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THE FABRICATION OF MULTILAYER CERAMIC – METAL LAMINATES

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ABSTRACT

As surgical techniques advance, surgical instruments must advance alongside them. Recent advances in minimally invasive surgeries require the use of an endoscope, which must contain precise, specialized surgical instruments fabricated at the mesoscale. These instruments are often made from stainless steel or yttria-stabilized zirconia, but these materials have inherent flaws. The aim of this thesis is to develop a steel-zirconia layered composite to optimize the mechanical properties of these surgical instruments. This composite was developed using a tape casting procedure. Non-aqueous steel and zirconia tape casting slurries were developed and cast as tapes. These tapes were laminated into a composite structure, binder was removed from the part through thermolysis, and the composite was sintered. Because the binder was removed from the composite in air, the steel layers were oxidized. This metal oxide was then partially reduced during sintering in forming gas. This oxidation and reduction led to delamination of the steel and zirconia layers. Another potential cause of delamination is stress at the steel-zirconia interface due to thermal expansion mismatch, strain on the tapes due to the tape casting process, or differing shrinkage rates during sintering of steel and zirconia. These, and many other, issues must be resolved before a mesoscale surgical instrument can be successfully fabricated from a multilayer steel-zirconia composite, but the work done in this thesis will provide a starting point for future work in the area.
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CHAPTER 1

Introduction

In the world of modern medicine, one of the primary goals is to minimize the risk a patient undergoes during a surgical procedure. Many formerly risky procedures have been updated to be minimally invasive, to reduce the risk of infection during surgery and decrease recovery time. These surgeries require precise instrumentation on the scale of microns to millimeters. Such mesoscale (defined by dimensions between 10μm and 1mm) instruments are often created from stainless steel or zirconia, but the single component materials have inherent limitations. The goal of this thesis is to evaluate the feasibility of fabricating steel and zirconia layered structures using a tape casting process to create a layered structure of the two materials. There are many property differences between steel and zirconia, not least of which is the thermal expansion coefficient and the thermophysical properties that control the particulate sintering process for the two materials. It will be demonstrated that tape casting is feasible, but the lamination and sintering processes are complicated and until properly optimized, delamination and macroscopic defects resulting from constrained sintering of the multilayer materials are typical of multilayer steel – zirconia materials.

Section 1.1 Literature Review

Section 1.1.1 Surgical Instruments

Many traditional minimally invasive surgeries are performed by creating a small incision in the patient. These surgeries utilize instruments that are long enough to reach the intended area of the body while being slim enough to minimize damage from the surgery. These surgeries are effective in lowering risk and reducing recovery time; however, a new, even less invasive
technique is being developed that will be applicable to certain procedures. This is called Natural Orifice Translumenal Endoscopic Surgery, or NOTES. NOTES uses the body’s natural orifices to perform procedures without making any external incisions. One such procedure, removal of the gall bladder through the esophagus and buccal cavity, is shown in Figure 1.1 [1].

Figure 1.1. Diagram demonstrating removal of the gallbladder through the esophagus and buccal cavity using natural orifice translumenal endoscopic surgery (NOTES) [1]. NOTES permits surgical interventions with minimally invasive procedures with shorter hospital stays and overall recovery time.

There are a series of medical and technological barriers that must be overcome before NOTES is widely useable in humans [2]. The increased complexity of these procedures requires continual advancement in endoscope design and technology [3]. Typical endoscopic surgical termination diameters range from 0.5 to 1.5 cm. Endoscopes house an optical camera as well as
one or, at most, two instruments selected for a particular procedure such as grasping, cauterization, retracting, etc. of a variety of instruments, which vary depending on the surgical procedure being performed. An example of one type of endoscope is shown in Figure 1.2, and a typical design for forceps designed at Penn State [4] to be included in an endoscope is shown in Figure 1.3.

Figure 1.2. Flexible endoscopes have diameters between 0.5 cm and 1.5 cm, depending on the intended use. The instruments contained within the endoscope are on the millimeter scale or smaller [3]. The instrument on the left is a grasping tool, similar to the forceps shown in Figure 1.3. The reference does not indicate the function of the instrument on the right, but it may be a suturing instrument.
Figure 1.3. Demonstration of a typical design for forceps to be included in a flexible endoscope. The forceps are closed or opened by extending or retracting the outer sheath indicated at the distal end of the instrument from the working end of the instrument [4].

The small scale of the endoscope requires instruments with specific designs tailored to the use of flexible endoscopes that are capable of extreme precision. The instruments also must withstand the relatively harsh physiological environment. Two typical instrument materials are stainless steel and zirconia. However, instruments fabricated from these materials have inherent limitations imposed by the respective material properties. A selection of property data for stainless steel and zirconia is shown in Table 1.1. Using the forceps design shown in Figure 1.3 as an example, a zirconia part could catastrophically fracture upon actuation, due to low damage tolerance with a fracture toughness in the 4 to 12 MPa m$^{1/2}$ range. The tips of the forceps may sag in a steel part, due to the lower elastic modulus of steel of 100 GPa in contrast to the higher elastic modulus of zirconia at 200 GPa, see Table 1.1 [5, 6].
Table 1.1. Bulk mechanical properties of stainless steel and zirconia. Stainless steel and zirconia are commonly used in the fabrication of endoscopic surgical instruments. A layered structure featuring stainless steel and zirconia should, in theory, combine the higher elastic modulus of zirconia with the higher fracture toughness of steel and be more ideal for mesoscale surgical instruments [7].

<table>
<thead>
<tr>
<th>Property</th>
<th>Stainless Steel*</th>
<th>Zirconia**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal Expansion Coefficient (K⁻¹)***</td>
<td>$17.5 \times 10^{-6}$ at 600K</td>
<td>$10.1 \times 10^{-6}$ at 600K</td>
</tr>
<tr>
<td>Elastic Modulus (GPa)</td>
<td>100</td>
<td>200</td>
</tr>
<tr>
<td>Fracture Toughness (MPa m¹/²)</td>
<td>50-170</td>
<td>4-12</td>
</tr>
<tr>
<td>Fracture Strength (MPa)</td>
<td>485-570</td>
<td>900-2,400**</td>
</tr>
</tbody>
</table>

** Bend strength values from Ashby [5] and Antolino et al. [9]
*** Thermal expansion values from Yeo (steel) [10] and Hayashi (zirconia) [11].

To compensate for the material limitations inherent to the monolithic materials, a laminated multiple layer composite of steel and zirconia could present a desirable combination of properties if the processing issues in making such a laminated structure could be overcome. In theory, the steel will bridge any cracks that form in the zirconia, preventing the part from failing [7]. The zirconia, meanwhile, should increase the overall elastic modulus, permitting the fabrication of high aspect ratio instruments such as the forceps shown in Figure 1.3. This laminated composite material would have a greater damage tolerance due to the more ductile steel, making the composite, at least in principle, ideal for use in endoscopic surgical instruments. However, the processing of multilayer laminates is not trivial. Not only is the sintering temperature generally lower for metals such as 316L stainless steel at 1,300 °C relative to the 3 mole percent yttria-stabilized zirconia at 1,400 °C (Hayes, Ph.D. Dissertation, 2011, pp. 57-59) [8], but the coefficient of thermal expansion is quite different ($17.5 \times 10^{-6}$ at 600K for stainless steel versus $10.1 \times 10^{-6}$ at 600K for yttria-stabilized zirconia, Table 1.1). The CTE mismatch can lead to strains high enough in the sintered material that delamination will take place between the different material layers. One of the processing modifications that permit
overcoming some of the thermal and physical differences between the two materials is to use a lower density in the metal particulate layers to compensate for the tendency of the metal to sinter at lower temperatures than the ceramic. However, such a broadly based study is beyond the scope of the current thesis. The more modest processing goals include the fabrication of dense tape cast metal and ceramic layers, and an evaluation as to whether the dense layers can be processed as prepared or if there is a need to use processing strategies such as deceasing the packing density in the metallic layers to minimize defects in the sintered materials.

**Section 1.1.2 Tape Casting**

The science of colloidal and interfacial chemistry is critical to wet powder processes such as tape casting [12-15]. The ceramic or metal particles in a tape casting slurry must be well dispersed to prevent the particles from agglomerating and settling out of suspension. The tape casting slurry must also include a binder, to impart flexibility and strength to the green ceramic parts. A final additive to a tape casting slurry is a plasticizer, which decreases the glass transition temperature of the binder so the tape is flexible at room temperature. There can be overlap among the various organic additive functions. For example, a binder can serve as a dispersant, or a dispersant as a plasticizer [13].

