

DEVELOPMENT OF POROUS CERAMICS WITH GRADED COLUMNAR PORE
STRUCTURES VIA FREEZE-TAPE CASTING

by

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ABSTRACT

Freeze-tape casting is a new processing technology that can generate continuous columnar-graded pore structures utilizing a wide variety of ceramic and/or metallic powders. The uni-directional solidification and subsequent freeze drying of yttria stabilized zirconia (YSZ) based aqueous cast tapes is being evaluated for various applications including fuel cells, filtration/separation membranes, and catalyst supports. The degree of pore divergence, pore packing, and pore orientation can be actively tailored by altering the solids loading, freezing rate, and tape pulling speed. The effects of solids loading and freezing rate is discussed with respect to morphology of ice growth. SEM and density data is reported to establish the breadth of tailorability and extent of anisotropy in the frozen tapes.

The freeze cast structure of ceramic materials is highly porous. The production of freeze cast, YSZ-based tapes include tape casting techniques and high temperature sintering steps. SEM analysis is displayed at varying angles relative to casting direction to provide further insight of the morphology of these materials. Results of varying solids loading and freezing temperature studies are discussed in detail. Compressive strength data by ASTM standard methods was resultant of concentric ring-on-ring testing and is further explained. Freeze cast structures appear to be potentially desirable over traditional pore formers for various applications.

INTRODUCTION

Thesis Overview

Freeze-tape casting is a relatively new ceramic processing technique that utilizes traditional tape casting methods to create pore morphologies and structures not achievable through traditional pore forming routes. This new method creates a continuous columnar-graded pore structure throughout the tape. Due to the viscosity of the slurry, as well as the method of solvent removal, these tapes can be uniformly cast very thin and up to a few millimeters thick. Thicker porous ceramics can easily be cast when utilizing dies on the Mylar tape carrier. Such ceramic structures appear to be beneficial for use in many applications requiring aspects of liquid and gas transport, some of which will be discussed later in further detail.

There are a wide variety of materials that can be processed using this method, as the processing system is highly materials independent. However, the material needs to be in a form that can be mixed into a homogeneous slurry. The common types of materials used in ceramic processing are discussed along with their properties. These properties can be important depending on processing method and intended application.

Common ceramic processing methods are described in detail. Some are more beneficial than others depending on the desired resultant size and shape of the processed ceramic. Slurry preparation methods and ingredients are explained in following sections. The specific ingredients used in the freeze casting process are given as well as a full explanation of the process itself. A brief description of the transport characteristics in

porous materials is given, as well as information about future experimentation to quantify the characteristics of these pore structures.

An extensive solids loading, freezing rate and microstructural characterization study was conducted on porous ceramic bodies fabricated by this novel process. Density measurements and scanning electron microscopy were used to analyze the pore structures in order to establish the processing-microstructure-properties relationship of these porous cast substrates. The freeze cast process was additionally studied to optimize the casting rate, organics content, and repeatability of the process. In addition to the processing, the mechanical properties were evaluated by means of ring-on-ring flexural testing to evaluate the strength characteristics of these pore morphologies. The results of these studies on the freeze tape casting system are discussed in an effort to develop the means of manipulating porous ceramics for various applications.

ADVANCED CERAMICS

Ceramic materials are utilized for many different applications in a variety of fields. There are many types of ceramics, each with unique individual properties. Some examples of common ceramics include glasses, cermets, heavy clays, abrasives, and some dielectric materials. Advanced ceramics have been used in many engineering applications for the last 40 years. The possible uses of these ceramics are seemingly limitless; however, it is necessary to know the inherent weaknesses of ceramics and their respective processability to ensure their use is applicable to a specific situation. [1]

These materials are compounds that are usually composed of metallic and nonmetallic elements. The classification of a ceramic falls into one of three categories: Oxides, such as alumina and zirconia; non-oxides, which include nitrides, borides, and silicides; and composites, which are reinforced combinations of oxides and non-oxides. [2]

Oxides

Oxide ceramics “are non-metallic, inorganic compounds that include oxygen, carbon, or nitrogen [3].” These materials can be used for long periods of time at high temperatures with minimal degradation due to their high melting point. Attributable to their range of electrical and mechanical properties, oxide ceramics are ideal for use in chemical and materials processing, high voltage power applications, as well as in bricks, cement, and other structural applications. These materials can be processed by a number

of techniques, such as slip, tape, and pressure casting, as well as extrusion and injection molding. [2, 3]

Determining the best oxide depends on the properties that are desired. Modulus of elasticity, density, purity, and grain size are just some of the properties that vary with each compound. Generally, these ceramics have low thermal conductivity, are highly resistant to oxidation, and are electrically insulating. Depending on the elements within the compound, the price of oxide ceramic powder can range from fairly low to rather high. [2, 3]

Non-oxides

Non-oxide ceramics are widely used for their thermal and mechanical properties. These ceramics generally have high thermal conductivities and are extremely hard, but are much more likely to oxidize at high temperatures than oxide ceramics. Also, some non-oxides have a little electrical conductivity, so they may not be applicable in certain situations. Depending on the intended application, a carbide may be more appropriate than a nitride for a specific task. For instance, some carbides are strong enough to be used in body armor due to their high strength. They are also able to withstand a higher thermal shock than nitrides. However, if a situation called for a material of high thermal conductivity, the nitride would most likely be chosen over the carbide. Those are just a few examples of the advantages of non-oxides. They have a wide range of uses due to their unique properties. [2, 4]

Composite Ceramics

Composite ceramics utilize a combination of oxide and non-oxide ceramics in a reinforced matrix. Fibers or whiskers of non-oxide ceramics, and sometimes metal particulates, are incorporated into oxide ceramics to create these composites. Often this is done to toughen and strengthen the ceramic to aid in the resistance of failure. To do this, the reinforcing material is combined in such a way as to resist any cracking. If the material should start to fail under a load, for example, the fibers should help to maintain the structure and prevent a catastrophic failure. When processed at high temperatures, the compounds within the composites have been known to react with one another, creating new compounds within the structure. These compounds can increase the electrical conductivity of the material that, along with the strength benefits, can make these composites very desirable for certain applications. [5, 6]

Porous ceramic composites are useful in applications where thermal insulation is important, such as space shuttle reentry. These ceramics, containing upwards of 90% porosity, have very high thermal shock resistance and toughness. However, the large porosity, and thus low density, of the material decreases its elastic modulus. These properties will be discussed in the following section.

Ceramic Properties

Ceramics are used for numerous applications due to their unique properties, such as hardness and compressive strength. The structural, thermal, electrical, and other properties of these materials make them desirable for bricks, voltage insulators, and oven

tiles, for instance. In order to design a ceramic for a specific application, it is necessary to understand the properties that certain ceramics possess. A few common characteristics are examined in this section.

Elastic Properties

All solids materials have a modulus of elasticity defined as the amount of stress necessary to produce a unit elastic strain. Generally, ceramics have higher elastic moduli than other classes of materials, due to their high bond strengths. The oxides tend to have strong ionic bonds while the non-oxides have strong covalent bonds. Also, the elements that the ceramic materials are composed of generally have low densities because they have loosely packed structures. The high elastic modulus paired with low density can be very beneficial; the material is very strong with minimal weight. However, ceramics are able to withstand greater compressive forces than tensile forces, as they have a propensity to fracture before yield strength is achieved. [1, 7]

Hardness and Toughness

Ceramics compounds are widely considered the hardest of solid materials. Hardness is determined by how much a material plastically deforms under an applied force. Since ceramics have practically no plasticity, they are much harder than metal materials. Some of the hardest ceramics are used commercially as abrasives for grinding, polishing, and cutting. Hardness of materials is usually measured using a diamond pyramid indenter or hard steel bearing which is pressed into the material. The value of hardness is related to the force of the press and a form of the projected area of the

indenter or bearing. The equations for hardness vary with which scale is being utilized. There are a number of different scales used to determine hardness; some basically tell whether the material is hard or soft while others are more specific and are utilized better when calculations are involved. Ceramics are so hard because the ionic or covalent bonds within them provide large resistances to dislocations. The diamond indenter is used instead of the steel bearing with ceramic hardness tests because steel is softer than most ceramics; the steel would fail before the ceramic. [1, 7]

Though ceramics tend to be hard, they are not always tough. Toughness is a measurement of how resistant a material is to fracture and its ability to resist additional fracture once failure has been initiated. Some ceramics are fairly brittle due to non-uniform porosity, but if the pores are formed properly, the ceramic structure surrounding those pores will be dense, making the structure tough. However, if a ceramic is sintered improperly, thermal stresses can cause small cracks to form. Once a crack is initiated the material can often fail fairly quickly. Unlike metals, the tip of a crack in a ceramic has practically no plastic zone. The less plasticity there is at this location, the less the crack energy is dissipated. A ceramic is only as tough as its longest crack. In some instances the fracture toughness can be increased by incorporating a compound different than that of the ceramic material. For example, alumina, a common ceramic with low toughness, can be strengthened with the addition of iron oxide or titanium oxide. [1, 7, 8]

Thermal Conductivity

The thermal conductivity of ceramics varies by their structure, but is generally low regardless. Since the bonds within them are either ionic or covalent, there are little to

no free electrons. The amount of free electrons within a material is a large factor in how effective the transfer of energy, by heat, will be within the material. Even semiconductive ceramics generally have little thermal conductivity until the material reaches elevated temperatures. However, free electrons are not the only determining factor of a material's conductivity; the vibrations of the crystal lattices of a material are also important. These vibrations are low with both ionic and covalent bonding. With the covalently bonded ceramics, the oxygen disrupts cooperative oscillations of the lattice. The structure formed with ionic bonding limits lattice movement as well. These low thermal conductivities paired with their high melting temperatures make ceramics ideal for high temperature applications. [1, 8]

Electrical Conductivity

The electrical conductivity of a material is highly dependent on the transport of ionic and electron charge. In ceramics there is a large amount of interference with this transport, limiting mobility and thus causing the material to have low conductivity. Also, as with thermal conductivity, electrical conductivity is dependent on the amount of free electrons. The lack of free electrons with both covalent and ionic bonding gives such materials poor conductivity. However, an increase in temperature tends to enhance the electrical conductivity of these materials. The reason for this is the elevated temperatures increase the ionic diffusion as well as allow more electrons to jump from the valence band to the conduction band energy levels. The extent of porosity in a material can greatly affect its conductivity; while the empty space within a pore is able to allow heat transfer, it cannot effectively transport a charge. [1]

GENERAL PROCESSING

The objective of the freeze casting process is to develop a thin, porous ceramic. To do this, the ceramic of interest must be prepared as an aqueous slurry. This slurry contains the ceramic powder, a solvent, a dispersant, and a binding agent. Depending on the percent of solids in the slurry, it may be necessary to add a thickening agent to increase the viscosity prior to casting. Each ingredient of the slurry serves a specific purpose at some point in the process. During the sintering process the binders and any excess agents are burned out leaving a substrate composed primarily of the ceramic powder, in which each particle of the powder is chemically bonded with neighboring particles.

Ceramic Powder

The ceramic powder used most often in tape casting for fuel cell related components is Yttria-Stabilized Zirconia (YSZ). It has high oxygen ion conductivity and maintains good mechanical properties at relatively high temperatures. There are a fairly wide variety of YSZ powders on the market today. These vary by particle size, molecular percentage of Yttrium Oxide (Y_2O_3), and purity; the properties depend on the method of synthesis. There are factors that need to be considered when using different types of YSZ. For example, nano-powders tend to have lower sintering temperatures than those of micro-powders, but properly stabilizing such small grains can be difficult.

[9]

The ceramic powder is the most important part of the slurry. During the casting process the powder is formed into the desired size and shape. After this is done and the solvent is removed, the ceramic is held in place by the binding agents. At this point the green tape can be carefully cut into specific shapes and sintered.

A number of things occur during the sintering process. At a certain temperature the binding agents and any other additives will start to burn out. While this is occurring, the ceramic particles come into contact with one another. Smaller grains combine into larger grains via a thermodynamic reduction in surface area. While the particles combine, small pores that once existed between particles are filled in with the newly merged grains. This densifies the structure, which causes the entire structure to shrink, generally between 15% and 25%. The extent of which the structure densifies is determined by the sintering cycle and the effect of this on the organic and inorganic additives in the system. The temperatures, dwell times, and heating rates all affect this densification. Higher green densities yield higher sintered densities and shrinkage effects are lessened. The end result is a solid consisting of only the ceramic with the precise amount of porosity when necessary.

Solvent

A solvent is used in the slurry to allow the ceramic particles to mix freely and uniformly. It must be able to dissolve the other additives to make a completely homogeneous mixture. The amount of solvent used is determined based on the percentage of solids desired within the slurry. This percentage determines how viscous

the slurry will be and affects the density of the resulting green tape. After the tape is cast, the solvent must be removed to allow it to take its green structure. How quickly the solvent is removed is important with typical drying methods; if done improperly, the resultant tape could have defects that could include warping, large voids, wrinkling, and general unevenness.

Depending on the method and equipment available for the processing, either an aqueous or non-aqueous solvent will be used. Also, the type of solvent used determines what other types of ingredients will need to be added. The most widely used solvents are non-aqueous due to their quick evaporation and lack of hydrogen bonding. This bonding complicates dispersion, making achieving high solids loads and proper nano-particle suspension more difficult. Some alcohols can be used, such as ethanol and methanol, as well some more volatile solvents such as xylene or methyl ethyl ketone. In some cases it is not good to have a very fast drying rate; the slurry can start drying while before it is even cast. The dried part in the slip, generally called the “skin”, will then be pulled along with the liquid part of the slurry leaving defects in the tape. To prevent these kinds of defects, it may be necessary to use more than one organic solvent to alter the drying rate. These combinations of organic chemicals, when done properly, can also make the slurry safer and/or aid in the dissolving of ingredients. [10]

Aqueous, or water-based, solvents are used less often mostly because the drying rate is harder to control and high surface tension exists, resulting in poor wetting of molds or Mylar. Also, it becomes necessary to have additives that will easily dissolve in the water and homogeneously mix. It is often desirable to have a binder that disperses rather

than dissolves to produce non-soluble green bodies. Water is much cheaper than the non-aqueous solvents and is much safer to handle [10]. Unfortunately, it is often necessary to have extra equipment to evaporate the water in these slurries. In the process of freeze casting, water is used instead of organic solvents due to its freezing temperature and ability to be sublimed. This will be discussed further in the tape casting section.

Dispersant

After the ceramic is combined with the solvent a dispersant is added. The dispersant basically coats the individual particles to separate them from each other by steric hindrance. When the particles are not able to come into contact with one another the slurry becomes homogeneous. The better the slurry is dispersed, the more even and dense the green tape will become.

