation model are used to describe the infiltration pressure and dishing, respectively. Additionally, an experiment that was intended to eliminate dishing but caused other defects is presented since it greatly reduced the roughness variation between the sides of the parts and could potentially increase the reliability of LM-RIF produced parts.

The concept of rapid infiltration forming (RIF) exploits the shear thinning nature of the particulate suspension by applying a shear rate though a squeegee. The RIF process is a manual process, which makes it highly operator dependent, but also very flexible. Attempts were made to automate the process by modifying a screen printer, but ultimately the inability of the screen printer to change squeegee angle and pressure, and to make rapid multiple passes made adapting a screen printer to RIF impractical at this stage of process development. Figure B-1 shows an example of a mold filled using a screen printer. Figure B-1 image (a) shows streaking on the right half of the mold surface, and image (b) shows bubbles highlighted by the arrows. Streaking is likely caused by squeegee deformation, while bubbles are formed in the corners of the mold cavities due to trapped air. Both of these defects can be eliminated by making multiple passes and varying the squeegee pressure and angle. An automated RIF process is
desirable and could be made to work, however, the flexibility of the manual RIF process allowed the squeegee parameters to be better understood if only qualitatively. These parameters will be discussed in this appendix.

![Figure B-1](image_url)

Figure B-1: These two images are optical images of a mold filled using a modified screen printer. (a) The streaking on the right side of this image is caused by squeegee deformation. (b) Bubbles can be entrained in the parts generally at the corners of the mold cavities.

### B.2 Reimer Flow Model

The infiltration pressure generated by the RIF process as a function of squeegee rate and angle can be estimated using an existing fluid dynamics model for screen printing that assumes creeping flow. The Reynolds number \( (Re) \), given in equation [B.1], for the casting process in simple shear is \( Re = 0.006 \) assuming the following values: 25\( \mu \)m characteristic length \( (L) \) (mold thickness), 5 cm/s average fluid velocity \( (V) \), 3.27 g/cm\(^3\) suspension density \( (\rho) \), and 0.65 Pa·s viscosity \( (\eta) \).

\[
Re = \frac{\rho VL}{\eta} \quad [B.1]
\]

Since the Reynolds number is significantly below unity, the creeping flow assumption is valid. According to the model by Reimer, the pressure created along a flat surface by a
The streamlines for the flow equation in the Riemer model are depicted in Figure B-2 for a squeegee angle of 45°. Figure B-3 (a) plots the infiltration pressure (P) versus distance (r) for a squeegee angle of 45° to the surface of the mold assuming a viscosity (η) of 0.65 Pa·s (high shear viscosity), and a squeegee velocity (V) of 10 cm/s. Figure B-3 (b) plots the infiltration pressure (P) versus the squeegee angle (α) at a fixed distance 20 µm in front of the squeegee tip. From Figure B-3 (a) and equation [B.2], infiltration pressure decreases with a (1/r) dependence on the mold surface away from the point of contact between the squeegee and the mold. From Figure B-3(b), the effect of decreasing the squeegee angle is to increase the infiltration pressure. During casting, it is advantageous to make a first pass at a low squeegee angle to ensure the mold cavities are filled at high pressure, and a final pass at a high squeegee angle to remove the suspension on top of the mold cavity (overburden) at low pressure. The squeegee deformation is not captured by the Riemer model, but pressure against the squeegee exerted by the suspension is of a similar form to equation [B.2]. Therefore, during the final squeegee pass at high angle, the squeegee will deform less which prevents suspension from flowing underneath and remaining above the mold cavities. However, with less hydraulic pressure against the squeegee, the squeegee is free to deform into the mold cavities and cause dishing. The
“buffing” solution applied in Chapter 4 circumvents the squeegee deformation by wearing away the overburden using a large contact area, hence lower pressure, to minimize disturbing the suspension within the mold cavity. Qualitatively, the information gathered from Riemer’s model allows the operator to precisely fill the mold cavities. An extension to the model to include squeegee deformation could accurately predict the overburden thickness; however, this extension is only suitable when the vertical force applied to the squeegee, and the squeegee speed and angle can be precisely controlled in an automated process.