A variety of chemicals can be added to serve as a dispersant by modifying interparticle forces [15]. As the particle size of the solid powder decreases, the surface area of the particles increases, increasing the amount of dispersant needed for particulate surface coverage and dispersion of the particles. Long chain molecules which adsorb to the surface of the solid particles are often used, and function as shown in Figure 1.4 [14]. These molecules provide a repulsive force strong enough and long range enough into the bulk solution between interacting particles to overcome the attractive van der Waals forces between particles.
Figure 1.4. Steric stabilization of particles in a colloidal suspension. The polymer, typically at a MW of approximately 15,000, adsorbs to the surface of the particle, interacting and overcoming the attractive van der Waals energy between the particles to maintain the particulate in a dispersed state in the suspension [14].

The organic binder is another category of polymer that is included in a tape casting slurry. Binders are usually high molecular weight polymers with long chain molecules [13]. The binder is soluble in the chosen solvent for the slurry. Addition of binder changes the rheology of the suspension, decreasing both Bingham yield point and viscosity, to yield a shear thinning suspension as shown in Figure 1.5 that permits tape cast formation.

Tapes are usually cast onto a polymer sheet such as Mylar, which is polyethylene terephthalate coated in silicone. The slurry must wet the surface of the Mylar, to create a uniform sheet of the specified thickness. Binder often serves as a wetting agent, modifying the contact angle of the slurry on the carrier film to wet the desired surface [13]. Binder also modifies the viscosity of the slurry, making the suspension shear thinning as shown in Figure 1.5, with viscosity decreasing with increasing shear rate. The shear thinning behavior permits the slurry to be cast by passing it under a blade, while ensuring that after it has been cast (and therefore the shear removed) the Bingham yield point (Figure 1.5) is high enough for the tape to
retain the cast shape and dimensions.

**Figure 1.5.** Typical rheological data for tape cast ceramic suspensions. (Top) Shear stress vs. shear rate for a ceramic suspension with a Bingham yield point, \( t_B \), at \( \sim 10 \text{dyn/cm}^2 \). (Bottom) The viscosity vs. shear rate for the same ceramic suspension showing that the definition for apparent viscosity in the current work is the viscosity at high shear rate extrapolated to zero shear rate. The suspension shown is shear thinning with shear rate decreasing and viscosity decreasing as a function of increased shear rate. The combination of a Bingham yield point and shear thinning behavior with relatively low viscosity (apparent viscosity is equal to about 60cP at high shear rates) means that the tape cast process can be used for this suspension with minimal dimension change for the cast tape as well as control over the thickness of the cast tape via the doctor blade apparatus shown in Figure 2.3. (Data from J.H. Adair, private communication) [16].
The amount of binder in a suspension is critical. If too little binder is included, the tape will develop cracks upon drying, due to inadequate polymer interconnectivity. If too much is included, the ceramic will have voids upon binder burnout from regions of higher organic binder concentration in the tape [13]. An important addition to a suspension is a plasticizer. The plasticizer modifies the glass transition temperature of the binder, softening the binder below 25 °C. While the binder imparts strength to the tape for handling during the lamination and dicing steps, the plasticizer makes the tape flexible and plastic, ensuring it can be handled with minimal defects and to promote plastic flow during the lamination process. In most aqueous and non-aqueous processes, the powder, solvent and dispersant are mixed and then milled for specified time to a specific surface area, usually determined via particle size distribution analysis. Following milling, plasticizer and binder are added and the slurry further mixed while still in the mill. Mill media is separated from the slurry by passing through a screen. The slurry is then cast by passing it under a doctor blade, which passes over a carrier material, often a sheet of polymer coated with silicone. Drying kinetics is a complicated science, which will not be explored in depth here. A mechanical model of drying is explained in detail by Scherer [17], but is beyond the scope of the current study.

Dried tape is cut and stacked into the desired shape of the final product. The stacked tapes are then laminated, using a combination of warm pressing and uniaxial pressure. A typical temperature and pressure are 70 °C and 2000 to 3000 psi [12]. The lamination process ensures mechanical integrity of the multilayer structure with intimate contact among the layers to, at least theoretically, improve the quality of the final sintered part. After lamination, the binder is removed by thermolysis. The material is heated, often in air, but sometimes in a more inert atmosphere such as nitrogen if the metal is prone to oxidation at the burnout temperature, to the point where the polymer additives combust, leaving an unsintered body with no polymer
Following binder removal, the part is sintered. The part is heated to high temperatures, typically in the range of 1100 °C to 1500 °C, which densifies the material through a three-step process [16]. These steps are neck formation between particles, bulk densification from about 75% theoretical density (TD) to about 93%TD, and final densification to greater than 99%TD. The initial sintering stage, neck formation, is characterized by surface diffusion to form necks among the sintering particulates with no bulk densification. The intermediate stage is characterized by bulk diffusion processes that eliminate particulate surfaces. During intermediate sintering, grain growth (i.e., grain boundary diffusion) competes with bulk diffusion eliminating open porosity. The final stage of densification above about 93%TD where isolated pores are obtained in the microstructure is characterized by grain boundary diffusion with eventual, but difficult, elimination of pores at triple points in the microstructure [18].

**Section 1.2 Research Considerations**

**Section 1.2.1 Manufacturability**

Instruments for minimally invasive surgery must be extremely precise and reliable. As such, the manufacturing techniques used to fabricate them must be equally precise. The fabrication techniques described in this document were all performed on a lab scale. Tape casting, however, is a process that is easily expanded to a much larger scale, simply through utilization of equipment that permits longer tapes and handling equipment for larger numbers of parts. Similarly, the slurries used for tape casting are all based on volume and weight percent, and as such can be readily formulated in larger batches. The fabrication and lamination of the multi-layered steel-zirconia structure is directly scalable from lab to industrial scale, and would certainly be feasible. As a metric for the scalability of the process, over 50 billion multilayer
capacitors are annually manufactured by the process used in this thesis [12].

Section 1.2.2 Economic Issues

The raw materials used in fabrication of the steel-zirconia layered composite vary in price. Stainless steel powders relatively expensive at over $100/kg, but zirconia powders are less expensive at about $20US/kg and readily available, as are the myriad solvents and organic materials used. Tape casting equipment has a large up-front cost on the order of $50,000US, but operating costs are very low. Overall, tape casting is an economically viable method of fabricating a layered ceramic-metal composite on a large scale as exemplified by the large number of multilayer capacitors fabricated that range from a few $0.01US to several dollars for each of the over 50 billion manufactured annually.

Section 1.2.3 Health, Safety and Ethical Issues

One of the motivations to develop the multilayer ceramic-metal composite is to create better non-invasive surgical instruments. These instruments, combined with the more advanced medical procedures they would enable, could drastically lower the risk associated with surgical procedures, as well as the time needed to recover from surgery. These instruments would go a long way towards helping NOTES through clinical trials, making sure it is safe and ethical for use in humans.

During formulation of the slurries, various organics and solvents are used. Some of these are harmful if inhaled in large quantities, so care must be taken with proper ventilation and collection of the fumes. In a laboratory setting, much of the preparation of the steel slurry in particular is done in a fume hood, due to the presence of xylenes, which are highly volatile and flammable. The zirconia slurry contains Darvan C, which includes ammonium polymethacrylate and can be harmful if inhaled. At a larger scale, fully robotic, completely
enclosed facilities can be used in which human interfaces with the manufacturing process are almost completely eliminated as used for the thermal conduction module manufactured by IBM in Fishkill, NY [16, 19] with minimal impact on the environment or personnel.

Section 1.2.4 Sustainability

One of the biggest drawbacks to tape casting is that it does not generally form a net shape for the product. For example, the surgical instrument fabrication requires a cutting operation after lamination for the complicated forceps shape in Figure 1.3. A large rectangular tape is created, and the end product is cut from this tape via one of a number of methods. The amount of wasted material can be minimized through clever placement of the ultimate components, but there will likely be some wasted material, which will either need to be disposed of, or a method for reusing waste materials will need to be developed for a specific material system. On the lab scale, some slurry is lost before tape casting, during the milling process, due to slurry adhering to the media. In an industrial setting, this loss would be minimized through utilization of a continuous milling process.