A dispersant can also have the ability to ionically charge the particles so that they repel one another. The ceramic particles must have their secondary bonds “broken” to properly be repelled. This secondary bond consists of Van der Waals (VDW) forces attract particles together based on their positive and negative regions, or dipoles. In order to reverse this bonding, the dispersant must induce a larger ionic charge to the particles than those of the VDW forces. [8]

The amount of dispersant necessary to properly homogenize a slurry is often minimal. Generally, no more than an amount equal to 2% of the ceramic powder mass is necessary for the milling phase. An excess of dispersant can cause agglomeration of particles by the bridging of dispersant chains. This is practically negligible when calculating the masses of the various ingredients for solids loading. The equation for this

will be explained in further detail later. When a slurry is milled in excess, it is possible that the dispersant coatings will break down, causing the particles to agglomerate. At this point the slurry becomes slightly “chunky”. Once this occurs, additional dispersant can be added in an effort to regain homogeneity, but this may be futile.

Binders

The binding agents are widely considered the most important additives of the slurry. The binders hold everything together once the solvents have been removed. The green tape relies on the binders to give it its strength, durability, and flexibility, as well as other properties. Without binders, the resulting tape would be like wet sand; it would look nice and smooth initially, but would crumble when handled. Once the tape is dry, it needs to be able to be cut and prepared for sintering without being damaged. [10]

There are essentially two types of binders that are used with tape casting. These are the polyvinyls and the polyacrylates. The decision of which one to use often depends on which solvent is being utilized. Binders with high molecular weight are often used because they produce stronger green tapes due to their higher viscosity. The binder contains polymer chains that form a matrix over all of the ceramic particles of the tape and hold them together. Sometimes it is desired to use binders with lower molecular weights to lower the viscosity in order to increase solids loading. However, these binders have smaller polymer chains and greatly reduce the strength of the green tape. [10]

It is also necessary to choose a binder that will properly react with the atmosphere in which it is being sintered. For example, some binders won't be properly removed if sintered in a reducing environment, as they require oxygen for proper decomposition.

However, as previously mentioned, the end result of sintering should be a ceramic structure devoid of any binding agents. [10]

CERAMIC PROCESSING TECHNIQUES

In order to use a ceramic for any application, ceramic materials must be formed into a desired shape by some processing method. This process is done utilizing fine powders that undergo a heat treatment process to bond the individual particles together. There are many methods to obtain a desired ceramic structure of varying size and shape. Each method utilizes various equipment and ingredients to create a desired result. Though this research was specifically related to the merging of tape casting and freeze casting technologies, other methods of ceramic forming techniques have been examined and contrasted with the most commonly used practices that are described in detail in this section.

Dry Pressing

Dry pressing is done by either uniaxially pressing material in a metal die or isostatically pressing the material of interest. These methods are fairly simple to do and can be used to create basic sizes and shapes with relative consistency. Powder particles are packed together densely by applying a pressure. This pressure determines how dense the green body will be.

Uniaxial Die Pressing

In this processing method, dry powder is compacted into a die. The die is often one that produces a green body with a fairly straightforward shape, such as a cylinder or cube. Generally this method is used to create specimens that are not as tall as they are wide (aspect ratio less than one), based on the method of compaction. To process a raw

material using this method, the powder is measured out and poured into the die.

Occasionally it is necessary to mix a binder or plasticizer with the material in order to achieve desired properties. While the material is being pressed the particles do two things. First, the grains rearrange themselves to fill in large voids. Then the grains deform to fill in the smaller voids. The end result is a sample of dimensions determined by the die shape, amount of material, and pressure applied. A typical pressing process is shown in Figure 1. After compaction the component should yield sufficient strength for handling prior to the sintering process. [11, 12]

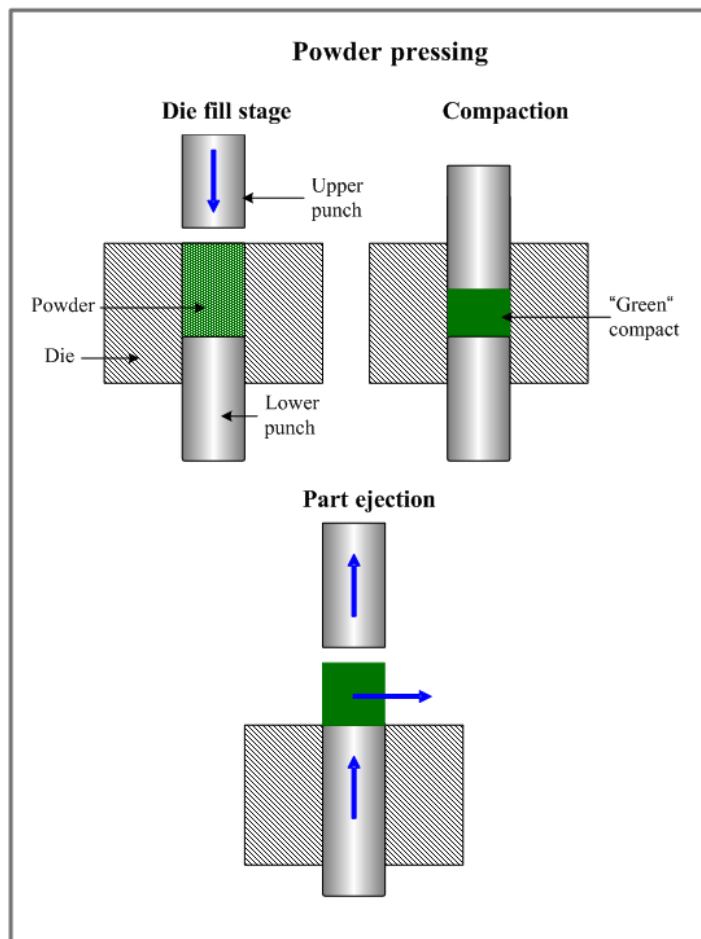


Figure 1. Uniaxial Die Pressing Process. [12]

Isostatic Pressing

This method involves applying a uniform pressure to a contained material. This is done in one of two ways. The first is called wet-bag pressing in which the material of interest is measured and placed in a flexible rubber mold. This mold is then placed within an oil-filled pressure vessel. The press applies a uniform pressure to the mold, forming the material to the desired shape. This is displayed in Figure 2 (a). Once this is complete, the mold is removed from the oil and the green sample can be retrieved. This method is often used when it is necessary to create a complex shape or large size.

The second method of isostatic pressing is called dry-bag pressing. This method is similar to the wet-bag press. With the dry-bag, a mold is already contained within the pressure vessel. The dry material is then added to this mold in the proper amount. The mold is sealed up and an item, such as a metal core, can be added for the mold to form around for a specific shape. This method is displayed in Figure 2 (b). The pressure is then slowly released and the green body is removed from the mold. Since the mold is fixed within the pressure vessel, this method is often preferred over wet-bag pressing; it is easier to produce many samples in less time with dry-bag pressing. [11]

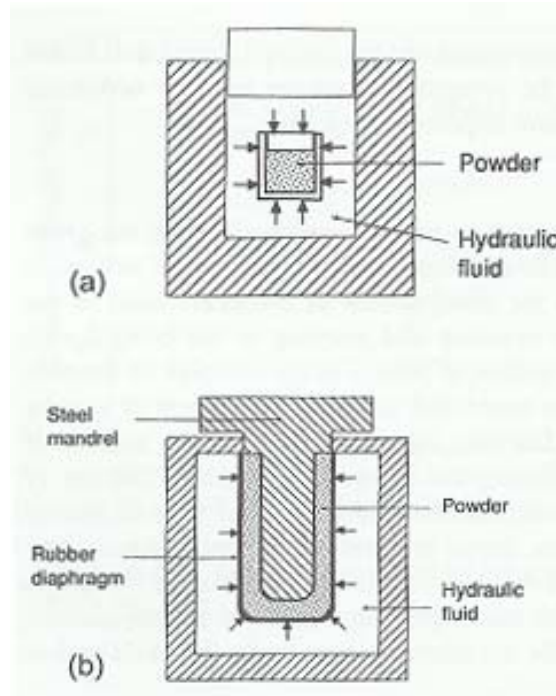


Figure 2. (a) Wet-bag and (b) dry-bag isostatic pressing. [11]

Spraying

Another method of ceramic processing is spray application. This is done to apply a very thin layer of ceramic, usually onto another material. This process is useful for applying an anode and cathode for an electrolyte supported fuel cell, for example. Often a slurry is made with the ceramic, an organic solvent, a dispersant, and a binder. A much smaller amount is needed than with the casting methods and it is much less viscous. The slurry is applied with the use of an airbrush sprayer. A disadvantage to this system is that the application thickness is difficult to regulate when done manually. After properly applied, the system is allowed to dry. This occurs fairly quickly with the use of an organic solvent. It may be desired to perform more applications after each drying process to achieve proper thickness and achieve proper leveling. Examples of a common airbrush

applicator and anode-sprayed electrolyte (applied via spraying method) are displayed in Figure 3.

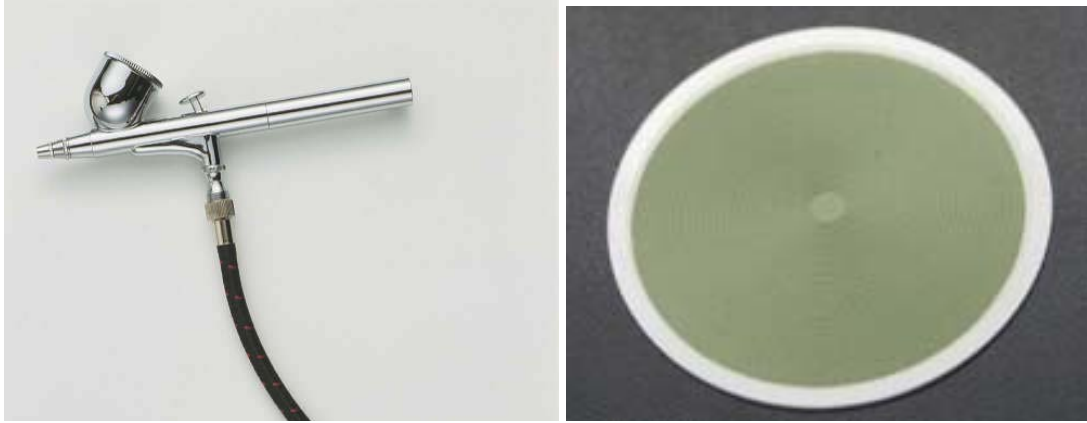


Figure 3. Example of Airbrush (Left) and Application of Method (Right). [13, 14]

Injection and Extrusion

Ceramics can also be “plastically” formed. Some of the common methods of this include extrusion and injection molding. In both cases, a molding additive containing polymeric chains is combined with the ceramic powder and processed with a machine. For the injection molding process, the ceramic material is fed into an injection chamber where it is heated to produce a viscous mass. A pressure is then applied to inject the viscous material into a mold. The mold cools and the result can be sintered. A diagram of a typical injection molding process is shown in Figure 5. With extrusion, the material is pressed through a shaped nozzle to produce a result with a uniform cross section. The process is similar to injection molding, but the material is not heated in the process. [11]

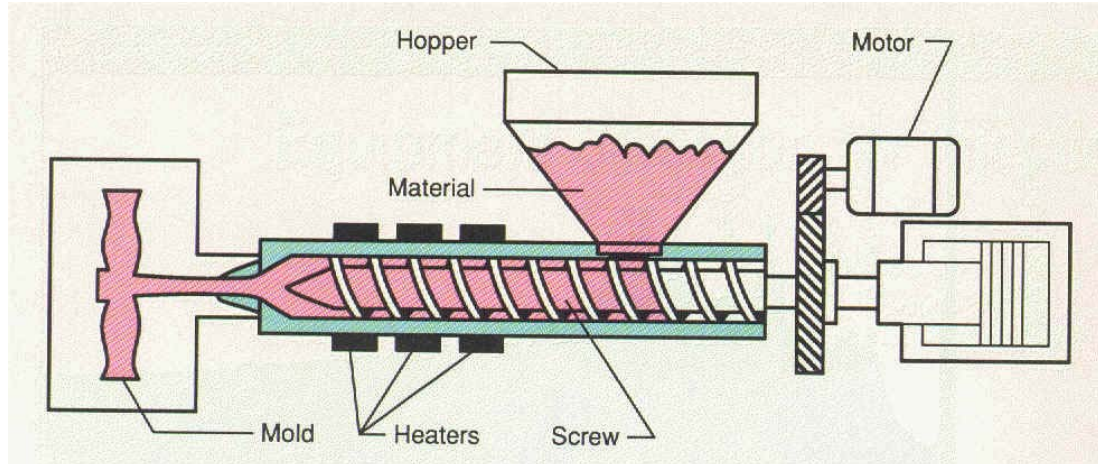


Figure 4. Example of Injection Molding Machinery. [15]

Slurry Casting

The two most common casting methods used today are slip casting and tape casting. Each technique requires suspending material particles in a liquid to create a slurry and then removing the liquid once it is cast. However, the technique of which the liquid is removed varies by casting method. When the casting is complete, a green dense ceramic material that can then be sintered is produced.

Pressure and Gel Casting

Pressure casting and gel casting are not as heavily utilized as other methods, but can be used to make various shapes with the use of molds. Pressure casting uses capillary forces to form the ceramic. A slurry is poured into a porous metal or plastic mold and a pressure is applied to speed up the capillary action of the pores in a process that accelerates traditional slip casting. The solids of the slurry build up on the mold and

a cast is produced that can be further processed by sintering. An example of a pressure casting apparatus is displayed in Figure 4. [11]

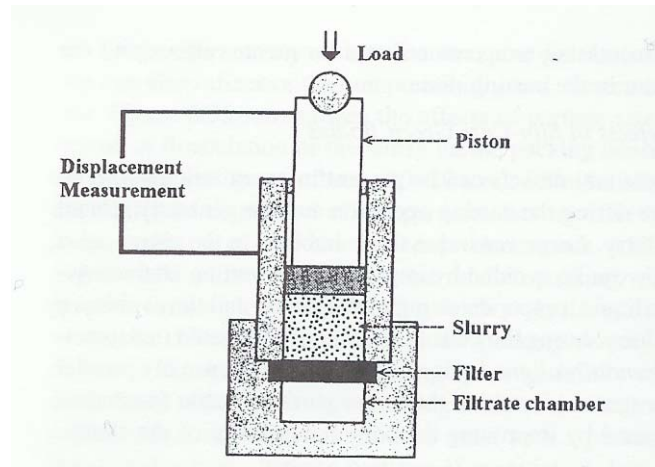


Figure 5. Example of a Pressure Casting Apparatus. [11]

Gel casting also uses a mold, but no pressure is applied. A mold is used to contain an aqueous slurry with an added monomer ingredient and the material undergoes a polymerization process. This bonds the ingredients in a gel-like suspension in-situ. The gel, while still wet, is removed from the mold and undergoes steps in drying, binder burnout, and finally sintering. [11]

Slip Casting

The first step of the slip casting technique involves creating a slurry with the desired material and solvent. It is also necessary in the slurry making process to include a dispersant and some binding agent. The process of making a slurry, as well as a description of the ingredients, can be found in the Freeze-Tape Casting Experimental Procedure section.