Figure B-2: This image, taken from Riemer, depicts a model of creeping flow due to a squeegee moving across a flat surface (labeled screen in image). The distance between the streamlines is inversely proportional to the velocity gradient and directly proportional to pressure. The maximum pressure according to this model is generated at 1/3 the squeegee angle or 15° for the 45° squeegee shown here.
**Figure B-3:** Infiltration pressure as calculated using the Riemer model\(^5\) for a suspension with a viscosity of 0.65 Pa·s, and squeegee velocity of 10 cm/s. (a) The infiltration pressure decreases as a function of \((1/r)\) where \(r\) is the distance in front of the contact point between the squeegee and mold. A 45° squeegee angle is assumed. (b) The infiltration pressure increases if the squeegee angle (angle between front edge of squeegee and the top of mold) is decreased. The infiltration pressure is calculated at a distance \((r)\) of 20 \(\mu\)m in front of the squeegee contact point.

### B.3 Squeegee Deformation

Dishing was a major defect eliminated in Chapter 4 through the use of a buffing process, which is an engineering solution to a problem originating from squeegee deformation into the mold cavity. The obvious solution is to use a harder squeegee, however, harder squeegees cannot conform to the mold surface and the squeegee rides on the high points, which leaves thick suspension in some areas of the mold surface. This over layer of suspension permanently attaches all the parts within that area together after sintering. This effect, called skipping, was also observed with harder squeegees in the stencil printing of solder pastes.\(^6\)

Mannan *et al.* provide a model that describes dishing, or “scooping” in their study, as a soft squeegee deforms into an aperture.\(^6\) The authors employ a static model to
predict the shape of the scooping, and a dynamic model to predict the depth of the scooping. Although, their model falls short in describing the scooping depth solely from the boundary conditions and elastic properties of the squeegee, it empirically describes the scooping depth profile and explains the effect of squeegee speed, vertical force applied to the squeegee, and aperture width on the scooping depth. The empirical nature of the model arises because it was discovered that a linear elastic model overestimated the squeegee deformation 2-3 fold.\textsuperscript{6} Despite its limitations, the Mannan \textit{et al.} model can be used to explain the dishing profile in the LM-RIF process observed in Chapter 4. Unfortunately, the manual squeegee action used in the LM-RIF process limits the model’s predictive capability since the squeegee pressure, angle and speed are highly variable in hand casting. The one quantitative metric that the Mannan \textit{et al.} model can be used for is the shape of the dishing or scooping. However, since the model is semi-empirical, it must assumed that the squeegees used in the LM-RIF process behave like those in the Mannan \textit{et al.} study. The LM-RIF squeegee had a hardness of 60 Shore A, which is roughly comparable to the 70-75 Shore A squeegee used by Mannan \textit{et al.}\textsuperscript{6} However, the mold cavities in the Mannan \textit{et al.} study were 150 $\mu$m $\times$ 625 $\mu$m laterally and 152 $\mu$m thick versus the LM-RIF mold’s lateral dimensions of 33 $\mu$m $\times$ 415 $\mu$m and 23 $\mu$m thickness. The difference in mold size makes it more likely that the squeegee will contact more than two sides of the mold cavity in the LM-RIF process for a given squeegee contact patch (length $\times$ deformed width). According to Mannan \textit{et al.}, this would have the effect of decreasing the amount of dishing since the squeegee is more strongly supported.\textsuperscript{6} Despite these limitations the findings of Mannan \textit{et al.} are still thought to be relevant to the LM-RIF process and will be summarized, followed by a
quantitative fit of the dishing profile of the LM-RIF using the static model by Mannan et al.