Section 1.2.5 Environmental Issues

Both the steel and zirconia slurries use organic components, which must be removed through a burnout process before the parts can be sintered. In an industrial setting, this would create some amount of pollution that would need to be dealt with via chemical scrubbers on the vent duct. As discussed in section 1.2.4, there is also some waste as a result of the fabrication of the surgical instruments from the laminated tape that needs to be disposed of or reused, but this waste can be minimized through efficient arrangement of the components.
CHAPTER 2

Materials and Methods

Section 2.1 Statement of Work

As minimally invasive surgical procedures evolve, more advanced and more precise surgical equipment is needed. The aim of this project is to develop a layered composite of steel and zirconia for future use in surgical instruments contained in endoscopes. The project plan is as follows:

1. Develop appropriate slurries for tape casting of 316L stainless steel and yttria-stabilized zirconia.

2. Cast the steel and zirconia slurries into tapes; assemble the tapes into a layered composite structure. Remove the binder from the layered composite and sinter it; examine the weight loss and volume shrinkage of the composite through these processing steps.

3. Examine the microstructure of the steel, zirconia and composite parts using optical microscopy.

4. Assemble the results of the study into a thesis and poster. Present the results at the Annual Student Awards Convocation on April 18, 2011 during the Material Science and Engineering Department Poster Competition.
Section 2.2 Materials and Equipment

The materials used in the completion of this thesis, as well as the sources of these materials, are as follows. 316L micro melt stainless steel powder was obtained from Carpenter Powder Products, Reading PA. TZ-3Y yttria-stabilized zirconia powder was obtained from Tosoh Corporation, Japan. 99-100% hydrolyzed polyvinyl alcohol was obtained from Kodak, Rochester NY. Polyvinyl butyral, Menhaden fish oil, polyalkylene glycol and polyethylene glycol-400 were obtained from Richard E. Mistler Inc. Tape Casting Warehouse, Reading, PA. Xylenes were obtained from J. T. Baker, Phillipsburg NJ. Butyl benzyl phthalate, ethanol and xylenes were obtained from Aldrich, Milwaukee WI. Darvan C was obtained from R. T. Vanderbilt Company, Inc, Norwalk, CT. 3 micron, 1 micron and 0.05 micron diamond slurries used in polishing were obtained from Allied High Tech Products Inc., Compton CA.

Particle size of milled zirconia powder was analyzed using a Brookhaven Instruments Corporation ZetaPlus Zeta Potential Analyzer, Brookhaven, NY. Tapes were cast on a Richard E. Mistler, Inc. Tape Caster, Reading PA. Tapes were laminated using a Carver Laboratory Press, Wabash IN. Parts were sintered in a CM Inc. Rapid Temp Furnace, Bloomfield, NJ. Sintered parts were mounted using an Allied High Tech Products Inc. TechPress 2, Compton CA. Mounted parts were polished using an Allied High Tech Products Inc. MetPrep 4, Compton CA. Samples were imaged using an Olympus BX60M optical microscope, Center Valley PA, with an attached Zeiss AxioCam MRc camera, Allied High Tech Products Inc., Reading PA. Samples were also imaged using a Zeiss Axiovert 200 MRT optical microscope, Allied High Tech Products, Reading PA, with an attached Zeiss AxioCam MRc.

Section 2.3 Experimental Procedure

Section 2.3.1 Steel Slurry and Tape

Steel-zirconia layered composites were prepared using a series of processing steps. A
diagram of the process is shown in Figure 2.1 [12]. First, steel and zirconia tape casting slurries were prepared. The resulting steel and zirconia slurries are cast as tapes, and then cut and stacked into components. These parts are laminated to form a green body, the organics are burned out, and the parts sintered. A procedure for creating multilayer ceramic capacitors was used as a model.

![Diagram of the processing steps for typical multilayer ceramic capacitor fabrication](image)

**Figure 2.1.** An overview of the processing steps for typical multilayer ceramic capacitor fabrication [12]. A similar process is used for this thesis, with the exception of the electroding, dicing and termination and lead attachment steps.

The first step in the fabrication process is to create individual steel and zirconia tapes. Before development of suitable tape casting slurries, the size of the particles was determined as particle size relates to surface area for the dispersed particles in suspension and affects the amount of dispersant needed. Particle size data for steel had been previously acquired by Hayes [8]. Steel particle size was analyzed using a sedimentation approach (Horiba CAPA 700, Irvine, CA) for as-received powder, after 1 hour of milling and after 20 hours of milling. This data,
along with SEM images of each of the powders, is shown in Figure 2.2.

**Figure 2.2.** (Top) Particle size distributions of the as-received 316L stainless steel powder, the particles after a 1 hour attrition mill, and after a 20 hour attrition mill. Data was obtained using a sedimentation approach (Horiba CAPA 700, Irvine, CA). The bottom row shows scanning electron microscope images corresponding to each of the particle size distributions.

A non-aqueous formulation for tape casting of nickel, taken from Mistler [20], was used as a starting point for a steel tape casting slurry. The formulation for the steel slurry developed is summarized in Table 2.1.
Table 2.1. Non-aqueous steel tape casting slurry formulation used in this thesis. It was adapted from a formula for tape casting nickel from Mistler [20]. The formulation is based upon a xylenes-ethanol solvent with the biologically derived dispersant, Menhaden fish oil, and polyvinyl butyral and butyl benzyl phthalate as binder and plasticizer, respectively.

<table>
<thead>
<tr>
<th>Slurry Formulation</th>
<th>Density (g/cm³)</th>
<th>Weight %</th>
<th>Volume %</th>
<th>Rel. Weight</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>316L SS powder</td>
<td>8</td>
<td>83.56</td>
<td>35.78</td>
<td>83.56</td>
<td>95.05</td>
</tr>
<tr>
<td>Menhaden fish oil</td>
<td>1</td>
<td>0.33</td>
<td>1.14</td>
<td>0.33</td>
<td>0.38</td>
</tr>
<tr>
<td>Xylenes</td>
<td>0.86</td>
<td>6.04</td>
<td>23.95</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.79</td>
<td>6.04</td>
<td>26.07</td>
<td>0</td>
<td>0.00</td>
</tr>
<tr>
<td>Butyl Benzyl Phthalate</td>
<td>1.12</td>
<td>2.01</td>
<td>6.16</td>
<td>2.01</td>
<td>2.29</td>
</tr>
<tr>
<td>Polyvinyl Butyral</td>
<td>1</td>
<td>2.01</td>
<td>6.9</td>
<td>2.01</td>
<td>2.29</td>
</tr>
</tbody>
</table>

Dry Tape: 4.95% Organic

In this slurry, Menhaden fish oil serves as the dispersant, polyvinyl butyral as the binder, and butyl benzyl phthalate as the plasticizer. Menhaden fish oil (MFO) is a biologically derived material, and as such can have considerable variation in properties among different batches [15]. The exact mechanisms through which MHO functions are not well understood, but it is highly effective in a wide variety of non-aqueous solvents. Xylenes are used as one of the solvents in this slurry due to Menhaden fish oil not being very soluble in ethanol, the preferred solvent in a non-aqueous system with wide availability and modest environmental impact. Polyvinyl butyral (PVB) is a common binder for use in non-aqueous systems, and butyl benzyl phthalate (BBP) is an effective plasticizer for PVB.

Initially, it was intended that the steel powder be attrition milled as opposed to ball milled, as attrition milling is a significantly more efficient milling process [21]. The Menhaden fish oil was dissolved in the xylenes, and the mixture added to the attrition mill along with the
316L stainless steel powder, ethanol, and 3 millimeter stainless steel milling media. The mixture was then milled for four hours. At this point, the VB and BBP were added, and the slurry milled for an additional 20 hours. After the 20 hours, the majority of the solvent had evaporated, leaving slurry too thick to successfully tape cast. To prevent solvent evaporation, ball milling was used in a sealed vessel.

The slurry was prepared in the ball mill based on the same formulation and milling times. The resulting slurry had the appropriate rheology for tape casting. Rheology data could not be obtained due to rapid evaporation of the solvent. The slurry was sieved, to separate the slurry from the milling media. The sieved suspension was then placed in a vacuum furnace and de-aired for 5 minutes at 30 cmHg. After stirring for an additional 30 additional minutes to remove any remaining air bubbles, the slurry was cast as a tape by pouring it onto a sheet of Mylar (polyethylene terephthalate coated in silicone) and passing it under a doctor blade. The gap between the doctor blade and the Mylar film was set to 0.356 millimeters. A typical tape casting setup is shown in Figure 2.3[12]. The tape was dried in air for approximately 12 hours.