After the slurry is properly prepared it is poured into a mold of a specific design. The mold contains micropores all throughout its structure which act as capillaries. These pores use a capillary action to draw the liquid out of the slurry and into the mold. As this happens, a layer of material builds up on the inside of the mold. This process is shown in Figure 6.

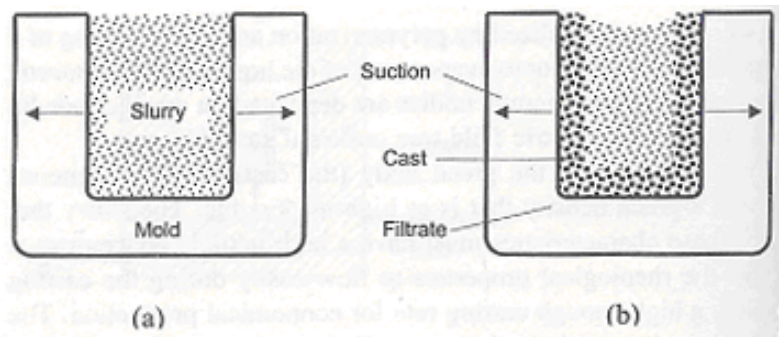


Figure 6. Slip Casting Process. [11]

When the desired thickness of solids is built up on the mold walls, the excess liquid is poured out. The material cast and mold are allowed to dry. As the cast dries it shrinks and separates from the mold walls and the cast can then be sintered. A full schematic of the process is displayed in Figure 7. The preparation of complex shaped molds can facilitate the fabrication of complex shaped slip cast parts both hollow and solid.

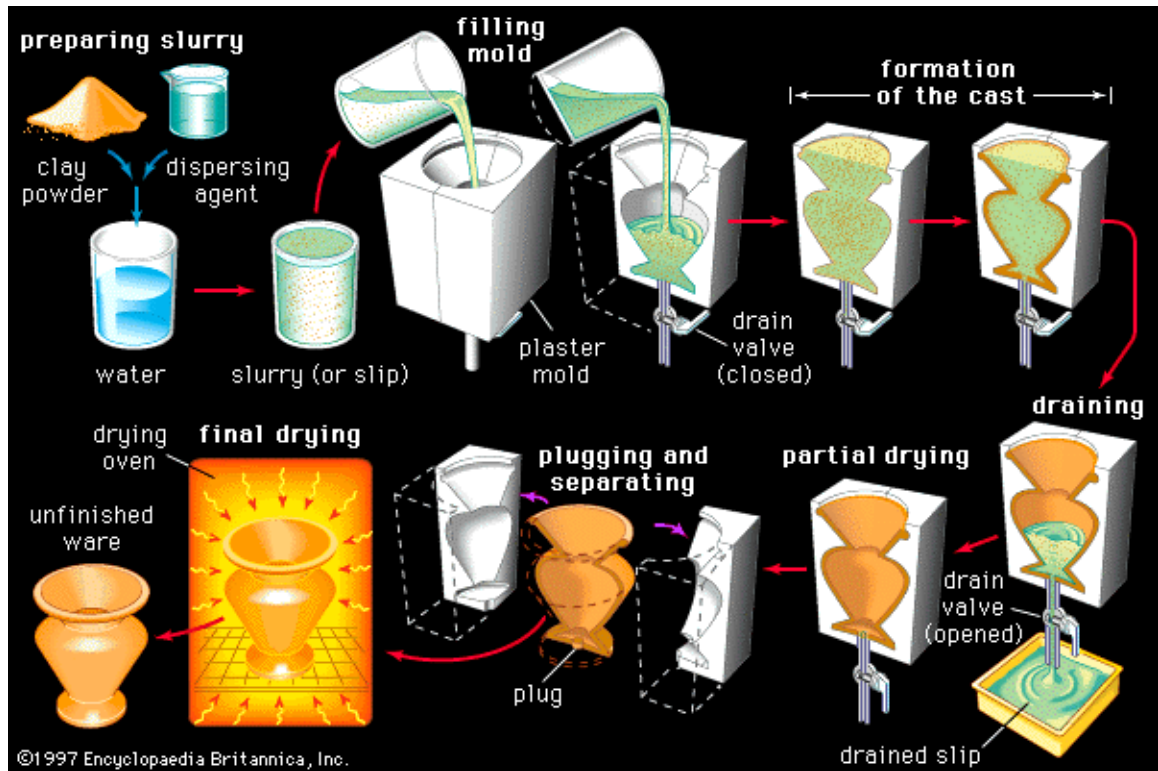


Figure 7. Stages of Slip Casting. [16]

Tape Casting

Tape casting has been used for decades to fabricate thin, uniform ceramic-based sheets. A detailed diagram of a continuous tape casting process used for developing multilayer resistors is shown in Figure 8. A slurry is created using a similar method as with slip casting. The slurry is generally cast onto a polyester film with a non-stick coating to allow the resulting ceramic material to be easily removed. The thickness of which the ceramic is cast is regulated with some form of “doctor” blade.

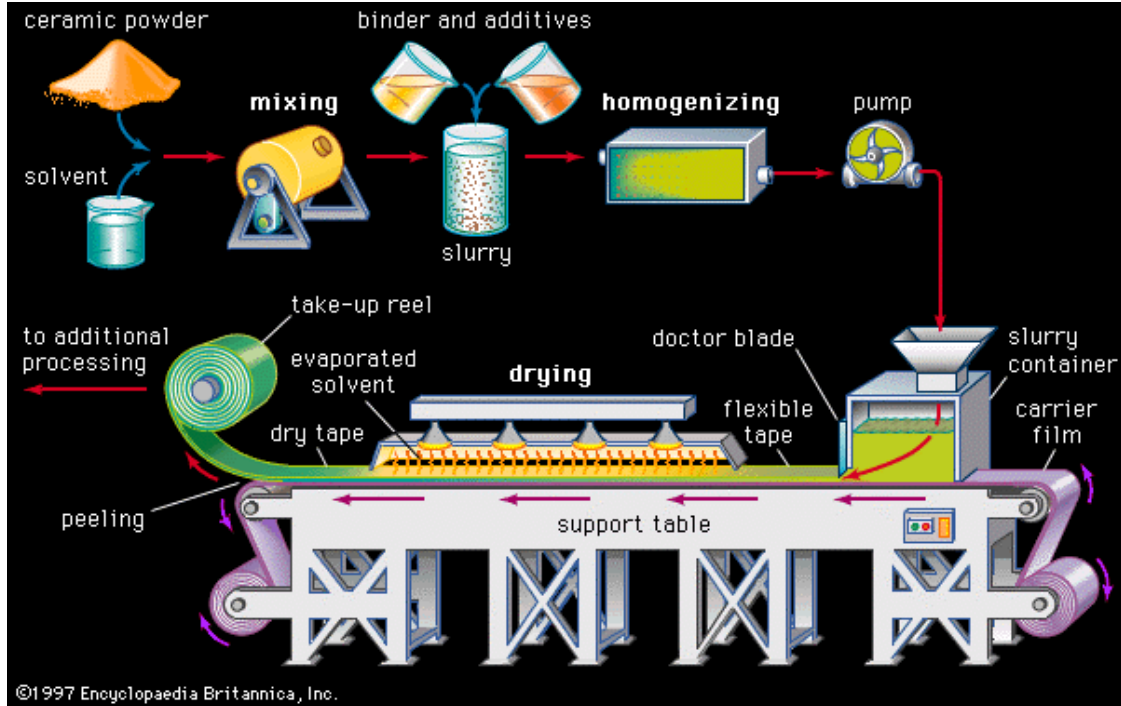


Figure 8. Continuous Tape Casting Process. [17]

A doctor blade, as shown in the figure, regulates the amount of slurry that gets pulled on the film. However, depending on the amount of slurry within the slurry container, hydrostatic forces may cause the slurry to be pushed out unevenly. This can be prevented with the use of a double doctor blade that utilizes two blades, as the name suggests. The doctor blade concept will be discussed in further detail in the Freeze-Tape Casting section. The slurry is poured into the stationary doctor blade reservoir and the slurry gets spread evenly along the moving film.

After the slurry is cast, the solvent evaporates out which aids in the production of a solid green tape. The speed of which the solvent evaporates is determined by the composition of the slurry, as well as any drying apparatus that may be utilized. Solvents are either aqueous (water) or organic; types of solvents are described in the following section. Since the slurry is cast onto a film, the only place the solvent can evaporate is

out of the exposed top surface. Because of this, the solvent must progress throughout the thickness of the tape to escape. This progression is known as diffusion. In order to dry the tape uniformly, the ideal situation is to have the diffusion rate equal to the evaporation rate. Unfortunately, this is practically impossible because the concentration of the solvent throughout the tape's thickness would have to remain uniform throughout the entire evaporation process.

The most common ways to increase diffusion rate are to use different binder concentrations and particle size. Heat is often applied to increase the diffusion rate, but this also increases the evaporation rate. It is necessary to ensure the diffusion rate is not significantly lower than evaporation in order to prevent a skin from forming. If a skin does form, the top of the tape will not allow proper diffusion to occur, which could result in deformities in the tape, such as wrinkling and curling. [10]

Binder Considerations for Common Processing

The approximate binder concentrations of the previously described processing techniques are displayed in Table 1. Injection uses the most amount of binder in an effort to make it plastic in nature for the forming phase. However, large concentrations of binders throughout a material must be slowly burned out in the sintering process. If not done properly, the material could have some debinding defects such as cracking, folding, and cavity formation. High concentrations can also be disadvantageous because they yield lower overall green densities. Low binder concentrations are not as important to the

sintering process, but the type of binder of interest and its burnout characteristics should be examined prior to sintering. [8, 11]

Table 1. Binder Concentrations Relative to Solid Content for Various Processing Methods. [11]

Processing Method	Binder Concentration
Dry Pressing	< 5%
Spraying	< 5%
Gel Casting	< 4%
Pressure Casting	< 2%
Injection	< 30%
Extrusion	< 5%
Slip Casting	< 0.5%
Tape Casting	10% - 30%

Freeze Forming

Freeze forming is a processing method that has become popular over the last few years. It involves freezing a suspension within a non-porous mold, removing the frozen material, and freeze drying it to remove the solvent. The result is a green body with the same shape as the mold. The density of the material is dependant on the solids loading; low solids content produces porous material. The typical processing method is outlined in Figure 9. This uses the same slurry processing steps as slip casting and tape casting. [18]

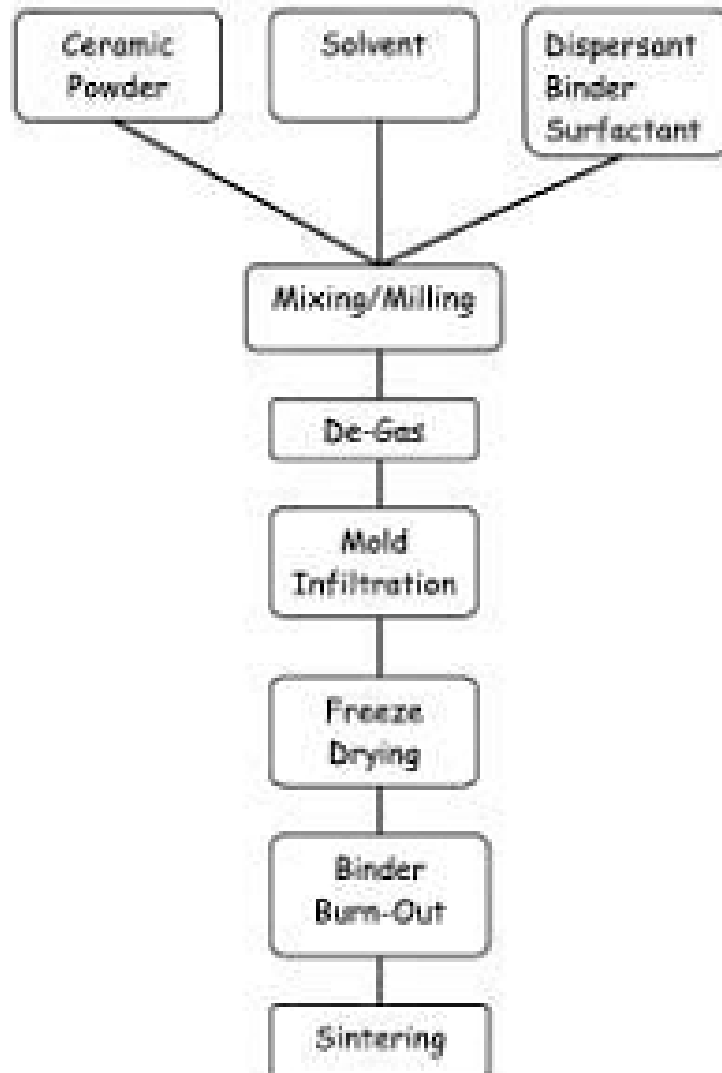


Figure 9. Freeze Forming Processing Schematic. [18]

This processing method is advantageous due to its ability to be conducted with non-toxic chemicals, the general ease of process, and its low binder concentrations, which allows for faster sintering cycles and minimal binder removal defects. Also, the material is easy to remove from the mold once it has been completely frozen and maintains a stable structure during transfer to the freeze-drying machine, as long as it is not held at an elevated temperature for sustained periods of time. A major advantage to

using sublimation is that it allows the structure to maintain its molded shape while the solvent is being removed. Since the ice is bypassing the liquid phase, and thus the volume decrease, as shown in Figure 10, capillary drying stresses become much less severe. In typical tape casting processes, these capillary stresses can cause warping of the material. [18]