Mannan et al. found that scooping depth decreased with increasing squeegee hardness, which has been qualitatively confirmed in the LM-RIF process. Additionally, softer squeegee blades are also more sensitive to aperture width variations, scooping to greater depths in apertures perpendicular to the squeegee direction compared to parallel apertures. Mannan et al. argue that differences between the scooping in perpendicular versus parallel apertures is due to squeegee deformation since a harder metal squeegee did not produce any difference in scooping based on aperture orientation. However, the squeegee deformed more into the perpendicular apertures than the parallel apertures in a static test despite the fact that the perpendicular apertures have less scooping. Ultimately the authors conclude that the decrease in scooping with perpendicular apertures is due to the higher paste pressure developed under perpendicular apertures because of the proximity of the mold wall to the squeegee edge. This proximity increases the paste pressure against the squeegee and thus decreases the scooping.

The geometry of the Mannan et al. static deformation model is given in Figure B-4. In this model, the deformation due to a vertical force (Q) applied to the top of the squeegee is considered. Rather than account for the 3-D deformation of the squeegee, Mannan et al. postulate that the shape of the scooped out region satisfies equation [B.3], where T is an empirical constant, E is the elastic modulus, z0 is the difference between the mold thickness (Hst) and maximum scoop depth (Λ) as defined in Figure B-5. Equation [B.3] models the squeegee curvature by applying a force equal to T(dz/dy)
along the squeegee edge which results in a squeegee shape similar to that shown in Figure B-5.6

\[
T \left( \frac{\partial^2 z}{\partial y^2} \right) - \frac{E}{L} (z - z_0) = 0
\]  

[B.3]

By applying the geometric boundary conditions, \( z = H_{st} \) at \( y = \pm A/2 \), the dishing or scooping profile is obtained and given in equation [B.4], where the \( \beta \)-parameter is equal to \( (E/LT)^{1/2} \), \( E \) is the elastic modulus, and \( L \) is the vertical distance between the application of vertical force and the squeegee tip.6

\[
z = \frac{H_{st} - z_0}{\cosh(\beta y)} \cosh(\beta A/2) + z_0
\]  

[B.4]

The effect of the \( \beta \)-parameter on the dishing profile is shown in Figure B-6 for a constant maximum dishing depth \( (H_{st} - z_0 = \Lambda) \) of 4.5 µm and mold width \( (A) \) of 30 µm. Figure B-6 only captures the effect of the empirical parameter \( T \), since the elastic modulus \( (E) \), and squeegee height \( (L) \) are effectively held constant since these variables also affect the scooping depth \( (\Lambda) \) for a given applied force, which was held constant. Equation [B.4] can be used to fit the optical profilometry data for the LM-RIF process to determine the \( \beta \)-parameter for the squeegee used to fill the mold cavities described in Chapter 4. Figure B-7 shows the curve fits to optical profilometry data of filled mold cavities. The maximum dishing depth \( (H_{st} - z_0) \) and mold width \( (A) \) was measured for each mold cavity using the optical profilometry data and then held constant in the fit equation. The data was fit using the \( \beta \)-parameter and the translational constants, \( z_o \) and \( y_o \), to correct for the baseline of the profilometer. For the five curve fits in Figure B-7, the \( \beta \)-parameter was 0.24±0.07 µm\(^{-1}\) compared to 0.013 µm\(^{-1}\) for the \( \beta \)-parameter in Mannan et al. This order
of magnitude difference arises from the empirical T constant since the elastic modulus and squeegee height, L, should be similar since the squeegees have approximately the same hardness and are made from the same material, polyurethane. Therefore, this model as limited applicability since the T constant is empirical and the results state the obvious result that a softer squeegee will deform more. Additionally, the human factor in the LM-RIF process limits the utility of improving the model since the model parameters are be highly variable.