![Figure 2.3](image.png)

**Figure 2.3.** A typical tape casting equipment featuring a double doctor blade apparatus to prepare colloidal films. The instrumentation shown is similar to the setup chosen for this experiment, though only one doctor blade was used [12]. The slip, or slurry, is passed under the doctor blade through the motion of the carrier film driven via a motorized chain.
Section 2.3.2 Zirconia Slurry and Tape Fabrication.

The initial goal for the zirconia suspension was to develop an aqueous tape casting slurry. The as-received powder was imaged using optical microscopy; an example of the powder is shown in Figure 2.4.

**Figure 2.4.** As-received Tosoh TZ-3Y yttria-stabilized (3 mole percent Y$_2$O$_3$) zirconia, optically imaged using an Olympus BX60M microscope. Average agglomerate size before milling is 60 microns [22].

Particle size data for milled zirconia powder was obtained using dynamic light scattering (DLS). The particle size distribution after 48 hours of ball milling is shown in Figure 2.5. Ball milling was effective at reducing the size of the particles; average agglomerate size before milling was 60 microns by volume, as found by Antolino et al. [22], while after 48 hours of ball
milling the average particle size is approximately 550 nm with a small percentage of the particles near 150 nm. In contrast, Antolino et al. [22] achieved a volume weighted average diameter at 120 nm using aqueous dispersion approaches based on an electrosteric dispersion mechanism. In the non-aqueous suspension, the steric approach does not yield the completely dispersed state, consistent with the more modest repulsive energy associated with steric vis-a-vis electrosteric dispersion [23].

![Size Distribution of Ball Milled 48h Tosoh Zirconia](image)

**Figure 2.5.** Particle size distribution of zirconia powder after 48 hours of ball milling. There is a large peak at approximately 550 nm, with a finer particle distribution centered at 150 nm. Milling produced a significant improvement from the large size in the as-received powder at about 60 μm, see Figure 2.4 [22].

The dispersant in the zirconia slurry was ammonium polymethacrylate, added in the form of Darvan C, R.T. Vanderbilt, Norwalk CT. The binder was 99-100% hydrolyzed polyvinyl alcohol (PVA) from Kodak, Rochester NY, and the plasticizer was polyethylene glycol 400 (PEG 400) from Richard E. Mistler Tape Casting Warehouse, Reading PA. The first slurry prepared contained 30% zirconia by volume, with 5% PVA relative to zirconia. Each of the following slurries features twice as much PEG 400 as PVA by weight, to properly plasticize
the system. The zirconia slurry formulations also feature 4 weight % Darvan C relative to zirconia. The high concentration of Darvan C is due to the relatively small zirconia particle size. The zirconia, water and Darvan C were added to a mill jar with 3-millimeter zirconia milling media and milled for four hours. The jar was removed from the mill, the PVA and PEG 400 added, and the slurry milled for another 20 hours. This slurry was so dispersed that a high enough apparent viscosity and Bingham yield point were not obtained with the slurry too fluid to be successfully tape cast, and also did not wet the Mylar sheet enough.

Therefore, to determine an appropriate solid loading and binder content for the aqueous zirconia tape casting slurry, a series of slurries were prepared. These slurries had solids loading of 30, 32, 35, 38 and 42 weight % zirconia with each containing 8% binder relative to zirconia by weight. A second series of slurries was also prepared, featuring PVA content relative to zirconia weight equal to 5, 7, 10, 15 and 20%. Each of these slurries contained between 30 and 35% zirconia solids loading. None of the slurries created was appropriate for tape casting; each had too low a viscosity and too low a Bingham yield point to retain their shape after being passed under the doctor blade. It was determined that a non-aqueous zirconia slurry should be developed as an alternate process.

The non-aqueous zirconia tape casting slurry was adapted from Mistler [20] and is summarized in Table 2.2. This formulation is similar to that used in the steel slurry, but with the addition of polyalkylene glycol (PAG) as a second plasticizer. It also features a higher percent of dispersant relative to solid, due to the smaller particle size of the zirconia as compared to the steel. The Menhaden fish oil was dissolved in the xylenes. The zirconia powder, ethanol, and xylenes-Menhaden mixture were added to a mill jar with 3 millimeter zirconia milling media. This mixture was milled for 20 hours, in order to properly coat the zirconia particles with dispersant. After this, the PVB, BBP and PAG were added, and the
slurry milled for an additional 20 hours. The slurry was sieved to separate the slurry from the milling media. It was de-aired in a vacuum furnace at a 25 cmHg vacuum for 5 minutes, and stirred for 30 minutes to remove any remaining air pockets. It was then cast as a tape on a Mylar sheet in a similar procedure to that used for the steel slurry, as shown in Figure 2.3. The blade gap set to 0.278 millimeters. The tape was then allowed to dry overnight.

Table 2.2. Non-aqueous zirconia tape casting formulation used in this thesis, adapted from Mistler [20]. The formulation is based upon a xylenes-ethanol solvent with the biologically derived dispersant, Menhaden fish oil. Polyvinyl butyral serves as the binder, and butyl benzyl phthalate and polyalkylene glycol serve as plasticizers.

<table>
<thead>
<tr>
<th>Slurry Formulation</th>
<th>Density (g/cm³)</th>
<th>Weight %</th>
<th>Volume %</th>
<th>Relative Weight</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yttria stabilized Zirconia Powder</td>
<td>6.05</td>
<td>61.83</td>
<td>19.54</td>
<td>61.83</td>
<td>89.13%</td>
</tr>
<tr>
<td>Menhaden fish oil</td>
<td>1</td>
<td>1.32</td>
<td>2.52</td>
<td>1.32</td>
<td>1.90%</td>
</tr>
<tr>
<td>Xylenes</td>
<td>0.86</td>
<td>15.3</td>
<td>33.85</td>
<td>0</td>
<td>0.00%</td>
</tr>
<tr>
<td>Ethanol</td>
<td>0.79</td>
<td>15.33</td>
<td>36.92</td>
<td>0</td>
<td>0.00%</td>
</tr>
<tr>
<td>Polyvinyl Butyral</td>
<td>2.49</td>
<td>3.08</td>
<td>2.36</td>
<td>3.08</td>
<td>4.44%</td>
</tr>
<tr>
<td>Butyl Benzyl Phthalate</td>
<td>1.25</td>
<td>1.56</td>
<td>2.38</td>
<td>1.56</td>
<td>2.25%</td>
</tr>
<tr>
<td>Polyalkylene glycol</td>
<td>1.25</td>
<td>1.58</td>
<td>2.42</td>
<td>1.58</td>
<td>2.28%</td>
</tr>
</tbody>
</table>

Dry Tape: 10.87%
Organic

Section 2.3.3 Lamination, Binder Removal and Sintering

After the steel and zirconia tapes were dry, the next step was to assemble steel, zirconia and steel-zirconia composite green bodies. The tapes were each cut into 1-inch squares using a razor blade. The thickness of the tapes was measured using calipers; the steel tape was 0.25 mm thick and the zirconia tape 0.10 mm thick. The squares were then stacked on top of each other. In an attempt to combat the strain put onto the tape during the tape casting process, which can
cause anisotropy in the sintered part [24], tapes were rotated 90° relative to the tape casting direction for alternating layers during stacking. The steel tape, labeled TC Steel, was stacked 10 layers thick; the zirconia tape, labeled TC Zirconia, was 20 layers thick. Two different composite structures were designed. One had a 1:1 ratio of steel tapes to zirconia tapes, layered in an alternating fashion; this was labeled TC Composite 1. The second composite had a 1:2 ratio of steel tapes to zirconia tapes; this was labeled TC Composite 2. After the parts were stacked, they were laminated to create a green body. The stacked parts were placed into a 1-inch square aluminum die. They were hot uniaxial pressed at 75 °C for 20 minutes at the lowest pressure at which the die would not shift in the press, just enough to slightly compact and laminate the green body. The pressure was low enough to not be registered by the meter on the press. The dimensions and weight of each part were measured. A summary of the parts fabricated for this thesis, using both tape casting and dry pressing, is shown in Table 2.3.
Table 2.3. A summary of designations used to refer to the parts fabricated during the course of this project. The tape cast steel and zirconia parts (TC Steel and TC Zirconia) were bisected after binder removal and the halves sintered under different conditions (half 1 of each sample was sintered for 2 hours at 1300 °C, half 2 for 4 hours at 1300 °C). Aside from the tape cast steel and zirconia samples, the designations remain consistent through each processing step (lamination, binder removal and sintering).