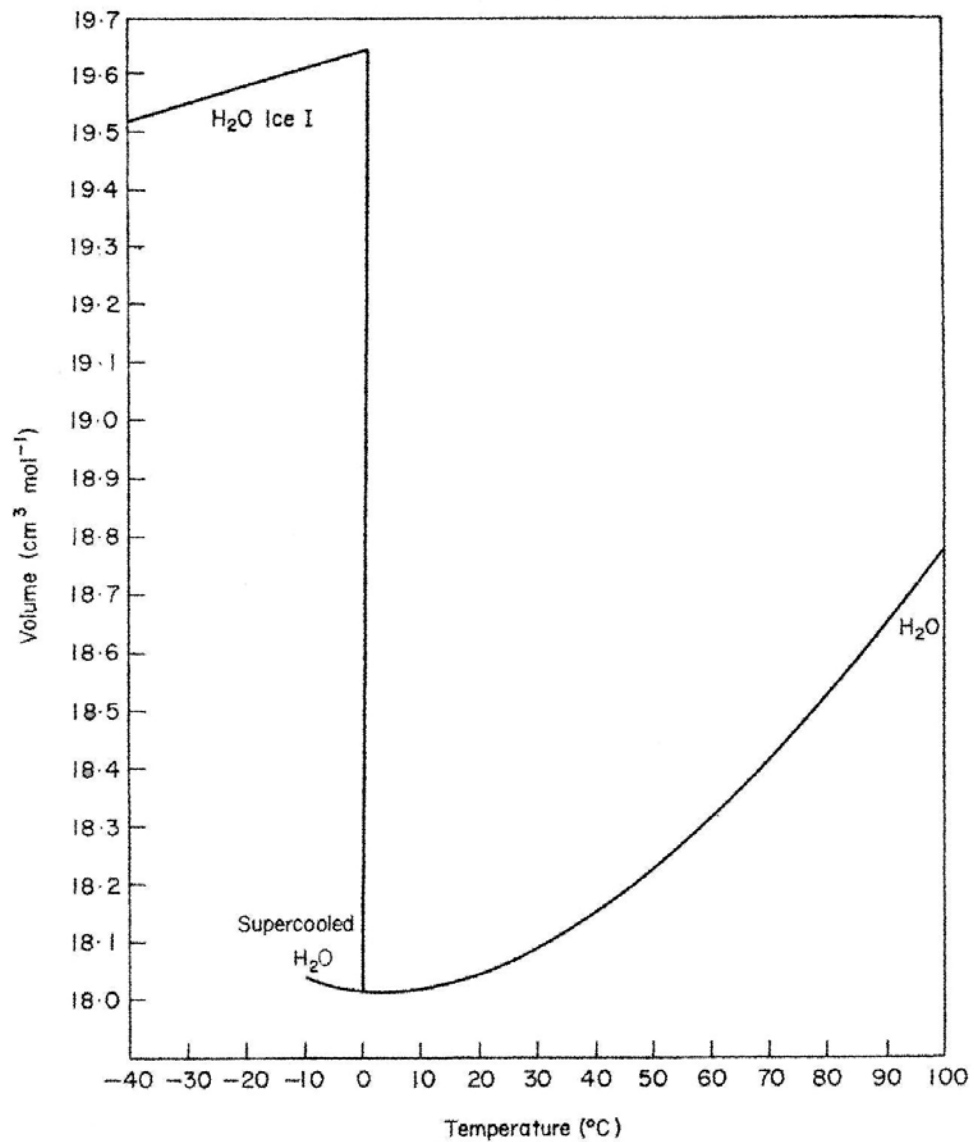


Figure 10. Temperature vs. Volume at Phase Change for H₂O. [18]

General Pore Forming

Most processing techniques will produce a slightly porous green body due to the solvent removal process or, in the case of die pressing, packing orientation due to lack of sufficient pressure. During the sintering process, these pores are reduced to greatly densify the material. However, in some cases it is desirable to make a porous ceramic. This may be desired for filtration or fuel cell applications. One way to make a porous ceramic is to introduce thermal fugitives to the material prior to the sintering phase. A thermal fugitive is a substance that will decompose at a specific temperature. Carbon/graphite is a thermal fugitive commonly used in pore forming.

Pore formers are added to the processing material and thoroughly mixed, often by combining a measured amount of the thermal fugitive with the ceramic powder and adding water or an organic solvent as well as a dispersant. This combination can then be milled until the mixture achieves homogeneity. At this point, the slurry can be used for casting or the solvent can be removed from the mixture to result in a properly mixed dry powder. A common method for solvent removal, for this application, is to quickly freeze the suspension with the aid of liquid nitrogen. Once completely frozen, the mixture is placed in a freeze-dryer and the solvent is sublimated. Since water has a higher freezing temperature than most organic solvents, it is frequently used as the mixing suspension for this method. Once the water has completely sublimed the resulting powder can be processed by one of the dry powder processing methods previously described. Casting of

materials with pore formers is also possible. The material powder/pore former mixture is processed as it would if pore formers had not been included.

Once the processing is complete, the material is sintered. As the temperature increases, the particles of the ceramic or metal start binding together. While this is occurring, the thermal fugitive breaks down leaving voids, thus producing a porous structure. Different pore formers have dissimilar burnout energy, which should be considered when determining which to use. Also, some can be quite costly, such as glassy carbon or graphite powder, while others, such as cornstarch and wood particulate, can be relatively cheap. However, the type that is used determines the size and shape of the pores. Images of the effects of different pore formers are shown in Figure 11.

Varying thermal fugitive concentrations and/or particle size can be utilized to make unique structures. For example, tapes can be processed with different pores throughout the thickness. To accomplish this, a number of thin tapes are cast with altered thermal fugitive content. Samples can be removed from each of the green tapes and stacked on top of each other. This stack is then uniaxially pressed and laminated together, resulting in a single structure with varying pore layers. Once sintered, these samples can be used for situations such as filtration, with pores ranging in size throughout the thickness. Most processing methods cannot form this layered porosity without the aid of pore formers and multiple lamination steps. However, the freeze-tape casting method outlined in the following chapter develops this porosity with much greater ease. [8]

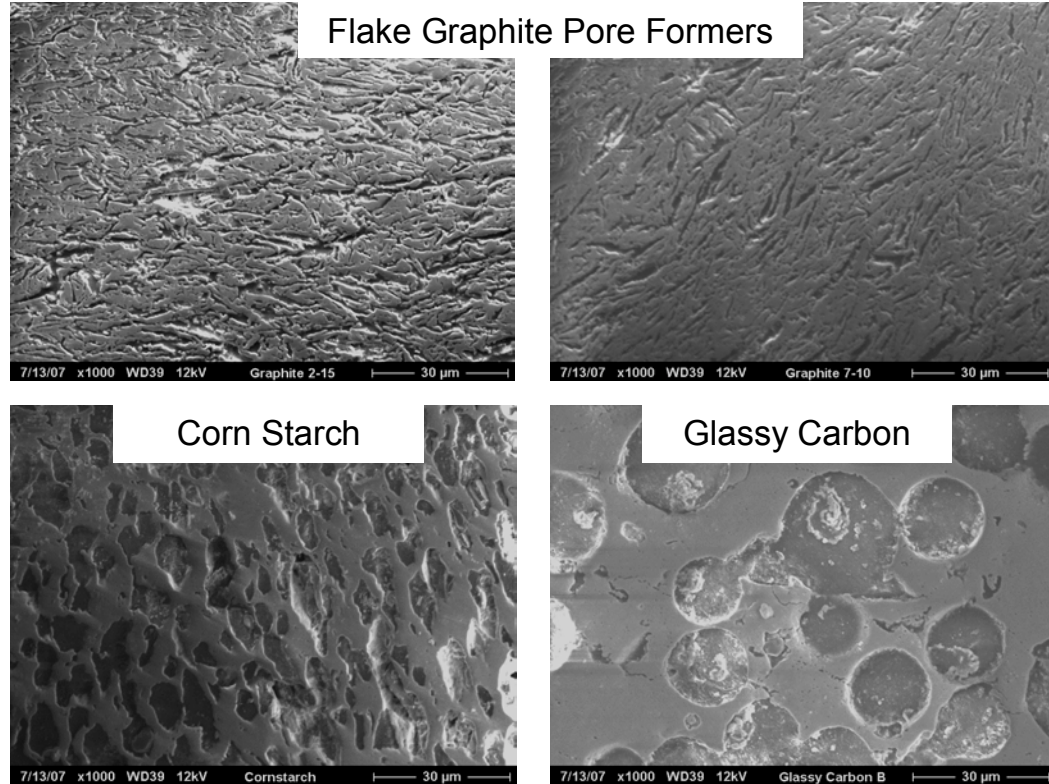


Figure 11. Thermal Fugitive Effects on Pore Structure.

There are some methods of forming pores that do not require the use of high temperature. One example of this includes combining NiO with the material of interest. As with the thermal fugitives, NiO can be introduced into a slurry and processed by any of the previously described methods. The material is sintered with its desired heating cycle to produce a dense ceramic. However, the NiO is still within the material, unlike the thermal fugitives that degrade during sintering.

Putting this type of sample in a reducing environment can form small pores as NiO is reduced to Ni metal. This is accomplished by heating the sample to a predetermined level, much lower than the melting temperature, while flowing a type of forming gas over it. The gas reacts with NiO, removing the oxygen atoms, which gives it some porosity. The Ni can then be etched or used as is for catalyst applications.

However, depending on the density of the sintered sample, the pores formed through reduction may not be large enough to allow the gas to flow within the material, leaving dense NiO contained within. Also, if the sample is to be used in high temperatures in oxygen rich environments, the material will re-oxidize and lose its porosity.

A more effective way to give porosity to samples containing NiO would be to remove the Ni. This way, oxidation would not become an issue. In order to do this, the sample is first reduced as previously explained. Once this is accomplished, the sample is submerged in boiling nitric acid. As it boils the nickel is leached from the sample. When properly leached, the end results would have a porosity ratio approximately equal to the percentage of NiO that was initially combined with the material. Though this seems to be an effective method of inducing porosity, it is not as safe or easy as using thermal fugitives. [19]

FREEZE-TAPE CASTING EXPERIMENTAL PROCEDURE

The procedure for the freeze-tape casting process involves some preparation prior to casting. The ceramic slurry must be prepared based on the intended properties of the sintered tape. In addition to properly adjusting the doctor blade, the tape casting bed must be cooled and other machinery must be ready. The following is an explanation of the steps taken during the freeze-tape casting experimentation.

Slurry Preparation

All of the previously mentioned slurry ingredients must be mixed properly. Care must be given in measuring to ensure the resulting tapes are comparable for evaluation. A couple things must be considered when starting the slurry. First, the solids content, or solids loading, should be determined, as this will establish how much solvent should be included. Second, the mass of the solids being added should be thought out because this, combined with the solids loading calculations, essentially determines how long the tape will be when it is cast.

Ball Milling

Ball milling, also known as dispersion milling, is the slurry mixing process that was utilized in the freeze casting experiments. With this method, “balls” are used in conjunction with dispersant to thoroughly mix the slurry until properly homogenized. The “balls” are made from YSZ that has been highly compressed to create small, hard cylinders of varying sizes. The compressed YSZ balls are used because they only consist

of YSZ and thus will not contaminate the system; if metal balls are used, there is a possibility that particles of metal could combine with the slurry. The balls are placed in a container with all of the slurry ingredients, capped off, and placed on a rotary ball mill. This mill consists of two rollers spaced enough to keep the container suspended between them. A motor of adjustable speed rotates one of the rollers, while the other spins freely.

Prior to ball milling, the ingredients are measured out. The YSZ is measured first and placed in the container. Based on the aforementioned solids loading equation, the appropriate amount of water is added. This water is deionized both to prevent any change to the dispersant effects and to avoid any possible contamination that might come from tap water. Darvan-C, an ammonium based dispersant used with some special ceramics, is added in the amount of 1% of the solid mass [20]. At this point, five-millimeter and ten-millimeter ball milling media are added. The amount of each necessary for proper mixing varies based on solids loading. The container is placed on the rollers and allowed to mill for 48 hours.

Equipment Preparation

Prior to the casting, a few things need to be set up. The casting bed needs to be cooled in order to properly freeze the water within the slurry. This is accomplished with a ThermoNESLAB ULT-80 circulating refrigeration bath. Attached to the unit is a copper tube that runs along the underside of the tape caster, in contact with the aluminum slab. This is well insulated to prevent unwanted heat transfer. The refrigeration unit

circulates cooled methanol throughout the tube to cool the caster to below 0 C. This must be turned on three to five hours prior to the casting.

A VirTis AdVantage Freeze Dryer is used after the tape is cast and completely frozen. The freeze dryer is used to sublime the water out of the tape and maintain its structure during the process. The structure must remain solid throughout the sublimation. In order to do this, the tape is first placed on a shelf within the unit and a vacuum is pulled. The shelf needs to initially be below freezing to ensure heat transfer from the shelf to the tape does not cause it to revert back to a liquid state. This is set to cool to -20 C about three hours prior to the cast. Additionally, a condenser within the unit is turned on to attract excess moisture.

The final thing to set up is the double doctor blade. This assembly, displayed in Figure 12, rests, immobile, on the moving Mylar film. The aluminum frame of the doctor blade uses a surface that angles down to the film in the direction of pull. On either side of the inclined surface are walls that contain the slurry as it is being cast. Two doctor blades are attached to the frame. These blades limit the height of which the slurry is cast and are adjustable with the use of springs and micrometers. The first blade is set to a height slightly greater than the second, which is set at the intended casting height.

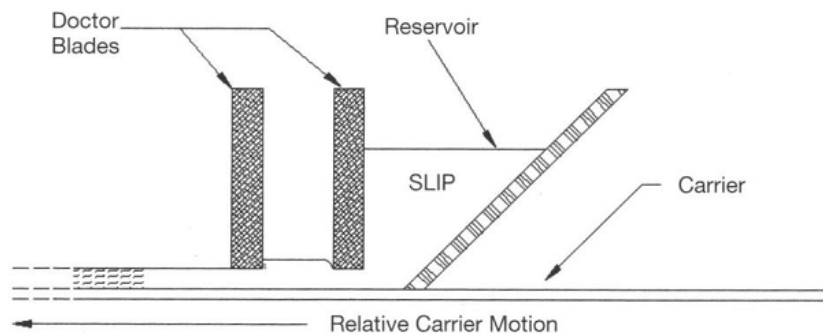


Figure 12. Double Doctor Blade Assembly. [10]

A small distance separates the two blades. In this gap lies the “casting pool” which is at a thickness greater than that set height of the first blade. The reason for this is that the slurry in the reservoir causes hydrostatic pressure at the deepest point, which makes it want to squeeze under the first blade rather than just being pulled. Within the casting pool this pressure is significantly lower, assuming the difference in height of the two blades is not considerable. The equations for hydrostatic pressure will not be discussed, as they were not used to obtain results. [10]

Prior to casting, the blades are zeroed out on a flat surface. The micrometers used are set to the intended height by hand. Obviously some variability comes from this method; tapes may be uneven as a result.