Figure B-4: The geometric variables in the Mannan et al. model for the scooping of paste by a squeegee from an aperture are shown here. This image was taken from Mannan et al.6

Figure B-5: The geometric variables in the Mannan et al. model showing dishing.6
Figure B-6: The effect of the $\beta$-parameter given in equation [B.3] is shown for the geometry of a mesoscale 30 $\mu$m wide, 24 $\mu$m deep bend bar mold cavity.
Although the Mannan et al. model shows that dishing can be limited by changing the squeegee parameters, the balance between obtaining conformal contact and...
minimizing squeegee deformation into the mold will always result in either dishing or an over layer of suspension over the mold. Of course, squeegee deformation is less important for thicker molds since 4 µm of dishing in a 400 µm mold is only 1% of the thickness versus 24% in a 17 µm thick mold. However, dishing becomes very significant for molds with a large area such as those shown in Figure B-8. The transmission optical images in Figure B-8 show that as the mold width increases for the same mold length (400 µm), dishing is deeper in the wider parts as evidenced by the increase in transmitted light through the wider samples. Therefore, if parts with a high area to thickness ratio are to be made reliably, dishing has to be minimized. The engineering solution of buffing described in Chapter 5 is not likely to be as effective in wide area parts that do not have large areas of solid SU8 to reduce the pressure. In Appendix A these large areas would likely result in the thermolysis cracks shown in Figure A-1. Another solution of sealing the top of the molds was tried unsuccessfully; however sealing has the potential to not only improve dishing for high area molds but also improve the roughness, therefore, the strength of the parts.
B.4 Sealing the Mold Cavities

In this experiment, 25 µm thick molds were cast as described in Chapter 4, then, a top layer of mylar film was applied that effectively seals the mold. The molds were then dried and the top layer of mylar was removed prior to sintering. A glass layer was also tried but resulted in suspension deposited overtop of the mold surface in the lower sections of the mold surface since the glass is less conformal. Ultimately, bubbles were trapped under the mylar and incorporated into the parts. Additionally, the pressure gradients created under the flexible mylar film resulted in bulk fluid flow between the mold cavities, which emptied some cavities and overfilled others. Drying cracks were also prevalent in the mylar coated samples. Figure B-9 shows the defects produced by
the mylar seal. The surface covering was therefore abandoned in favor of the buffing approach since the buffing process did not produce additional defects and significantly reduced dishing to less than 1 \( \mu \text{m} \). However, the mylar film did produce very smooth upper surfaces (Green part \( R_q < 100 \) nm, \( R_t < 500 \) nm) in the parts as shown in Figure B-10. If large area parts are produced, then the sealed mold cavities should be further explored.

Figure B-9: This optical image in transmission shows defects that are typical when a mylar film or other surface layer is applied to the filled mold cavities. Drying cracks and bubbles are prevalent throughout the parts. Each bend bar mold shown is approximately 415 \( \mu \)m long.
Figure B-9: The height of the green parts while still in the mold cavities was measured by optical profilometry. The graph shows the height of the line scans depicted in the images below the graph for cavities that were filled and then buffed versus cavities that were filled and then sealed with a mylar film. The surfaces of the mylar sealed bend bars after the mylar is removed are much smoother than the buffed surfaces. It must be noted that the profilometer scan for the mylar sealed bend bars shown here was atypical in that no cracking or bubbles were seen. The colors in the contour plots are not consistent with each other in terms of the height scale.
Appendix C

Sintering of macroscale zirconia

C.1 Introduction

The grain size of mesoscale parts was measured and analyzed in Chapter 5. This appendix summarizes the grain size of identically processed macroscale samples of the same 3Y-TZP material.