<table>
<thead>
<tr>
<th>Green Samples</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape Cast Steel Part*</td>
<td>TC Steel</td>
</tr>
<tr>
<td>Tape Cast Zirconia Part*</td>
<td>TC Zirconia</td>
</tr>
<tr>
<td>Tape Cast Composite Part 1</td>
<td>TC Composite 1</td>
</tr>
<tr>
<td>Tape Cast Composite Part 2</td>
<td>TC Composite 2</td>
</tr>
<tr>
<td>Dry Pressed Steel Part 1</td>
<td>DP Steel 1</td>
</tr>
<tr>
<td>Dry Pressed Steel Part 2</td>
<td>DP Steel 2</td>
</tr>
<tr>
<td>Dry Pressed Zirconia Part 1</td>
<td>DP Zirconia 1</td>
</tr>
<tr>
<td>Dry Pressed Zirconia Part 2</td>
<td>DP Zirconia 2</td>
</tr>
<tr>
<td>Dry Pressed Composite Part 1</td>
<td>DP Composite 1</td>
</tr>
<tr>
<td>Dry Pressed Composite Part 2</td>
<td>DP Composite 2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>2 Hour Sintering – 1300 °C</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape Cast Steel Part*</td>
<td>TC Steel 1</td>
</tr>
<tr>
<td>Tape Cast Zirconia Part*</td>
<td>TC Zirconia 1</td>
</tr>
<tr>
<td>Tape Cast Composite Part 1</td>
<td>TC Composite 1</td>
</tr>
<tr>
<td>Dry Pressed Steel Part 1</td>
<td>DP Steel 1</td>
</tr>
<tr>
<td>Dry Pressed Zirconia Part 1</td>
<td>DP Zirconia 1</td>
</tr>
<tr>
<td>Dry Pressed Composite Part 1</td>
<td>DP Composite 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4 Hour Sintering – 1300 °C</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tape Cast Steel Part*</td>
<td>TC Steel 2</td>
</tr>
<tr>
<td>Tape Cast Zirconia Part*</td>
<td>TC Zirconia 2</td>
</tr>
<tr>
<td>Tape Cast Composite Part 2</td>
<td>TC Composite 2</td>
</tr>
<tr>
<td>Dry Pressed Steel Part 2</td>
<td>DP Steel 2</td>
</tr>
<tr>
<td>Dry Pressed Zirconia Part 2</td>
<td>DP Zirconia 2</td>
</tr>
<tr>
<td>Dry Pressed Composite Part 2</td>
<td>DP Composite 2</td>
</tr>
</tbody>
</table>

* Only one tape cast steel part and one tape cast zirconia part were laminated. The parts were bisected before sintering.
The step following lamination is binder removal, performed by holding the parts at a temperature above the boiling point of the binder, but below the sintering temperature of the steel or zirconia. This burns out any organic in the system, preparing it for sintering. For this project, the burnout temperature was chosen to be 600 °C. The furnace was ramped from room temperature to 100 °C at 5 °C per minute, then to 600 °C at 1 °C per minute. The temperature increase rate was chosen to slowly remove the organics as the part increased in temperature with the aim for slow removal of the organic combustion gases, though a lower rate such as 0.3 °C per minute may have been more ideal due to the small particle size of the zirconia. If organic is removed via the formation of combustion gases, parts can deform by bloating, or even suffer from catastrophic failure; slow temperature increase helps to combat this occurrence. The furnace was set to dwell at 600 °C for 12 hours, to ensure that all organics were removed. The weight and dimensions of each part was measured, to determine weight loss and shrinkage during binder burnout. For comparison with the tape cast parts, dry pressed steel, zirconia, and steel/zirconia composite parts were prepared; designations for these samples are summarized in Table 2.3.

The final step in the processing of the parts was sintering. The parts were heated to high temperature and became densified parts. The dry pressed parts were sintered under the same conditions as the tape cast components. The parts were sintered at 1300 °C with dwell times of either 2 or 4 hours; which parts were sintered under which conditions can be seen in Table 2.3. For both dwell times, a ramp rate of 5 °C per minute up to 1300 °C was used, along with a cooling rate of 10 °C per minute down to room temperature. Due to the presence of steel in the parts, sintering was performed in a reducing atmosphere of forming gas, with 5% hydrogen and the balance nitrogen. After sintering, the dimensions and weights of the tape cast and dry
pressed parts were measured, to determine weight loss and volume shrinkage during the sintering process.

**Section 2.3.4 Microstructural Analysis**

After sintering, TC Steel 1 and 2, TC Zirconia 1, TC Composite 1, DP Steel 1 and 2 and DP Zirconia 1 were examined using optical microscopy. The parts were mounted and polished to obtain high quality images of the microstructures. The parts were first rough polished, ending with 12-micron grit sandpaper. They were then polished using an Allied MetPrep 4 automatic polisher, Compton CA. 3 micron, 1 micron and 0.05 micron diamond slurries were obtained from Allied High Tech Materials Inc., Compton CA. The first polishing step was a 20-minute polish with 3-micron grit diamond slurry and a force of 31 Newtons. The next step was a 10-minute polish with 1-micron grit diamond slurry and a force of 13N. The final polishing step was a 10-minute polish with 0.05-micron grit diamond slurry and a force of 4N. Due to the small grain size of the zirconia parts, they were thermally etched at 1100 °C for 30 minutes in air in an attempt to make the grains more visible. However, the grains of the zirconia could still not be identified, using either optical microscopy or scanning electron microscopy.

After polishing, a series of images were taken of the parts. Optical microscope images were taken of TC Steel 1 and 2, DP Steel 1 and TC Composite 1. The average pore size and average porosity of each steel part was calculated through image analysis with the program ImageJ. The image was converted to binary and de-speckled, and the fraction of pore (black) phase relative to steel (white) phase was calculated.

The measurements taken throughout this thesis had a certain amount of uncertainty. For the measurements of weight and dimensions for fabricated tape cast and dry pressed parts, there was an uncertainty of 5 relative to the smallest significant digit (i.e. if the value was 1.51, the
uncertainty would be ±0.005, for a total uncertainty of 0.01 and a relative fractional error of $0.01/1.51 = 0.0066$ or 0.66%. The fractional errors were added to describe the total fractional error for a calculated characteristic such as volume. This procedure was used because there was often only one sample for a given sample designation (see Table 2.3). This uncertainty is additive. For example, a sample with 0.005 uncertainty in each of its three dimensions would have a total uncertainty of 0.015. The porosity measurements were assigned a 95% confidence interval. This was possible due to the fact that porosity was measured using a series of images of the same sample.
CHAPTER 3
Results and Discussion

Section 3.1 Lamination, Binder Removal and Sintering

A solid steel part (TC Steel), solid zirconia part (TC Zirconia) and two composite parts (TC Composite 1, TC Composite 2) were laminated from the cast tapes at 75 °C for 20 minutes in an aluminum die under uniaxial pressure which was too low to measure using the scale on the uniaxial press. Only one of each type of part was fabricated. TC Zirconia stuck to the die and delaminated slightly, but was largely intact and still used in the succeeding processing steps. TC Steel, TC Composite 1 and TC Composite 2 did not stick to the die. The sides of TC Steel bowed out during lamination, making the width slightly larger in the middle than at the corners. This signifies that the steel part was over-pressed, which could result in elastic springback, possibly leading to delamination during sintering. After lamination, the dimensions and weight of the parts were measured. The data is summarized in Table 3.1, along with measurements taken after binder removal and change during the binder removal process. All percent changes are relative to the laminated (before binder removal) value; for example, TC Steel lost 3.4% of the weight of the laminated composite during the binder removal process.
Table 3.1. Weight, dimensions, volume and density of the fabricated steel, zirconia and composite parts after lamination. The parts were roughly square; width refers to the average dimension between the two sides. All percent changes are relative to the laminated (before binder removal) value; for example, TC Steel lost 3.4% of the weight of the laminated composite during the binder removal process.