Casting

One hour prior to casting, the viscosity of the slurry must be checked. If the slurry is not viscous enough, usually comparable to that of house paint ($\sim 3000\text{-}4000$ MPa*s), it may be desirable to add a thickening agent. The thickener used is VANZAN, which is a derivative of Xanthan gum, which: “increases viscosity, helps to stabilize emulsions, and prevents the settling of solids in a wide variety of applications.” [21]. If the slurry requires greater viscosity, the milling media is filtered out of the slurry, a small amount of VANZAN is added, and 20-millimeter milling balls are added and allowed to mill for one hour. At this point the slurry is checked again and the steps are repeated as necessary. However, should the viscosity of the slurry become too high, it is unlikely the

problem can be remedied without adding more liquid. Doing this will change the solids loading and alter the experimental results.

The final step with the slurry, preceding the cast, is to add the binding agents. Two binding agents are used in this process: Duramax B-1000 and B-1022 (Rohm and Haas Company). They are measured out and added as 13% and 12% of the ceramic mass, respectively. The B-1000 contains 55% solids and is used to add flexibility to the green tape, while the B-1022 has 45% solids and gives the tape stiffness. These properties only affect the tape after sublimation and before sintering. As previously mentioned, the solids content of each of the binders is factored into the solids loading equation.

The binders are added directly to the milling container and slowly mixed with the other ingredients. When this is done it helps remove any slurry attached to the container walls, decreases the viscosity of the slurry making it easier to filter, and aids in the general mixing of ingredients. The slurry with the binders should not be mixed vigorously. If this is done, the binders will often react giving the slurry a consistency similar to cottage cheese. Vigorous agitation also mixes air with the slurry causing bubbles to form. After slowly mixing for a few minutes, the slurry is strained to remove the milling media and any agglomerates that may have formed. This mixture is then slowly mixed for ten minutes prior to cast to ensure the binders are completely combined.

With the slurry prepared and all of the equipment set up, the tape can now be cast. The Mylar carrier is rolled up tightly on the casting side. Throughout the cast it is necessary to make certain that the carrier is tight and wrinkle-free. Any waves in the

carrier will cause a change in casting rate and therefore the tape will be uneven. The carrier pull rate is manually adjusted to approximately one-millimeter per second. As displayed in Figure 13, the ceramic slurry is poured into the reservoir and pulled along the freezing bed. A study was conducted at varying cooling temperatures to determine the effect of freezing rate on the tape structure. The temperature measured on the surface of the freezing bed was approximately half that, in Centigrade, of the refrigeration bath; a -80 C input would cool the bed to -40 C . Results of temperature tests will be explained later.

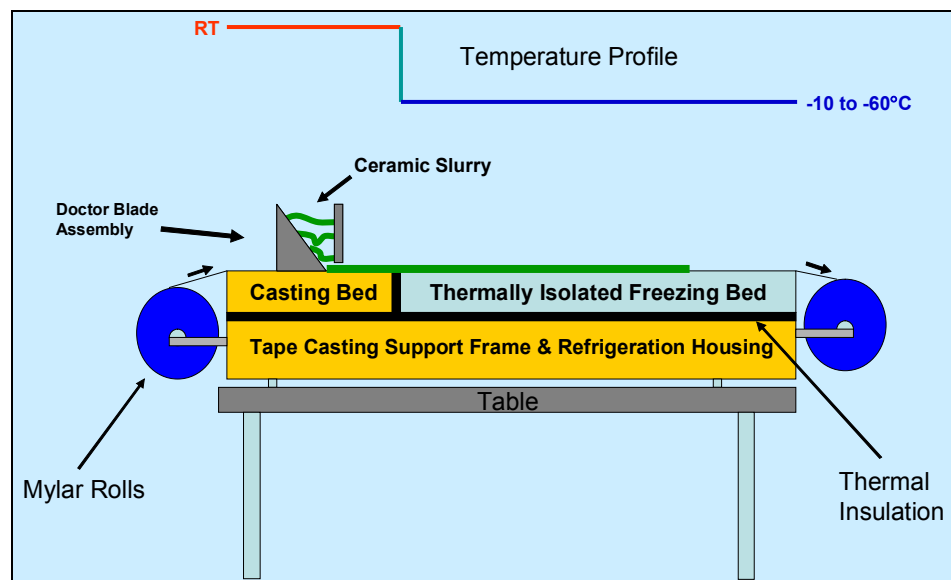


Figure 13. Freeze Casting Diagram. [8]

After the tape has been cast, it is allowed to completely freeze on the casting bed. This is generally complete a few minutes after the last of the slurry has come in contact with the bed. At this point, the Mylar is cut around the tape and that whole section is quickly transferred to the cooled shelf of the freeze-drying unit. The unit is sealed and a vacuum pump is turned on. Once a strong enough vacuum is pulled, the shelf

temperature is increased to 30 C. The whole unit is allowed to run for about 12 hours to sublimate the ice crystals that have formed within the tape. The resulting ceramic material is now considered the green tape.

Sintering

The final step in the casting process is sintering. This involves heating the green tape to a specific temperature in order to give the tape its desired properties. This may be achieved under a vacuum, in a reducing environment, or in ambient air. Sintering is conducted with a specific heating cycle that is decided based on the desired result. It involves ramping up the heat at an input rate, dwelling at a temperature, and ramping back down to ambient temperature. In order to optimize this it may be necessary to run tests on samples of the material of interest in a dilatometer and thermo gravimetric analyzer (TGA). The dilatometer utilizes a linear variable differential transducer (LVDT) to analyze the thermal expansion of the material while the TGA uses a balanced scale to determine the weight loss/gain vs. temperature. Both systems have very limited space for the sample and use a small furnace to mimic the conditions of the sintering process. This testing process can be time consuming, but if the results are analyzed properly, the ramp rates and dwell lengths can be determined in order to achieve the preferred mechanical characteristics. [1]

For the freeze casting testing, a study for optimizing the sintering cycle was not conducted; values for heating rate, max temperature, and dwell time were provided from previous studies to achieve reasonable results. The freeze cast samples are placed on an

aluminum oxide refractory sheet and placed into a box furnace. The heating cycle is programmed into the furnace interface as follows: Increase temperature from ambient conditions at a rate of $5^{\circ}\text{C}/\text{min}$ up to 1450°C , dwell at this temperature for two hours, and reduce the temperature at a rate of $10^{\circ}\text{C}/\text{min}$ until room temperature is reached. The entire cycle theoretically takes about 10 hours, as shown in Figure 14. This sintering cycle was used for all of the samples that were tested. Details of these tests follow in the results section.

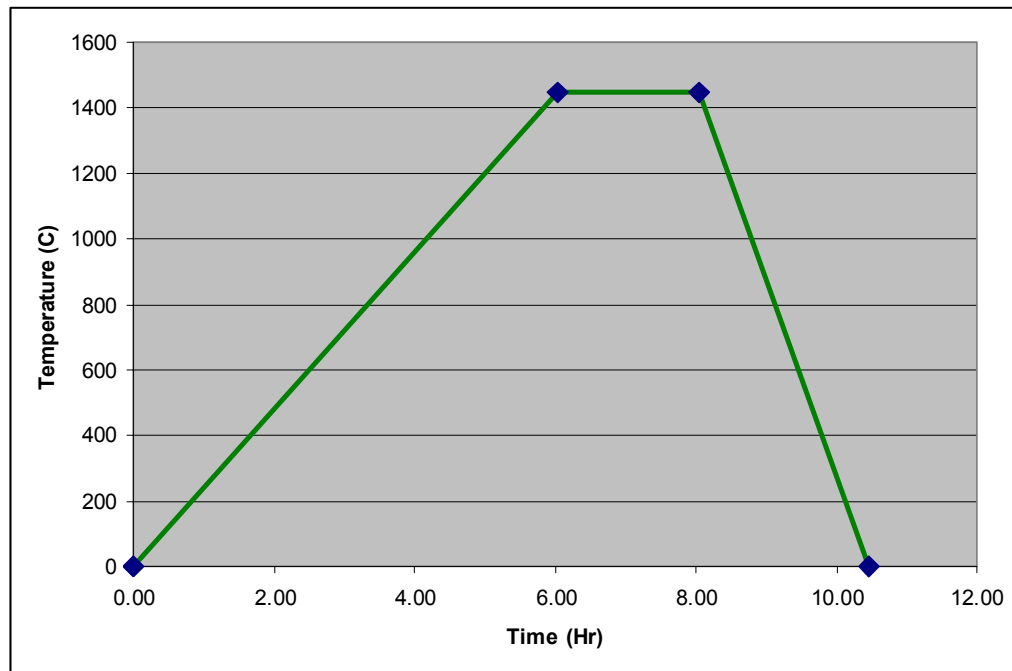


Figure 14. Freeze-Tape Casting Sintering Cycle.

RING-ON-RING MECHANICS

Description of Testing Apparatus

A study of mechanical strength was conducted on freeze cast specimens of 3YSZ (TZ-3YSZ, Tosoh Corporation, Japan). The tests were done using samples of 20%, 25%, and 30% solids loadings. In order to do this, the specimens had to be cut at a specific diameter in their green state and sintered to shrink to a specified testing diameter. It was decided that the final diameter would be 1.5". A testing process described by ASTM International was utilized for these experiments [22]. This process involves compressing a sample between two rings with the aid of machinery and data acquisition software.

Two test fixtures were machined for this experiment. The load fixture and support fixtures were manufactured according to ASTM C1499-05 standards using a typical aluminum. It is recommended to use hardened steel for these fixtures in normal circumstances, but due to the low fracture forces it was determined that such a hard material would be undesirable. A ring was machined on the underside of the load fixture that would apply force to the test sample. The support fixture was machined similarly. A ring was machined at the top of the fixture with a diameter slightly smaller than that of the specimen. Detailed dimensions of each fixture are described in Appendix A.

An Instron testing apparatus was used for this experiment. The position of each component involved in the test is displayed in Figure 15. The bottom support platen and both load rods were made of 6061-T6 Aluminum and supplied for the experiment. The bottom load rod is connected to the support platen and attached to the bottom of the

Instron test fixture. The support fixture is placed on top of the platen and contains machined air holes to prevent pressure buildup. Samples are individually placed and centered on the support ring of the lower fixture. On top of the sample rests the load fixture. This fixture has a similar pressure release hole as that of the support as well as a 120-degree conical section machined into the top for a steel ball to sit. This ball is used to equally distribute the compressive force that the machine will induce. At the top of the Instron test fixture, the top load rod is attached using a cotter pin. This load rod has a similar cone machined out of it, which will press on the ball as the test is being performed.

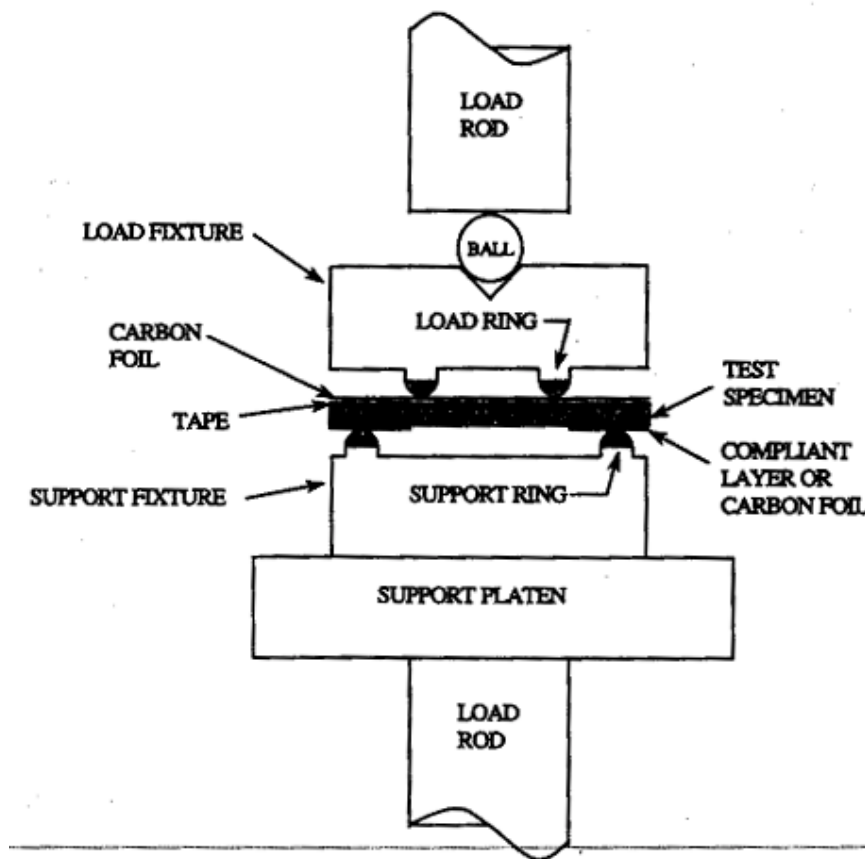


Figure 15. Equibiaxial Test Rig. [22]

Testing Procedure

Samples of 3YSZ that had been freeze cast at 20%, 25%, and 30% solid loadings were cut with a 2 1/8" arch punch. The size of the punch was determined based on shrinkage characteristics of this ceramic. It was determined that this diameter of green sample would shrink to a size a little larger than that of the test fixture. At least ten of each solids load was sintered using the temperature profile described in the Freeze Casting section. The dimensions of the sintered samples were recorded with a digital caliper of 0.01 mm resolution. The samples were checked for any cracks that may have occurred during thermal cycling. Any sample with visible flaws was removed so as to not skew the results.

The concentric rings were assembled as described in the previous section. Each sample was carefully centered on the support ring prior to its individual test. The load ring, with the steel ball on top, was then set atop the sample and aligned with the top load rod. The Instron machine was run with the use of special software (Bluehill). Prior to running any tests, a testing program had to be set up. This was aided by an interface that allowed dimensional data and a rate of compression to be input. An average diameter and thickness was input into the program as well as a compression rate of 2 mm/min. Also, it was set up so the Instron would start and stop manually.

Using the manual machine controls, the top load rod was lowered just above the load fixture and load was calibrated as zero in the software. The rod was then lowered slightly onto the steel ball and the compressive distance was calibrated. The program was then run and allowed to compress the sample. As the samples were compressed, the

program took constant data of compressive distance vs. compressive load. Once a sample reached failure, the program was stopped and the load rod was manually raised to allow the sample to be removed. After each test, the fractured sample was reassembled and held together with tape. Using the ASTM standard shown in Figure 16, each sample was analyzed to determine the strength of the failure. These results will be briefly discussed later.