The procedure for fabricating macroscale specimens is the same as that described for the mesoscale specimens in Chapter 5, with the exception that a larger mold was used. The heat treatments were identical for the mesoscale and macroscale samples including the 1200°C / 1hr pre-firing, and the heat treatments on the macroscale samples occurred in the same furnace run as the mesoscale samples. Macroscale and mesoscale samples were also heat treated at 1500°C for 1, 8, and 16 hours, but the mesoscale samples were microcracked from spontaneous tetragonal to monoclinic phase transformation and were therefore not mechanically tested in Chapter 5. The macroscale samples were mechanically polished using SiC paper with grit sizes progressing in order of 180, 320, 400, 600 grit followed by 3 μm, 1 μm, and 0.5 μm diamond slurry polishing. The grain boundaries were thermally etched at 1300°C for 30 minutes at a heating rate of 10°C/min. The linear intercept method was used to measure the grain size.

Figures C-1 and C-2 compare the grain size of the mesoscale samples (sintered surface images) to that of the macroscale samples sintered identically at 1400°C and 1500°C. Large grains, characteristic of exaggerated grain growth, can be seen in the
1400°C / 16 hr and 1500°C / 1, 8, 16 hr samples. Figure C-3 quantifies the grain growth in the macroscale samples. The binning and log-normal fitting was completed using the same method as described in the Materials and Methods section of Chapter 5. The log-normal equation used to fit the binned linear intercept data is given in Equation [C.1], where $F$ is the fractional frequency, $A$ is the area of the distribution, $w$ is the standard deviation or a measure of the distribution width, $G_{\text{avg}}$ is the average grain size, and $G$ is the grain size at the center of the bin.

$$F = \frac{2A}{wG\sqrt{2\pi}} e^{-\left(\ln\left(\frac{G}{G_{\text{avg}}}\right)\right)^2 / 2w^2}$$