<table>
<thead>
<tr>
<th>Laminated</th>
<th>Weight (g)</th>
<th>Thickness (mm)</th>
<th>Width (mm)</th>
<th>Volume (mm³)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC Steel</td>
<td>8.326(5)*</td>
<td>2.35(5)</td>
<td>26.5(5)</td>
<td>1650.29±10.72</td>
<td>5.05±0.033</td>
</tr>
<tr>
<td>TC Zirconia</td>
<td>2.859(5)</td>
<td>1.69(5)</td>
<td>26.0(5)</td>
<td>1142.44±7.99</td>
<td>2.50±0.018</td>
</tr>
<tr>
<td>TC Composite 1</td>
<td>5.651(5)</td>
<td>1.75(5)</td>
<td>27.0(5)</td>
<td>1275.75±8.93</td>
<td>4.43±0.031</td>
</tr>
<tr>
<td>TC Composite 2</td>
<td>5.098(5)</td>
<td>1.35(5)</td>
<td>29.5(5)</td>
<td>1174.84±9.40</td>
<td>4.34±0.035</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>After Binder Removal</th>
<th>Weight (g)</th>
<th>Thickness (mm)</th>
<th>Width (mm)</th>
<th>Volume (mm³)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC Steel</td>
<td>8.044(5)</td>
<td>N/A</td>
<td>26.8(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TC Zirconia</td>
<td>2.517(5)</td>
<td>1.71(5)</td>
<td>26.0(5)</td>
<td>1155.96±8.09</td>
<td>2.18±0.016</td>
</tr>
<tr>
<td>TC Composite 1</td>
<td>N/A</td>
<td>N/A</td>
<td>27.0(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TC Composite 2</td>
<td>N/A</td>
<td>N/A</td>
<td>29.5(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Change During Binder Removal</th>
<th>Weight Loss (%)</th>
<th>Thickness Change (%)</th>
<th>Width Change (%)</th>
<th>Volume Change (%)</th>
<th>Density Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC Steel</td>
<td>-3.4%</td>
<td>N/A</td>
<td>0.9%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TC Zirconia</td>
<td>-12.0%</td>
<td>1.2%</td>
<td>0.0%</td>
<td>1.2±0.53%</td>
<td>-13.0±5.9%</td>
</tr>
<tr>
<td>TC Composite 1</td>
<td>N/A</td>
<td>N/A</td>
<td>0.0%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>TC Composite 2</td>
<td>N/A</td>
<td>N/A</td>
<td>0.0%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*The (x) represents the uncertainty in the smallest significant figure. For example, 8.236(5) for the weight of the steel has an uncertainty equal to ±0.0005 for a total uncertainty equal to 0.001 and a fractional error equal to 0.1/8.326 or 0.012 or 1.2% error. The calculated values for volume and density have higher uncertainty, displayed as, for example, ±0.024, due to the inherent uncertainty in the weight and size values used in their calculation.

Following lamination, the binder was removed from the parts at 600 °C. This process makes the parts very fragile. The dimensions and weight of the parts were measured and are displayed in Table 3.1. TC Steel cracked and warped during binder removal. Hayes has recently shown that up to 0.15 weight percent oxygen and on the order of 0.4 weight percent nitrogen result from the burnout procedure air at 600 °C for 1 hour and sintering in the forming gas (5%H₂/N₂) atmosphere [8]. It is likely that the additional 12 hours of time at 600 °C will
lead to significantly more oxidation than the 1 hour procedure used by Hayes. Thus, delamination between the steel and zirconia layers may be expected because of the reactive interfaces present between the metal-oxidized metal, zirconia and the gases that may persist at the complex interfaces. The presence of oxidation is supported by the observation that TC Steel warped and cracked during binder burnout.

The composite parts also became partially delaminated. One steel layer delaminated from the surface of TC Composite 1, and a fragment broke off of TC Composite 2. The breakage of the samples was likely due to a combination of factors, but it is likely that the largest contribution was due to uncontrolled oxidation on the steel particulate surfaces. Other factors may also contribute. Strain imparted on the tapes during the tape casting process, combined with different shrinkage rates during sintering of oxidized and possibly actively decomposing metal oxides on the steel particles and zirconia, would have caused stress at the interface between the tapes, and could be a source of breakage. Another source of delamination could be the thermal expansion mismatch of the steel and zirconia layers (10.1x10^{-6}°C^{-1} at 600K for zirconia and 17.5x10^{-6}°C^{-1} at 600K for steel, Table 1.1), which could result in stress at the interface during both the heating and cooling cycles. The lamination process could also be a source of delamination. A higher temperature or longer time in the uniaxial press could help to alleviate residual stains due to lamination. A second lamination step could also be added, such as isostatic pressure.

Due to damage during binder removal, accurate weight loss and shrinkage data could not be calculated for every part. The volume and weight change calculations are shown in Table 2.3. The zirconia part underwent a weight loss of 11.9% through binder burnout, width stayed the same, and the thickness grew by 1.2 %of the initial length. The 11.9 % weight loss is reasonably consistent with the 10.9 weight % organic remaining after solvent removal for the
zirconia formulations (Table 2.2). In contrast, the steel part underwent a weight loss of 3.4%. This is considerably lower than the 4.35 weight % of organic remaining in the dried steel tape (Table 2.1). The discrepancy in the weight loss data for the sintered steel parts is consistent with an increase in weight due to steel oxidation. Thus, the weight loss data is consistent with metal oxidation during the burnout processes. At least some of the metal oxide formed during burnout will be reduced during sintering in the forming gas atmosphere. This reduction is likely to lead to delamination of the composite materials during the sintering process. The smaller specific volume of the metal relative to the corresponding metal oxide leads to the metal layer pulling away from the zirconia layer, which is observed on a macroscopic scale as delamination of the layers.

After binder removal, the parts were sintered, along with the dry pressed parts created for purposes of comparison. A summary of the parts and the conditions under which they were sintered is provided in Table 2.3. The dimensions and weights of the dry pressed parts are shown in Table 3.2, along with volume and density, as the tape cast parts were too damaged during binder removal to accurately measure dimensions with any certainty.
Table 3.2. Weight, dimensions, volume and density of the dry pressed steel, zirconia and composite parts before and after sintering. The parts were right cylinders before sintering; the steel and zirconia remained right cylinders after sintering. The steel and zirconia components of the composites shrank by different amounts; diameter was recorded for both the zirconia segment and the steel segment.