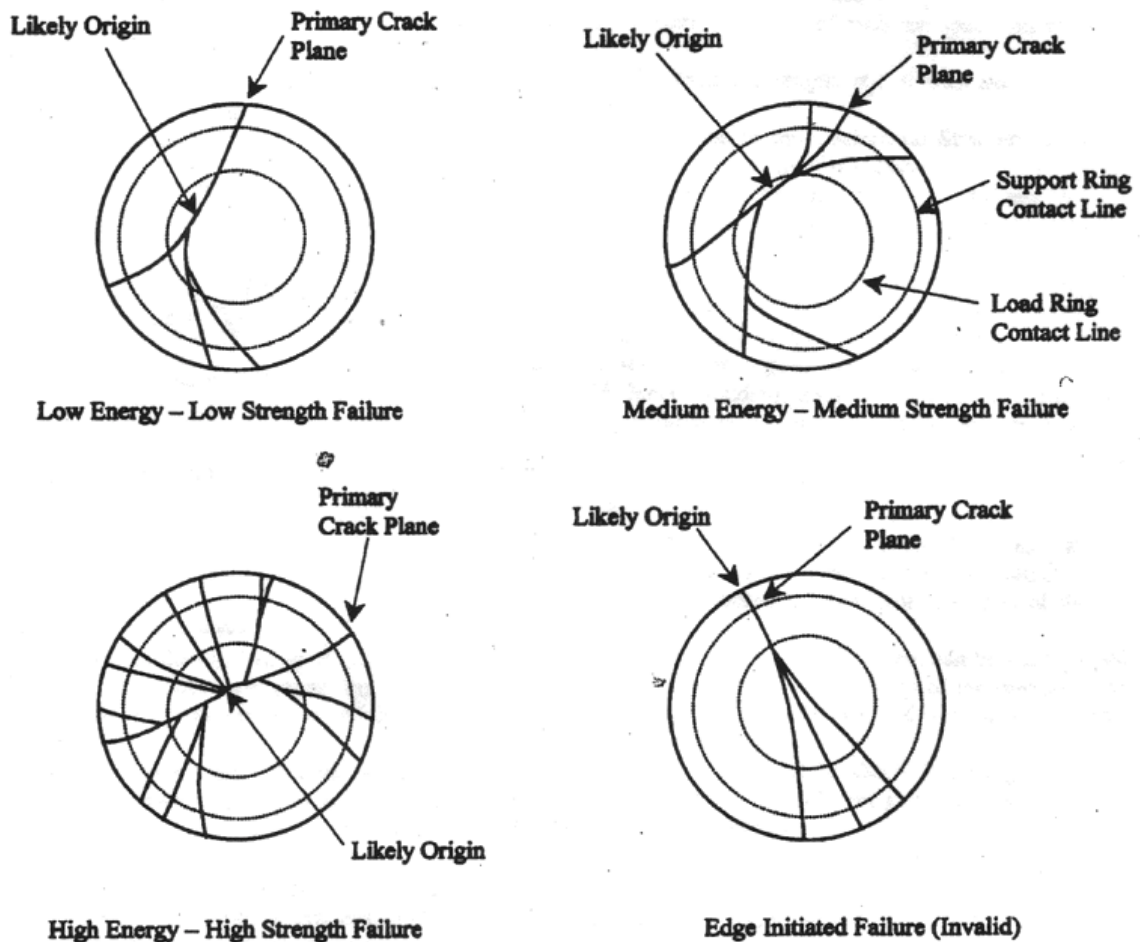


Figure 16. Typical Failure Patterns of Concentric Ring Test Specimens. [22]

Result Analysis

The C1499-05 ASTM standard manual provides an equation for calculating the equibiaxial strength of each sample. In this equation, shown as Equation 1, the equibiaxial strength (σ_f) is related to the fracture force (F), the sample height (h), Poisson's ratio (ν), support ring diameter (D_s), load ring diameter (D_L), and the sample diameter (D). The force is in Newtons, Poisson's ratio is dimensionless, and the height and diameters are in millimeters.

$$\sigma_f = \frac{3 * F}{2 * \pi * h^2} * \left[(1 - \nu) * \frac{D_s^2 - D_L^2}{2 * D^2} + (1 + \nu) * \ln \left(\frac{D_s}{D_L} \right) \right]$$

Equation 1. Equibiaxial Strength of Circular Sample by Concentric Load Testing. [22]

TRANSPORT CHARACTERISTICS

The tape that results from the freeze casting process has pores that extend from the base to the top with increasing diameter. The pores are all interconnected producing semi-conical columns of empty space throughout the material. Scanning electron microscopy (SEM) was used to capture images of the pore structures of some freeze cast specimens for analysis. After examining some images, it appears that their tortuosities are very low. Tortuosity is a term used to describe how many twists something, such as a pore, might have. The equation for this is shown below in Equation 2, where τ is tortuosity, L is the curved length of the pore, and C is the straight-line distance between the two ends of that curve [23].

$$\tau = \frac{L}{C}$$

Equation 2. Equation for Tortuosity. [23]

Using the SEM imagery, the apparent tortuosities of the freeze cast specimens can be compared to those of traditional pore formers. An example of this is displayed in Figure 17. The left image shows a freeze cast specimen at 70x magnification. The pore progression can be seen from the bottom to the top of the image. In the right image, glassy carbon was combined with 8YSZ and sintered to densify and remove the carbon. It is shown that not all of the carbon formed pores are connected to one another. In fact, some are completely separate. Though the image on the right is magnified at 1000x, the non-uniformity of both size and position is evident. If a line were to be traced from top to bottom along the pore edges, it is obvious that the distance would be greater with the

pore former. Thus, a fluid passing through the freeze cast specimens would travel further.

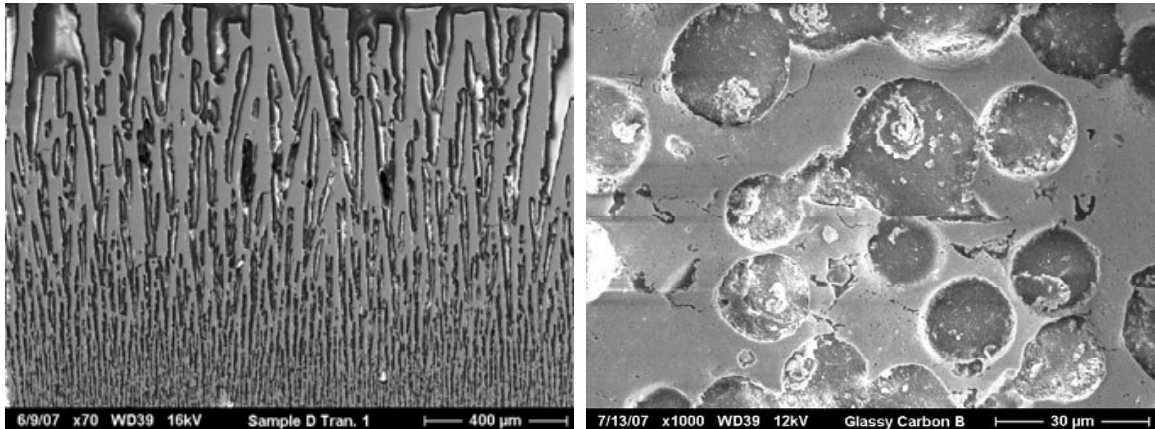


Figure 17. Freeze Cast (Left) and Glassy Carbon Pore Former (Right) SEM Images.

Hugo Schmidt and Laura Lediaev, of MSU's Physics department, are conducting a study of tortuosity. They have developed a mathematical model that can be used to model the tortuosity of a material. Some freeze casting experiments are being prepared to validate the modeling by experimental testing of freeze cast and pore formed ceramics. In these tests, a freeze cast ceramic is attached to a dense NiO pellet that was formed by dry pressing and sintering at 1500 C for two hours. To attach these, a small amount of cement is applied around the bottom edge of the freeze cast specimen, pressed to the NiO, and allowed to set. This whole combination is then carefully coated with a glass cement, except for a small exposed circular section at the top (large pore side). This seals off the NiO from any outside sources apart from what can pass through the YSZ pores.

The sample is then placed in a reducing environment at a specified temperature for a certain amount of time. This environment consists of a forming gas flowing over the sample. This gas enters through the top pores, reacts with the NiO, and leaves

through the pores. The reaction that takes place removes oxygen atoms from the NiO and “reduces” it to just Ni. A diagram of this process is shown in Figure 18.

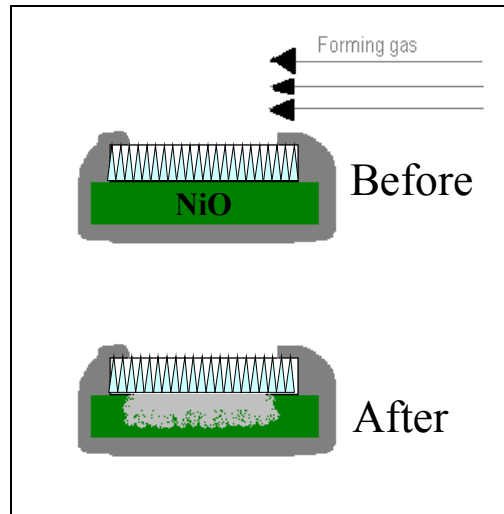


Figure 18. Process of Reducing Dense NiO.

Once the reduction has taken place over the desired amount of time, weight associated with NiO reduction can be used in the determination of the tortuosity. The modeling predictions require information from the reduction testing. These include surface area of exposure, thickness of porous YSZ, porosity of YSZ, density of NiO pellet, weight change from reduction, and thickness of reduced Ni. Other information required about the reducing environment includes temperature and pressure of reduction, flow of forming gas, duration of reduction, and the volume of space within the furnace.

INVESTIGATION RESULTS, OBSERVATIONS, AND DISCUSSION

Experimental Results and Discussion

The freeze casting process freezes the water within the cast slurry to produce a columnar pore structure. Studies were conducted to determine various characteristics of these structures. SEM was used to acquire images of the freeze cast structures for visual analysis. The results of each study are described in this section.

Casting Speed

The rate at which the Mylar carrier is pulled is an important part of the freeze-tape casting process. In order to develop a uniform tape, the pulling speed must not be greater than the rate that the ice crystals are formed. This was determined after many cast tapes with odd nucleation. A motor with adjustable speed pulls the carrier. Unfortunately, the adjustment for speed is based on the percentage of maximum pulling rate rather than in units of millimeters per minute. The rate was adjusted for each tape.

Initially, the ice crystals that formed during casting experienced non-uniform behavior because the tape was being quickly cast onto the freezing bed and then allowed to freeze. They progressed through the tape somewhat randomly, causing the defects shown in the left column of Figure 19. It was determined that these defects were caused by excessive casting speeds. Tapes continued to be cast at slower pulling rates until a uniform cast was achieved, such as that in the right column of the figure. After a few tests, it was determined that the casting rate that produced the best results was

approximately 1 mm/sec. This speed was used for all freeze-tape casts discussed in this work.

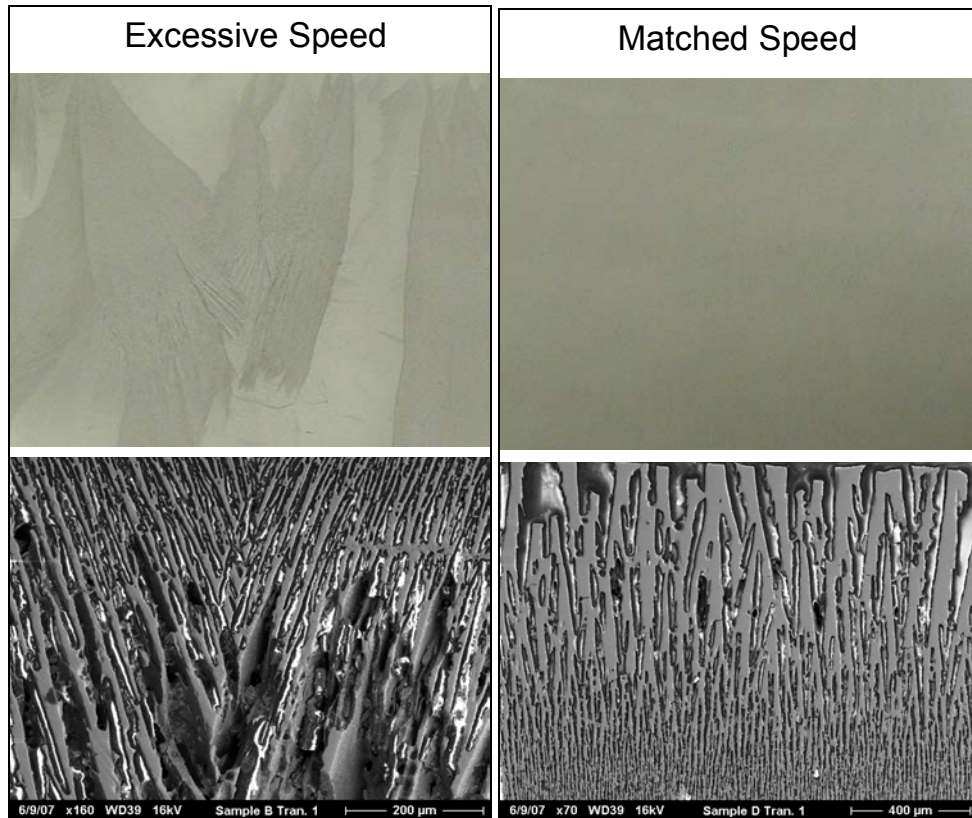


Figure 19. Effects of Casting Speed on Tape Uniformity and Pore Structure.

3D Morphology

A study of the 3D morphology of freeze cast tapes was conducted with the use of SEM. Four samples were cut from the same tape in a contained, uniform area. The tape that was used was formed from a slurry consisting of 66% NiO (99%, Alfa Aesar, Ward Hill, MA) and 34% 8YSZ (Tosoh). These samples were mounted and polished at different viewing angles related to the direction of cast. The mounting process simply involves suspending the sample in an epoxy filled die and allowing it to cure. The four

viewing angles were 0° , 45° , 90° , and 135° with 0° being the casting direction and moving clockwise.

The results yield substantial variation indicating a strong level of anisotropy. The ice crystals form a graded pore structure throughout the ceramic material; however, the morphology changes with orientation. As displayed in Figure 20, small ice crystals form at the base of the sample and grow larger up to the top. Each image within the figure shows the full thickness of each sample at the same magnification, oriented appropriately from top to bottom. In the 0° orientation, the structure appears to be columnar. The 45° and 135° appear to be slightly angled in opposite directions from one another while still maintaining a columnar appearance. The 90° orientation can cause some confusion since the other three views are all quite similar to each other.