Table C-1 summarizes the linear intercept distribution statistics for the macroscale specimens (polished and etched) and mesoscale specimens (focused ion beam polished) as a function of sintering temperature and time. There is a statistically significant difference to the 0.05 level between the average linear intercept distance of the mesoscale and macroscale specimens for all three isothermal soak times at 1400°C. However, the mean intercept distance is longer for the 1 hr macroscale specimen versus the mesoscale specimen, but shorter for the 8 hr and 16 hr specimen. The grains in the mesoscale specimen are slightly smaller than the macroscale specimen at 1 hr, but grow at a faster rate. Table C-2 summarizes the log-normal distribution fits to the binned linear intercept data. The standard deviation parameter ($w$) is similar between soak times within a particular soak temperature for the macroscale specimens, with the possible exception of the 1500°C / 8 hr parameter although the adjusted $R^2$ value is notably higher for this fit.
The similarity between the distribution widths supports the assertion that abnormal grain growth did not occur in the macroscale samples.
Figure C-1: A comparison between the grain size of mesoscale and macroscale specimens sintered at 1400°C. The mesoscale images are of the sintered surface and macroscale images are of a polished and thermally etched surface. Exaggerated grain growth is only observed in the 16 hr soak time mesoscale specimen.
Figure C-2: A comparison between the grain size of mesoscale and macroscale specimens sintered at 1500°C. The mesoscale images are of the sintered surface and macroscale images are of a polished and thermally etched surface. Exaggerated grain growth is visible in all the mesoscale samples and none of the macroscale samples.
Figure C-3: The binned linear intercept grain size distribution is log-normal. The frequency has been normalized so the sum of the bars in an individual histogram is 100. The linear intercept distance statistics are given in Table C-1 and the log-normal fit parameters are given in Table C-2.
Table C-1: A summary of the grain size intercept statistics for macroscale and mesoscale samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>log t (log hrs)</th>
<th>N total</th>
<th>Mean Size (µm)</th>
<th>Standard Deviation (µm)</th>
<th>Lower 95% CI of Mean (µm)</th>
<th>Upper 95% CI of Mean (µm)</th>
<th>Minimum (µm)</th>
<th>Median (µm)</th>
<th>Maximum (µm)</th>
<th>Avg. Intercept dist. x1.558 (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro</td>
<td>1400C/1hr</td>
<td>0.0</td>
<td>744</td>
<td>0.205</td>
<td>0.092</td>
<td>0.199</td>
<td>0.212</td>
<td>0.037</td>
<td>0.194</td>
<td>0.736</td>
</tr>
<tr>
<td>Macro</td>
<td>1400C/8hr</td>
<td>0.9</td>
<td>807</td>
<td>0.276</td>
<td>0.126</td>
<td>0.268</td>
<td>0.285</td>
<td>0.039</td>
<td>0.264</td>
<td>0.770</td>
</tr>
<tr>
<td>Macro</td>
<td>1400C/16hr</td>
<td>1.2</td>
<td>814</td>
<td>0.327</td>
<td>0.156</td>
<td>0.317</td>
<td>0.338</td>
<td>0.046</td>
<td>0.314</td>
<td>1.083</td>
</tr>
<tr>
<td>Macro</td>
<td>1500C/1hr</td>
<td>0.0</td>
<td>789</td>
<td>0.331</td>
<td>0.153</td>
<td>0.320</td>
<td>0.341</td>
<td>0.049</td>
<td>0.311</td>
<td>1.005</td>
</tr>
<tr>
<td>Macro</td>
<td>1500C/8hr</td>
<td>0.9</td>
<td>332</td>
<td>0.523</td>
<td>0.266</td>
<td>0.494</td>
<td>0.551</td>
<td>0.070</td>
<td>0.502</td>
<td>1.348</td>
</tr>
<tr>
<td>Macro</td>
<td>1500C/16hr</td>
<td>1.2</td>
<td>152</td>
<td>0.629</td>
<td>0.303</td>
<td>0.581</td>
<td>0.678</td>
<td>0.142</td>
<td>0.591</td>
<td>1.465</td>
</tr>
<tr>
<td>Meso</td>
<td>1400C/1hr</td>
<td>0.0</td>
<td>164</td>
<td>0.166</td>
<td>0.071</td>
<td>0.155</td>
<td>0.177</td>
<td>0.045</td>
<td>0.161</td>
<td>0.414</td>
</tr>
<tr>
<td>Meso</td>
<td>1400C/8hr</td>
<td>0.9</td>
<td>230</td>
<td>0.319</td>
<td>0.135</td>
<td>0.302</td>
<td>0.337</td>
<td>0.067</td>
<td>0.306</td>
<td>0.849</td>
</tr>
<tr>
<td>Meso</td>
<td>1400C/16hr</td>
<td>1.2</td>
<td>72</td>
<td>0.419</td>
<td>0.246</td>
<td>0.361</td>
<td>0.477</td>
<td>0.101</td>
<td>0.404</td>
<td>1.486</td>
</tr>
</tbody>
</table>

Table C-2: A summary of the log-normal distribution fitting parameters.