<table>
<thead>
<tr>
<th>Part</th>
<th>Weight (g)</th>
<th>Height (mm)</th>
<th>Diameter (mm)</th>
<th>Volume (mm³)</th>
<th>Density (g/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Unsintered Parts</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP Zirconia 1</td>
<td>0.720(5)</td>
<td>7.55(5)</td>
<td>6.40(5)</td>
<td>242.88±0.73</td>
<td>2.96±0.012</td>
</tr>
<tr>
<td>DP Steel 1</td>
<td>1.260(5)</td>
<td>8.27(5)</td>
<td>6.40(5)</td>
<td>266.05±0.66</td>
<td>4.74±0.014</td>
</tr>
<tr>
<td>DP Composite 1</td>
<td>3.830(5)</td>
<td>7.66(5)</td>
<td>12.84(5)</td>
<td>991.86±1.79</td>
<td>3.86±0.008</td>
</tr>
<tr>
<td>DP Zirconia 2</td>
<td>0.715(5)</td>
<td>7.80(5)</td>
<td>6.34(5)</td>
<td>246.24±0.74</td>
<td>2.90±0.012</td>
</tr>
<tr>
<td>DP Steel 2</td>
<td>1.225(5)</td>
<td>8.15(5)</td>
<td>6.34(5)</td>
<td>257.29±0.77</td>
<td>4.76±0.016</td>
</tr>
<tr>
<td>DP Composite 2</td>
<td>4.650(5)</td>
<td>10.03(5)</td>
<td>12.81(5)</td>
<td>1292.67±1.68</td>
<td>3.60±0.005</td>
</tr>
<tr>
<td><strong>Sintered Parts - 2 Hours</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP Zirconia 1</td>
<td>0.710(5)</td>
<td>6.63(5)</td>
<td>4.97(5)</td>
<td>128.62±0.51</td>
<td>5.52±0.028</td>
</tr>
<tr>
<td>DP Steel 1</td>
<td>1.250(5)</td>
<td>7.61(5)</td>
<td>5.80(5)</td>
<td>201.06±0.60</td>
<td>6.22±0.021</td>
</tr>
<tr>
<td>DP Composite 1 (Zirconia)</td>
<td>3.670(5)</td>
<td>6.60(5)</td>
<td>10.29(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>DP Composite 1 (Steel)</td>
<td>N/A</td>
<td>N/A</td>
<td>11.26(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Sintered Parts - 4 Hours</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP Zirconia 2</td>
<td>0.710(5)</td>
<td>6.85(5)</td>
<td>4.90(5)</td>
<td>129.17±0.52</td>
<td>5.50±0.027</td>
</tr>
<tr>
<td>DP Steel 2</td>
<td>1.221(5)</td>
<td>7.50(5)</td>
<td>5.70(5)</td>
<td>191.38±0.57</td>
<td>6.38±0.022</td>
</tr>
<tr>
<td>DP Composite 2 (Zirconia)</td>
<td>4.503(5)</td>
<td>8.58(5)</td>
<td>9.90(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>DP Composite 2 (Steel)</td>
<td>N/A</td>
<td>N/A</td>
<td>11.24(5)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Change During Sintering - 2 Hour</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP Zirconia 1</td>
<td>-1.39%</td>
<td>-12.19%</td>
<td>-22.34%</td>
<td>-47.04±4.47%</td>
<td>86.21±11.6%</td>
</tr>
<tr>
<td>DP Steel 1</td>
<td>-0.79%</td>
<td>-7.98%</td>
<td>-9.38%</td>
<td>-24.43±4.27%</td>
<td>31.27±7.50%</td>
</tr>
<tr>
<td>DP Composite 1 (Zirconia)</td>
<td>-4.18%</td>
<td>-13.84%</td>
<td>-19.86%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>DP Composite 1 (Steel)</td>
<td>N/A</td>
<td>N/A</td>
<td>-12.31%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td><strong>Change During Sintering - 4 Hour</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DP Zirconia 2</td>
<td>-0.70%</td>
<td>-12.18%</td>
<td>-22.71%</td>
<td>-47.54±4.52%</td>
<td>89.30±15.2%</td>
</tr>
<tr>
<td>DP Steel 2</td>
<td>-0.33%</td>
<td>-7.98%</td>
<td>-10.09%</td>
<td>-25.62±4.23%</td>
<td>34.00±12.4%</td>
</tr>
<tr>
<td>DP Composite 2 (Zirconia)</td>
<td>-3.16%</td>
<td>-14.46%</td>
<td>-22.72%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>DP Composite 2 (Steel)</td>
<td>N/A</td>
<td>N/A</td>
<td>-12.26%</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*The (x) represents the uncertainty in the smallest significant figure. For example, 8.236(5) for the weight of the steel has an uncertainty equal to ±0.0005 for a total uncertainty equal to 0.001 and a fractional error equal to 0.1/8.326 or 0.012 or 1.2% error. The calculated values for volume and density have higher uncertainty, displayed as, for example, ±0.024, due to the inherent uncertainty in the weight and size values used in their calculation.*
After sintering, the parts were examined. The pure steel and pure zirconia tape cast parts (TC Steel 1 and 2, TC Zirconia 1 and 2) were sintered without any cracking or part failure, but due to damage during binder removal and bisecting of the parts prior to sintering accurate measurements could not be taken post sintering. TC Steel 1 and TC Steel 2 were deformed, but this was due to the cracking and warping that occurred during binder removal. The pure steel and pure zirconia dry pressed parts (DP Steel 1 and 2, DP Zirconia 1 and 2), which were right cylinders prior to sintering, remained right cylinders after the sintering process was complete. DP Zirconia 1 is shown in Figure 3.1, and weight, volume and density change for the parts is summarized in Table 3.2. DP Zirconia 1 sintered to a final density of 5.52 g/cm³ and DP Zirconia 2 sintered to a density of 5.50 g/cm³. The theoretical density of yttria-stabilized zirconia is approximately 6 g/cm³; therefore the zirconia was sintered to approximately 91.7% of theoretical density. DP Steel 1 sintered to a density of 6.22 g/cm³, and DP Steel 2 sintered to a density of 6.38 g/cm³. The theoretical density of 316L stainless steel is 8 g/cm³; therefore the steel was sintered to between 77 and 80% of theoretical density.

![Figure 3.1. Macroscopic images of monolithic zirconia sample DP Zirconia 1 after sintering for 2 hours at 1300 °C. a) A view of the DP Zirconia 1 from the top. There is a small inclusion of steel on the surface due to steel powder remnants on the dry press die during fabrication of the part. b) A side view of DP Zirconia 1 after sintering. The part appears black due to contamination of the surface with steel powder and graphite lubricant remaining in the die during dry pressing. The part was a right cylinder before sintering, and remained a right cylinder after sintering.](image-url)
The composite parts were also examined. TC Composite 1, which was sintered for two hours, was severely warped. An optical image of the part is shown in Figure 3.2.

![Image of TC Composite 1 after sintering for 2 hours at 1300 °C. The composite warped and delaminated around the edges, but remained laminated in the center. The delamination is due to oxidation of the steel particulates during binder removal and the subsequent partial reduction of the metal oxide due to sintering in a forming gas atmosphere. Oxidation and reduction would occur at the edges of the sample first, resulting in delamination around the outside of the part while the center remained laminated.](image)

The center of TC Composite 1 remained laminated through the sintering process, but the edges became delaminated and warped. This deformation was likely due to a combination of factors. The primary cause was oxidation of the steel during sintering; the part would have oxidized from the edges to the center, resulting in delamination of the edges before the interior. Differing shrinkage rates, again due to oxidation of the steel, and thermal expansion mismatch between the steel and zirconia layers may also have been contributing factors.

TC Composite 2, which was sintered for four hours, broke into several fragments during the sintering process. One fragment is shown in Figure 3.3; the other parts are similar in size and shape. The fragment is severely warped; again, this is likely due to stress at the interface
between tapes due to differing shrinkage rates during sintering because of the oxidation and reduction effects during binder removal in air and sintering in forming gas, respectively.

Figure 3.3. Sever warping, delamination, cracking, and fracture of the parts is observed in the optical image of TC Composite 2 after sintering for 4 hours at 1300 °C in forming gas (5% H₂/N₂). The composite fractured into pieces during the sintering process. This fracture is likely due to oxidation of the steel during the binder removal and subsequent partial reduction of the metal oxide during sintering in the forming gas atmosphere. One fragment is shown in this figure; the others were similar in size and shape.

The dry pressed parts were composite parts (DP Composite 1 and 2) were examined after sintering. The dimensions and weights of the parts are displayed above in Table 3.2. The steel and zirconia sections of the composite underwent differing amounts of shrinkage during sintering, but the interface between the sections did not fail. This resulted in a change in the shape of the part from cylindrical pre-sintering to a “muffin” shape post-sintering. Images of the composite parts after sintering are shown in Figure 3.4. The diameters of the steel and zirconia segments of the composite were both recorded, due to the large difference in shrinkage between the segments. The shrinkage of the steel and zirconia sections of the composite is summarized in Table 3.2.
Figure 3.4. Images of the sintered composite steel-zirconia dry pressed parts after sintering at 1300 °C for two hours (a) and four hours (b). Prior to sintering, the samples were right cylinders. The steel and zirconia sections of the parts underwent different amounts of shrinkage during sintering due to the difference in particle size of steel and zirconia, but the interface between the sections did not fail. This led to a change in shape in the parts from cylindrical shape pre-sintering to a “muffin” shape post-sintering.

As seen in Table 3.2 and Figure 3.4, the steel underwent significantly smaller linear shrinkage than the zirconia. This is unexpected; at 1300 °C steel should sinter to a higher density, experiencing more linear shrinkage than zirconia. This serves to support the idea that the steel was oxidized during binder removal and partially reduced during sintering in forming gas.

Section 3.2 Microstructural Analysis

After sintering, the steel samples were polished and imaged using optical microscopy. The microstructures of the tape cast samples with different sintering times were compared, and the tape cast samples were compared with the dry pressed samples. Images of TC Steel 1 and 2, as well DP Steel 1, at 50x magnification are shown in Figure 3.5.
Figure 3.5. a) Optical microscope image of tape cast steel sintered at 1300 °C for two hours (TC Steel 1). b) Optical microscope image of tape cast steel sintered at 1300 °C for four hours (TC Steel 2). c) Optical microscope image of dry pressed steel sintered at 1300 °C for two hours (DP Steel 1). In images a) and b), the light phase is steel, the grey phase is a second phase that is likely metal oxide, and the black phase is porosity. In image c), it appears that the microstructure of DP Steel 1 resembles the acicular nature of the steel particles after milling (Figure 2.2).

The tape cast and dry pressed samples were relatively uniform across their surfaces; the above images in Figure 3.5 are representative. The surfaces of TC Steel 1 and TC Steel 2, in Figure 3.5 sections a) and b), are also quite similar; the microstructure of both samples appears to be based off of roughly circular grains. However, the grain structure of the dry pressed
sample, shown in Figure 3.5 section c, is quite different; the microstructure of DP Steel 1 appears to be oblong or acicular in nature. Porosity of the samples was calculated using the image analysis program ImageJ as relative area of pore (black) phase to steel (white) phase; this data is shown in Table 3.3.