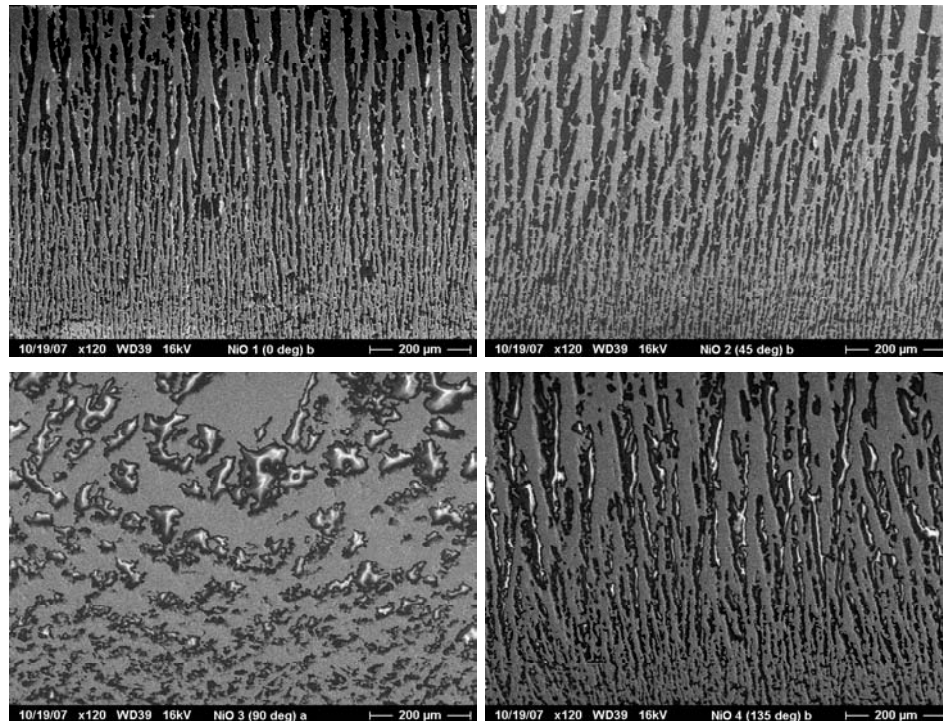


Figure 20. 0° (Top Left), 45° (Top Right), 90° (Bottom Left), and 135° (Bottom Right) Viewing Angles of Freeze-Tape Cast Material.

It appears that the structure of these freeze cast specimens can be compared to that of a cornfield. As one looks perpendicular to the cornrows, gaps can be seen between each of the corn stalks. However, if viewed parallel to the rows, all of the stalks are grown close together leaving very few gaps, which is comparable to what is seen in the 90° view. A visual aid is provided as Figure 21. This is essentially what is happening with the freeze cast specimens. The freezing process seems to form ice crystals in rows along the direction of the cast. These rows leave solids between them that are all connected to maintain a stable structure.



Figure 21. Cornfield (For Ceramic Structure Comparison). [24]

Solids Loading Study

The solids loading of the slurry determines how viscous the slurry will be as well as how dense the green tape will turn out. The definition of solids loading is described in Equation 3 as the total percentage of solids contained in the slurry. To properly calculate this, the amount of solvents in each of the additives must also be incorporated into the equation. Testing was conducted to determine which solids loadings appeared to satisfy the most desirable conditions consistently.

$$\% \text{ Solids} = \text{Powder Weight} / (\text{Powder Weight} + \text{Solvent Weight})$$

Equation 3. Solids Loading Calculation. [10]

A study of the effect of solids loading on structure was initially done using NiO/8YSZ (NiO, 99%, Alfa Aesar, Ward Hill, MA; TZ-8YSZ, Tosoh Corporation, Japan). Later, concentric ring-on-ring compressive strength testing was done on 3YSZ (TZ-3YSZ, Tosoh Corporation, Japan) at 5% intervals of solids load from 20-30%. The results of the first tests are described in this section while the 3YSZ results are discussed later. When using the above equation, both the solids loading and powder weight were determined and the amount of solvent, in this case water, had to be established. Any known amounts of water in the other ingredients were subtracted from total solvent weight. This provided the value of how much water would need to be added in the ball milling process.

Initial testing of pore structure variation due to changes in solid content was conducted using NiO/8YSZ. The study parameters started as a comparison between specimens with solids loadings ranging at 10% intervals from 10% to 50%. However, after successfully casting the 10% slurry, it was determined that the tape was much too brittle; it crumbled when touched after being sintered. Also, a 50% tape was impossible to cast, as the water content was too low to make a proper slurry. It was determined that even if it was possible to cast, the low water content would limit the ice growth, making it devoid of columnar grading. Thus, these two tests were removed, deemed beyond the scope of the study.

The test continued with the 20%, 30%, and 40% solids loadings. Each slurry was cast at the same temperature of approximately -30 C. After the freeze-drying process,

samples were cut from the tapes and sintered. Following sintering, the samples were fractured perpendicular to the casting direction and mounted in epoxy. SEM images were taken for each tape and compared with one another. Each solids loading is represented in Figure 22.

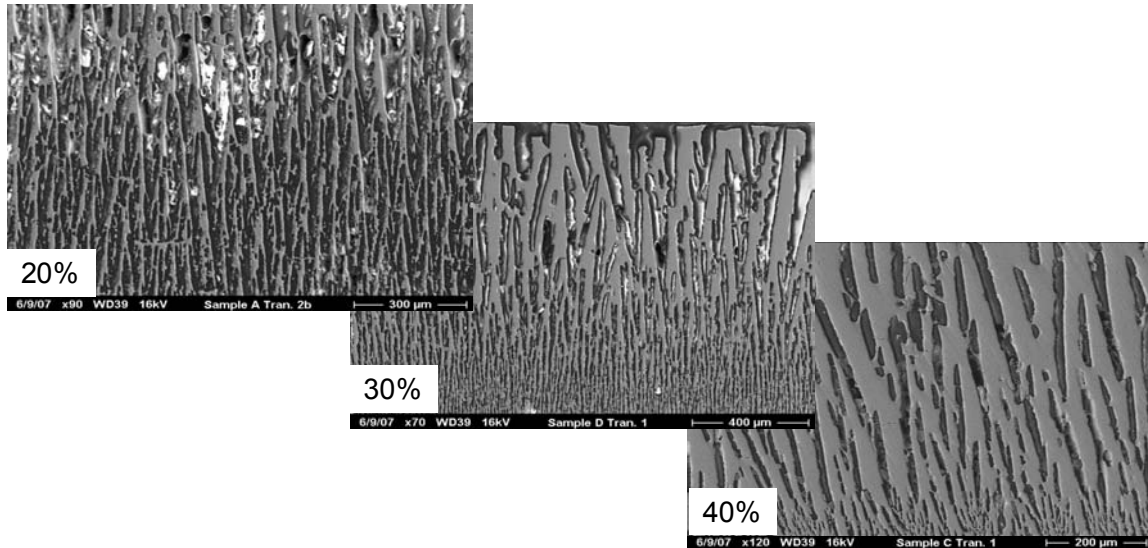


Figure 22. SEM Images of Varying Solids Loading. [25]

It can be seen that the structure varies greatly with solids loading. The 20% samples were fairly brittle and fractured easily when applying pressure with fingers. This is understandable considering the large pores and thin structure seen in the image. However, the pore structure appears to be ideal for applications that involve flow. Strictly based on the image, it appears the tortuosity is very close to one. There did not appear to be any clear difference in pore size from top to bottom, though there was a greater amount of pores on the base of the sample.

The 40% samples exhibited a much larger strength than that of the 20%. Since less water was used in this slurry than with the others, the density of the end result was fairly high. The formation of ice crystals appears to be more random than with the other

tapes. Many small crystals formed at the base of the tape, but immediately become large and fewer of them extending throughout the rest of the thickness. Ceramics of this structure do not appear to have quite the amount of pores as the 20% and 30% samples, but could be useful with filtration when fracture strength is necessary.

After examination of the 30% solids load samples, it appears that these may be the best suited for many applications, some of which will be described later. The pores start of small at the base and gradually increase to a larger diameter at the top, unlike the 40% that exhibits a quick change in pore size. Though the structure may not be as strong as that of the 40%, it is still comparatively stronger than the 20%. The tortuosity of the 30% solids appears close to one, so it may be desired for ease of flow. Samples of this type would likely be preferred over traditional pore forming methods when used for situations such as anode-supported fuel cells; traditional pore forming methods produce a much less predictable structure.

Freezing Temperature Study

The effect of freezing temperature on the tapes was also examined. In this study, slurries of 20%, 30%, and 40% solids loadings were freeze cast at various casting bed temperatures. The resulting tapes were processed and were examined visually and compared by their relative densities. Since the sintered samples were all fairly uniform in shape, a simple volumetric calculation was conducted using measurements acquired via digital calipers. The mass of each sample was measured on a laboratory scale accurate to 0.001 grams. The approximate density was then calculated for each sample using the basic equation of density being equal to mass divided by volume. This calculation was

done for each sample and compared to the theoretical density of solid NiO/8YSZ, which was calculated to be 6.67 g/cm^3 . The results are displayed in Figure 23.

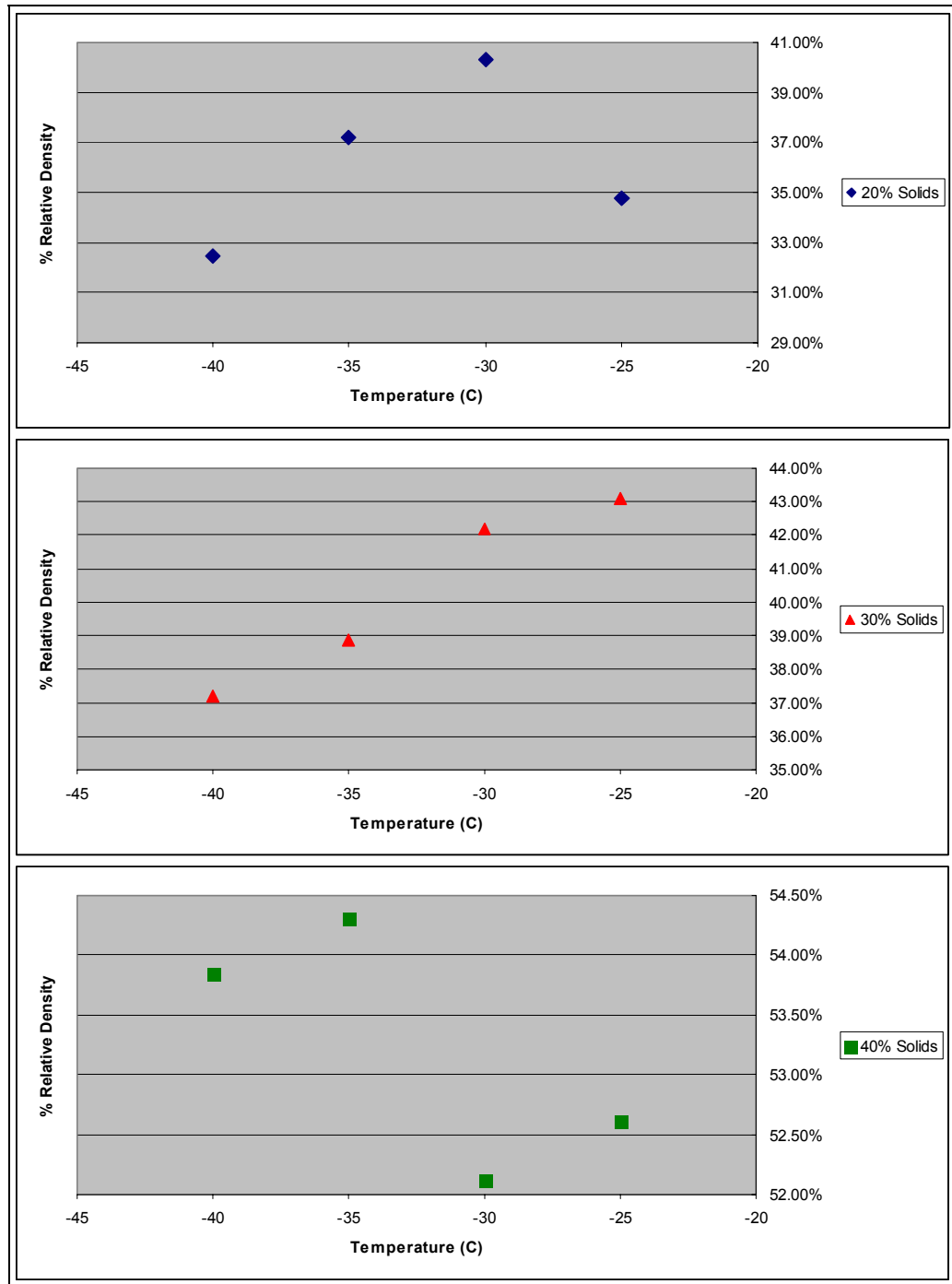


Figure 23. Temperature vs. Relative Density for 20%, 30%, and 40% Solids Loads.

As displayed in the figure, the results varied significantly between the solids loadings. It was expected that these would experience equal relative density distribution at each temperature, but this was not the case. However, based on the SEM images found in the solids loading study, it appears that the transition of pore structure was much greater from 30% to 40% than that of 20% to 30%. The three solids loading steps experienced average relative densities of 36%, 40%, and 53%, in increasing order.

A brief comparison of SEM images was conducted based on the freezing temperature of the cast. It was observed that as the freezing bed got colder, the pore alignment changed. The pores exhibited a tilt, angling away from the casting direction. An example of this is shown in Figure 24. These images were taken at a 90° angle to the direction of the cast. It appears that as the freezing temperature is increased, the pores approach a vertical orientation. If similar images were to be taken at other freezing temperatures, it may be possible to compare the angles in an effort to predict pore alignment in other cases.

Since no 3D modeling was conducted, this pore tilting is only speculation. It may be that more dendritic behavior appears as a result of the increased freezing rate. These dendrites might grow at angles away from the central ice crystal columns that simply push the solids into other orientations. This may make it appear that the pores are tilted, but perhaps they aren't at all. Accurate 3D imaging would be a very beneficial form of analysis for these samples.