<table>
<thead>
<tr>
<th>Sample</th>
<th>( G_{avg} ) (µm)</th>
<th>Std. Error ( G_{avg} )</th>
<th>( w ) (µm)</th>
<th>Std. Error ( w )</th>
<th>( A )</th>
<th>Std. Error ( A )</th>
<th>Adjusted ( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macro</td>
<td>1400C/1hr</td>
<td>0.196</td>
<td>0.010</td>
<td>0.572</td>
<td>0.035</td>
<td>10.786</td>
<td>0.617</td>
</tr>
<tr>
<td>Macro</td>
<td>1400C/8hr</td>
<td>0.272</td>
<td>0.015</td>
<td>0.554</td>
<td>0.062</td>
<td>10.411</td>
<td>0.876</td>
</tr>
<tr>
<td>Macro</td>
<td>1400C/16hr</td>
<td>0.326</td>
<td>0.012</td>
<td>0.521</td>
<td>0.035</td>
<td>10.068</td>
<td>0.572</td>
</tr>
<tr>
<td>Macro</td>
<td>1500C/1hr</td>
<td>0.325</td>
<td>0.011</td>
<td>0.530</td>
<td>0.032</td>
<td>10.167</td>
<td>0.526</td>
</tr>
<tr>
<td>Macro</td>
<td>1500C/8hr</td>
<td>0.521</td>
<td>0.053</td>
<td>0.687</td>
<td>0.076</td>
<td>21.887</td>
<td>2.158</td>
</tr>
<tr>
<td>Macro</td>
<td>1500C/16hr</td>
<td>0.632</td>
<td>0.046</td>
<td>0.605</td>
<td>0.072</td>
<td>21.171</td>
<td>1.928</td>
</tr>
<tr>
<td>Meso</td>
<td>1400C/1hr</td>
<td>0.167</td>
<td>0.011</td>
<td>0.496</td>
<td>0.058</td>
<td>5.190</td>
<td>0.522</td>
</tr>
<tr>
<td>Meso</td>
<td>1400C/8hr</td>
<td>0.329</td>
<td>0.015</td>
<td>0.463</td>
<td>0.039</td>
<td>10.182</td>
<td>0.761</td>
</tr>
<tr>
<td>Meso</td>
<td>1400C/16hr</td>
<td>0.426</td>
<td>0.053</td>
<td>0.708</td>
<td>0.077</td>
<td>21.682</td>
<td>2.377</td>
</tr>
</tbody>
</table>
C.2 Exaggerated Grain Growth in Y-TZP

In Chapter 5, it is proposed that a Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ eutectic forms a liquid phase that promotes exaggerated grain growth. The Y$_2$O$_3$-Al$_2$O$_3$-SiO$_2$ is reproduced in Figure C-4. An isothermal 1400°C section shows that a composition centered at 12Y$_2$O$_3$-22Al$_2$O$_3$-66SiO$_2$ by mol% melts at 1371°C. If the hypothesis that the eutectic phase is responsible for grain growth is true, then different grain growth kinetics can be expected between the mesoscale and macroscale specimens. Figure C-5 shows the average grain size ($G_{avg}$ by fit) as a function of sintering time. The average grain size is not affected significantly by the few exaggerated grains in the 1400°C / 16 hr specimen since the matrix grains far outnumber the exaggerated grains and dominate the average. The grain growth kinetics of the mesoscale specimens are faster than the macroscale specimen at 1400°C, showing a $t^{1/3.0}$ dependence versus a $t^{1/5.6}$ for the macroscale specimen. A grain growth exponent (n) of 5.6 is large, but not unreported for 3Y-TZP material from the same manufacturer. Mazaheri et al. report a grain growth exponent of 6 for 3Y-TZP and suggest the fine initial particle size may be responsible. However, the most likely explanation is that the difference between $G_0$ and G is not large enough in the macroscale samples to provide an accurate estimation of n, which has been shown to yield larger values of n. A ratio of $G/G_0$ of 3 or greater has been recommended for determining n, which was not satisfied in the macroscale specimen.
Figure C-4: The upper $Y_2O_3$-$Al_2O_3$-$SiO_2$ phase diagram taken from Bondar and Galakhov\(^8\) shows the terenary eutectic phase is 12$Y_2O_3$-22$Al_2O_3$-66$SiO_2$ by mole (the diagram is in weight percent) marked by a red “x.” The lower $Y_2O_3$-$Al_2O_3$-$SiO_2$ phase diagram taken from Kolitsch et al. shows the extent of liquid phase formation at 1400°C and is plotted in mole percent.
Normal grain growth is driven by a reduction in chemical potential between atoms on different sides of a curved grain boundary. The difference in chemical potential, shown as pressure ($P$) is given by equation [C.1], where $\gamma_{gb}$ is the grain boundary energy, and $r_1$ and $r_2$ are the principle radii of curvature.\textsuperscript{11}

$$\Delta P = \gamma_{gb} \left( \frac{1}{r_1} + \frac{1}{r_2} \right)$$ \hspace{1cm} [C.1]