**Table 3.3.** Average porosity of tape cast stainless steel samples sintered for two and four hours at 1300 °C and a stainless steel dry pressed sample sintered for two hours at 1300 °C. This data was calculated using the image analysis program ImageJ. Surface area fraction of pores is the percent of the total area that was occupied by black (pore) phase after the image was converted to binary; density of steel phase is the percent of the total area that was occupied by white (steel) phase. Average was computed from 5, 6 and 8 images of the surface for TC Steel 2, TC Steel 1 and DP Steel 1, respectively; 95% confidence interval was calculated.

<table>
<thead>
<tr>
<th></th>
<th>4 Hour Sintered Tape – TC Steel 2</th>
<th>2 Hour Sintered Tape – TC Steel 1</th>
<th>2 hour Sintered Dry Press – DP Steel 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Pore Size (square microns)</td>
<td>Average 13.5%</td>
<td>Average 8.9</td>
<td>Average 18.5%</td>
</tr>
<tr>
<td>Surface Area Fraction of Pores (%)</td>
<td>20.8%</td>
<td>17.3%</td>
<td>30.1%</td>
</tr>
<tr>
<td>Density of Steel Phase (%)</td>
<td>79.8%</td>
<td>82.7%</td>
<td>69.9%</td>
</tr>
<tr>
<td>95% Confidence Interval</td>
<td>±1.6%</td>
<td>±1.4%</td>
<td>±2.8%</td>
</tr>
<tr>
<td></td>
<td>±0.9%</td>
<td>±2.6%</td>
<td>±0.7%</td>
</tr>
<tr>
<td></td>
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<td></td>
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</tr>
</tbody>
</table>
The average porosity was highest in the dry pressed sample, at approximately 30% surface area. This is expected; the forming process of the dry pressed samples does not create as dense a green body as tape casting, especially in this case where the powders were not granulated to provide ideal die filling. The tape cast samples both were closer to 20% surface area porosity.

The zirconia tape cast and dry pressed samples were also imaged using optical microscopy. However, due to the small grain size in the parts, no useful information could be obtained via optical imaging. The samples were thermally etched at 1100 °C for 30 minutes, in an attempt to increase the visibility of the grains, but the process was ineffective. Both optical microscopy and scanning electron microscopy yielded no useable results; images appeared as a white image with the occasional defect but no visible grain structure.

The composite tape cast sample was imaged with optical microscopy. A series of images of the steel-zirconia boundary of the sample are shown in Figure 3.6.
Figure 3.6. A series of optical microscope image of a steel-zirconia composite fabricated using tape casting and sintered at 1300 °C for two hours (TC Composite 1). In each image, zirconia is the darker segment and the steel the lighter segment. a) A 10x magnification image showing the multilayered structure present in the composite. Cracking in the zirconia phase is evident. b) A close-up on an area of steel-zirconia interface of the sample featuring cracking. Though the zirconia phase is fractured, the steel phase appears to have bridged the crack, preventing total failure of the part. c) A close-up of a region of steel-zirconia interface where no cracking has occurred. The parting between the steel and zirconia phases is consistent with the idea that the steel oxidized during binder removal and was partially reduced during sintering in forming gas.

Section a) of figure 3.6 shows a view of several layers of zirconia and steel, demonstrating the multilayered structure in the composite. The dark layers in the structure are zirconia, while the light layers are steel. Cracking of the zirconia layers is evident from this
image. Section b) of Image 3.6 displays a close-up on a region of steel-zirconia interface where cracking has occurred. Again, the dark phase is zirconia and the light phase steel. From this image, it appears that though the zirconia is cracked, the part has not failed completely due to the presence of the steel layers. Though there is a significant amount of work still to be done before a layered composite fabricated using tape casting can be used to make mesoscale surgical instruments, this behavior is promising. The steel phase is intended to prevent failure of the part in the presence of cracking of the zirconia phase; this appears to have occurred. Section c) Figure 3.6 displays a close-up on a region of steel-zirconia interface at which no cracking has occurred. The parting of the steel and zirconia layers at this interface is consistent with the idea that the steel was oxidized and the metal oxide partially reduced during binder removal in air and sintering in forming gas, respectively.
CHAPTER 4

Conclusions

Stainless steel and yttria-stabilized zirconia were successfully cast as tapes and laminated into green bodies. The tapes were layered into monolithic steel and zirconia parts, as well as composite layered structures. The green bodies had binder removed through thermolysis in air, and were sintered in a forming gas atmosphere. The composite parts generally failed during the binder removal and sintering processes. It is theorized that the steel particulates were oxidized in air, and the metal oxide partially reduced during sintering in forming gas. This likely led to delamination of the steel layers from the zirconia and ultimately to failure of the parts. The sintered parts were also examined with optical microscopy. The zirconia layers of the composite were fractured, but the steel layers remained intact and held the part together, though delamination did occur. Parting observed at the interface of the steel and zirconia layers further reinforces the idea that the steel was oxidized and the metal oxide partially reduced. Multilayer steel-zirconia composites can be fabricated through tape casting, but binder removal and sintering need to be properly optimized before the composite will be able to be used for fabrication of mesoscale surgical instruments.
CHAPTER 5

Suggestions for Future Work

Significantly more work must be done before mesoscale parts can be fabricated from this stainless steel – yttria-stabilized zirconia multilayer composite. The lamination process must be optimized to create dense green bodies which will yield dense final sintered parts. A more suitable binder removal process must also be developed, to eliminate oxidation of the steel and prevent warping and cracking. Shrinkage of the zirconia relative to the steel must be taken into account, to prevent strain at the interface between steel and zirconia during sintering. The sintering process must be optimized to prevent warping and failure during sintering, as well as yield dense final parts. After a suitable composite structure has been developed, it must be fashioned into mesoscale parts to be used in mechanical testing, and the fracture toughness and Young’s modulus of the composite determined. Finally, if the mechanical properties of the composite are as desired, mesoscale surgical instruments must be fabricated from the multilayer composite.
REFERENCES


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Education:
Bachelor of Science in Materials Science and Engineering – Ceramics Option
The Pennsylvania State University Schreyer Honors College, University Park, PA.

Work Experience:
Manufacturing Intern, Merck & Company: Summer 2010
Lyophilization Process Deviation Management, located in West Point, PA under Justin Lucas
and Karim Younan. Examined the process of thawing Varicella virus bulk to be used in Chicken Pox vaccine manufacture.

Research Intern, Merck & Company: Summer 2009
Center for Materials Science and Engineering, located in West Point, PA under Eric Seymour and Steve Conway. Examined the porosity and pore size distribution of Simvastatin granules, and the relationship between those properties and the compound’s compaction and dissolution characteristics.

Maintenance Associate, Vertis Communications: Summer 2008
Carried out tasks as determined by the maintenance supervisor. Duties included reallocating facility storage space, painting and general maintenance.

Sales Associate, Dick’s Sporting Goods: Summer 2008
Assisted in the opening of a new location, including assembling shelving and organizing and stocking the shelves with initial product. Once the store was open, assisted customers in finding and purchasing appropriate sporting goods and equipment.

Relevant Coursework:
Thermodynamics of Materials * Materials Characterization * Crystal Chemistry
Kinetics of Materials * Phase Relations * Mechanical Properties of Materials * Biomedical Materials
Materials Methodology and Design * Processing of Ceramics * Glass Science
Technical Writing for Engineers * Global Management in Earth and Energy * C++ Programming
Electrical Properties * Optical Properties * Thermal Properties * Solid State Physics

Activities:
Vice President, Penn State chapter of Keramos 05/2010 to Present
(Treasurer since 2009, member since 2008)
Vice President, Penn State Material Advantage 05/2010 to Present
(Member since 2007)
Member, College of Earth and Mineral Sciences Undergraduate Student Council, 09/2008 to Present
Member, College of Earth and Mineral Sciences Dance Marathon Team, 09/2008 to Present
Member, Penn State Marching Blue Band, 08/2007 to 04/2008

Awards and Achievements:
Merck Science and Technology Fellowship 2009-2010
Penn State Schreyer Honors College Academic Excellence Scholarship 2007-2010
William and Estelle Turney Ceramics Science and Engineering Scholarship 2009
Eagle Scout, Troop 71, Doylestown, PA 2007
6 other scholarships since 2007