The free energy is reduced as an atom jumps from the high potential side (concave) of a grain boundary to the low potentials side (convex). The rate that atoms jump is proportional to the radius of curvature, which is proportional to the grain diameter. Thus, the rate of grain growth ($d(d)/dt$) is given by equation [C.2], where $d$ is the grain diameter and $k$ is a constant.\textsuperscript{11}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure_c5}
\caption{The grain growth kinetics of mesoscale specimens are faster than those of comparable macroscale specimen.}
\end{figure}
On integration equation [C.2] yields the parabolic grain growth law given by equation [C.3] where \( d_0 \) is the initial grain size at time zero.\(^{11}\)

\[
d^2 - d_0^2 = Kt
\]  

\[ \text{[C.3]} \]

The constant \( K \) is equal to \( 2k \) in equation [C.2], and is the product of a geometric constant \( \alpha \), the grain boundary energy \( \gamma_{gb} \), and the grain boundary mobility \( M_b \).\(^{13,14}\)

The constant \( K \) has an Arrhenius relationship with temperature as given in equation [C.4] where \( Q \) is the activation energy for grain growth, \( T \) is temperature, \( R \) is the ideal gas constant, and \( K_0 \) is a constant.\(^{14}\)

\[
K = K_0 \exp\left(\frac{-Q}{RT}\right)
\]  

\[ \text{[C.4]} \]

Therefore, with the curvature of the grain boundary as driving force for grain growth, the grains should growth at a parabolic rate with time. However, this is rarely observed because of drag factors such as pores, inclusions, or solute mobility.

Exaggerated grain growth is the growth of a single grain at the expense of surrounding grains and may be facetted or un-facetted like the grain growth observed in this study. Although the origin of why a single grain is favored to grow over its neighbors is still an active area of research,\(^{15}\) the growth of the exaggerated grain can be described using Hillert’s model.\(^{16}\) Hillert proposes three conditions for exaggerated grain growth.\(^{16}\)

1. Normal grain growth cannot take place due to the presence of second phase particles (or solute drag).
2. The average grain size is below the limit \( 1/2z \) (an abnormal grain must be at least twice the average grain size).
3. There is at least one grain much larger than the average.

However, simulations have shown that even if a grain larger than twice the average grain size is present, it does not grow abnormally if the grain boundary energy and mobility are the same for the abnormally large grain and the matrix grains.\textsuperscript{17} Thus, exaggerated grain growth only occurs if the large grain has a higher mobility or lower grain boundary energy than the surrounding grains.\textsuperscript{14}

In order to verify the cause of the exaggerated grain growth in the mesoscale specimen a detailed chemical analysis of the grain boundary phase would have to be completed, which is beyond the scope of this work since exaggerated grain growth does not occur for short soak times at 1400°C where the finest grain size is achieved and also the highest strength.

Appendix References


VITA

Nicholas E. Antolino

Nicholas Antolino was born in Doylestown, PA on September 19th 1978. He attended Old Saybrook Senior High School in Connecticut and graduated with high honors in 1996. After high school, Nicholas attended the New York State College of Ceramics at Alfred University until 2001. During his time at Alfred, Nicholas worked as a Co-op and again as a summer intern for Pratt & Whitney in East Hartford, CT. In 2001, Nicholas graduated from Alfred University *magna cum laude* with a B.S. degree in Ceramic Engineering. From Alfred, Nicholas joined Saint-Gobain Abrasives Research and Development in Worcester, MA as a Development Engineer. Nicholas left Saint-Gobain in 2004 as a Research Engineer to pursue a Ph.D. in Materials Science and Engineering at The Pennsylvania State University under the tutelage of Prof. James H. Adair. Prior to developing the LM-RIF process, Nicholas studied the chemically aided attrition milling of mixed phase alumina, the glycothermal synthesis of alpha-alumina, and the drying of hydrothermally synthesized zirconia.