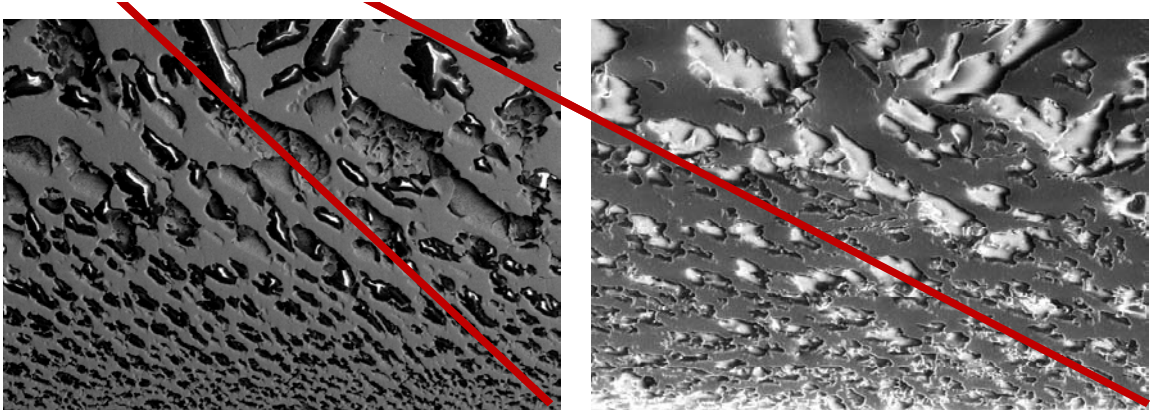


Figure 24. Observed Pore Tilting Difference From -20°C (Left) to -40°C (Right).

Equiaxial Compressive Strength Study

A compressive strength study was conducted as described in the section on Ring-on-Ring Mechanics. Failure load data was taken from eleven, ten, and twelve samples of 20%, 25%, and 30% solids load of 3YSZ, respectively. An example of the data collected from the Bluehill Instron software is displayed in Figure 25. As the test is conducted, the software program compiles the data of compressive load and compressive extension for every twentieth of a second. For this specific study, the value of load at fracture is the most important part. This occurs in the figure at the minimum value for each specimen. The program uses a negative load because it is in compression. The machining designs for the load and support fixtures are shown in Figures 26 and 27, respectively.

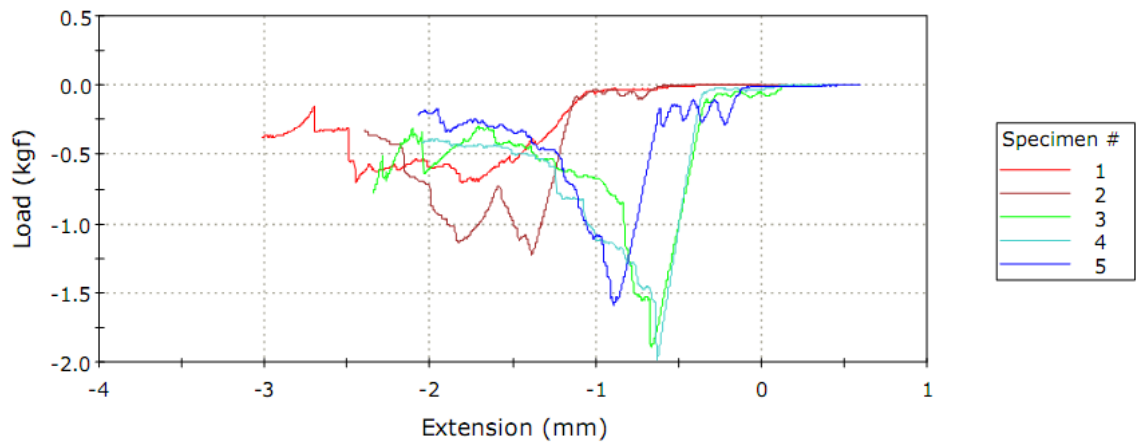


Figure 25. Example of Data Collected from Instron Tests.

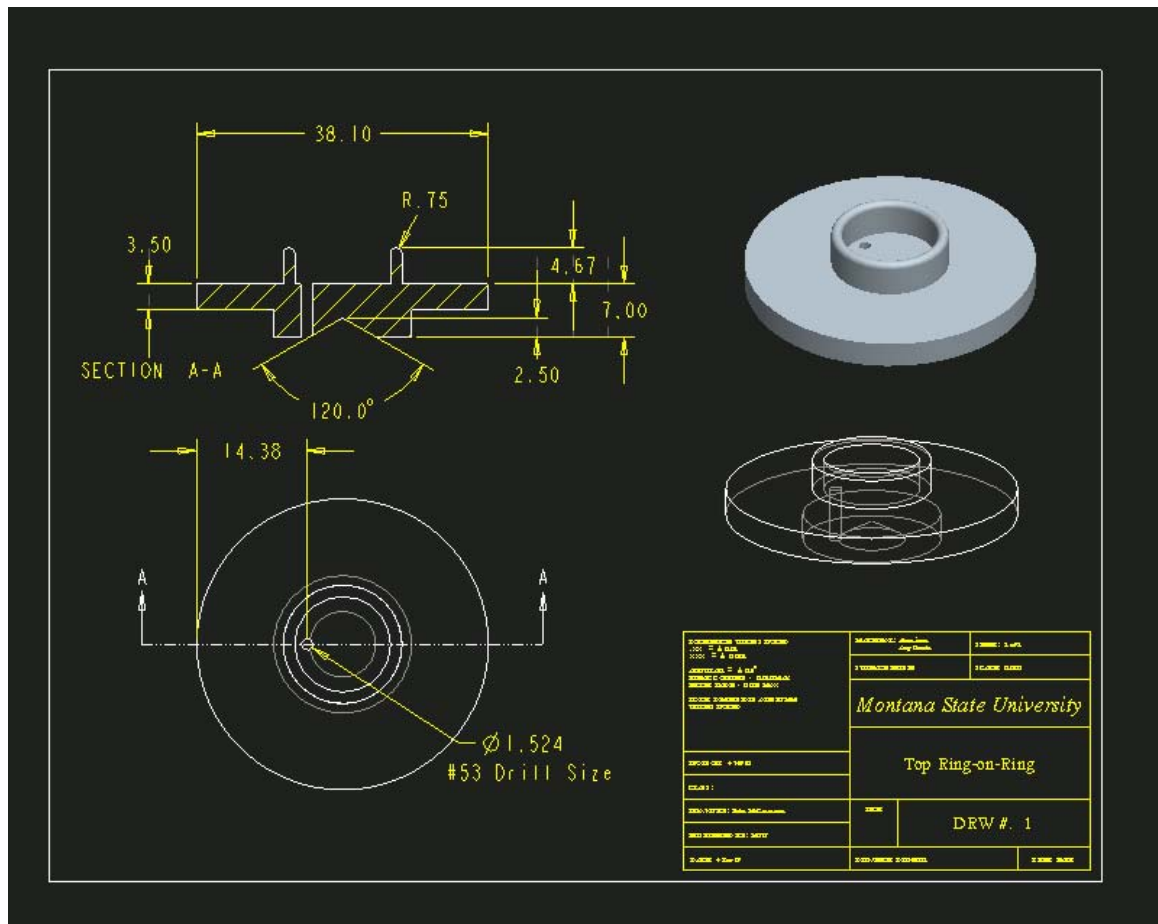


Figure 26. Design for Load Fixture for Ring-on-Ring Testing.

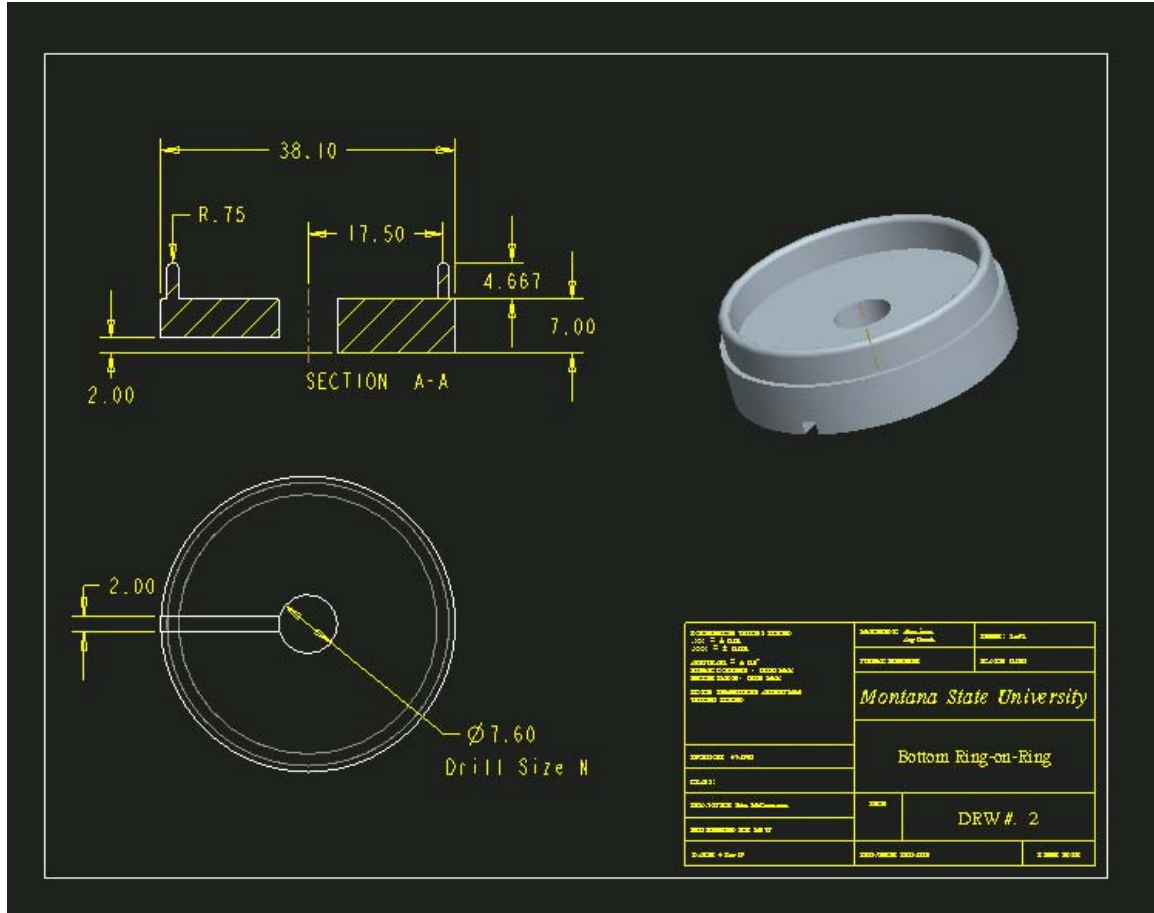


Figure 27. Design for Support Fixture for Ring-on-Ring Testing.

As mentioned in an earlier chapter, the fracture patterns of the samples can be examined to determine the likely origin of failure. Each sample was visually compared to the ASTM fracture pattern information (Figure 16). A large majority of the specimens exhibited high strength failure similar to that of Figure 28. As shown, the likely point of origin of samples such as these is at a location near the center. This is usually at a point at which the load ring was in contact. A few samples experienced medium energy and even fewer had low energy. Fortunately, none had edge initiated failure, indicating proper conduction of the test.

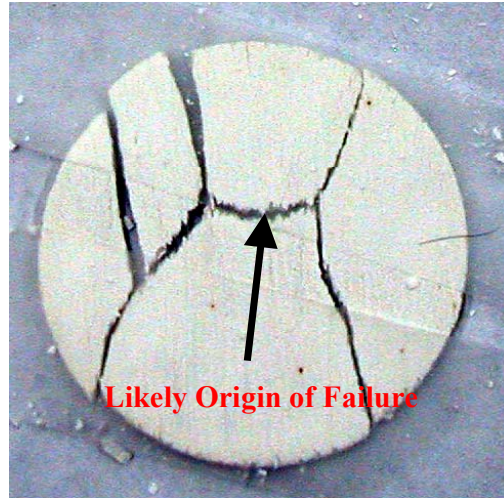


Figure 28. Example of Test Specimen after Failure.

After the data had been taken for all of the samples, a maximum value of compressive force was calculated. This force value only took into consideration the force exerted on the load fixture by the machine. Therefore, the force due to gravity applied by the load fixture had to be figured into this force. The failure stress of each specimen was calculated using Equation 1. The constant variables in the equation were Poisson's ratio and the diameters of the load and support rings as manufactured. A Poisson's ratio of 0.31 was used [26]. Each sample within each solids loading category had relatively the same diameter, so they were averaged for use in the calculations. The 20%, 25%, and 30% diameter means were 42.34 mm, 42.47 mm, and 42.52 mm. Plugging all known values into the equation produced the result shown in Table 2.

The values from Table 2 were then graphed (Figure 29). In this figure, the three solids loads were graphed by thickness and fracture stress. The results of 20% solids loading were reasonable. These samples exhibited a fairly linear trend with varying thickness not appearing to be a factor. The mean stress was 3.14 MPa with a 1.02 MPa

standard deviation. It was expected that these samples would not be able to withstand as much stress as those with higher solids content due to the greater porosity.

Table 2. Concentric Ring-on-Ring Test Results.

20% Solids Loading	Sample Thickness (mm)	Failure Stress (MPa)	25% Solids Loading	Sample Thickness (mm)	Failure Stress (MPa)	30% Solids Loading	Sample Thickness (mm)	Failure Stress (MPa)
1	1.63	1.78	1	1.35	4.80	1	1.36	6.92
2	1.66	2.95	2	0.84	12.73	2	0.93	10.55
3	1.74	4.13	3	1.41	6.67	3	1.06	14.86
4	1.74	4.33	4	1.35	6.62	4	1.42	8.51
5	1.67	3.79	5	1.59	8.13	5	1.38	7.40
6	1.25	1.91	6	0.94	6.52	6	0.77	11.94
7	1.81	3.55	7	0.87	5.71	7	1.18	13.82
8	0.88	3.12	8	1.57	9.51	8	1.25	7.02
9	1.72	1.53	9	0.75	6.18	9	0.75	17.16
10	1.72	3.16	10	0.56	16.59	10	1.02	10.55
11	1.30	4.32				11	0.85	14.93
						12	1.02	11.30

The 25% solids specimens had two unusually high failure stresses, but were otherwise fairly consistent. These had an average of 8.35 MPa with a standard deviation of 3.68 MPa. The general trend of the 30% samples appeared to be a decrease in failure stress as thickness of the samples increased. This may be due to the pores becoming larger as the samples are cast thicker but could also be coincidence. The average for these was 11.3 MPa with 3.42 MPa standard deviation. These results provide further insight into the effects of solids loading. The thin struts of the 20% solids dramatically reduce the strength of the specimens indicating that 25% is an optimal balance between strength and high porosity.

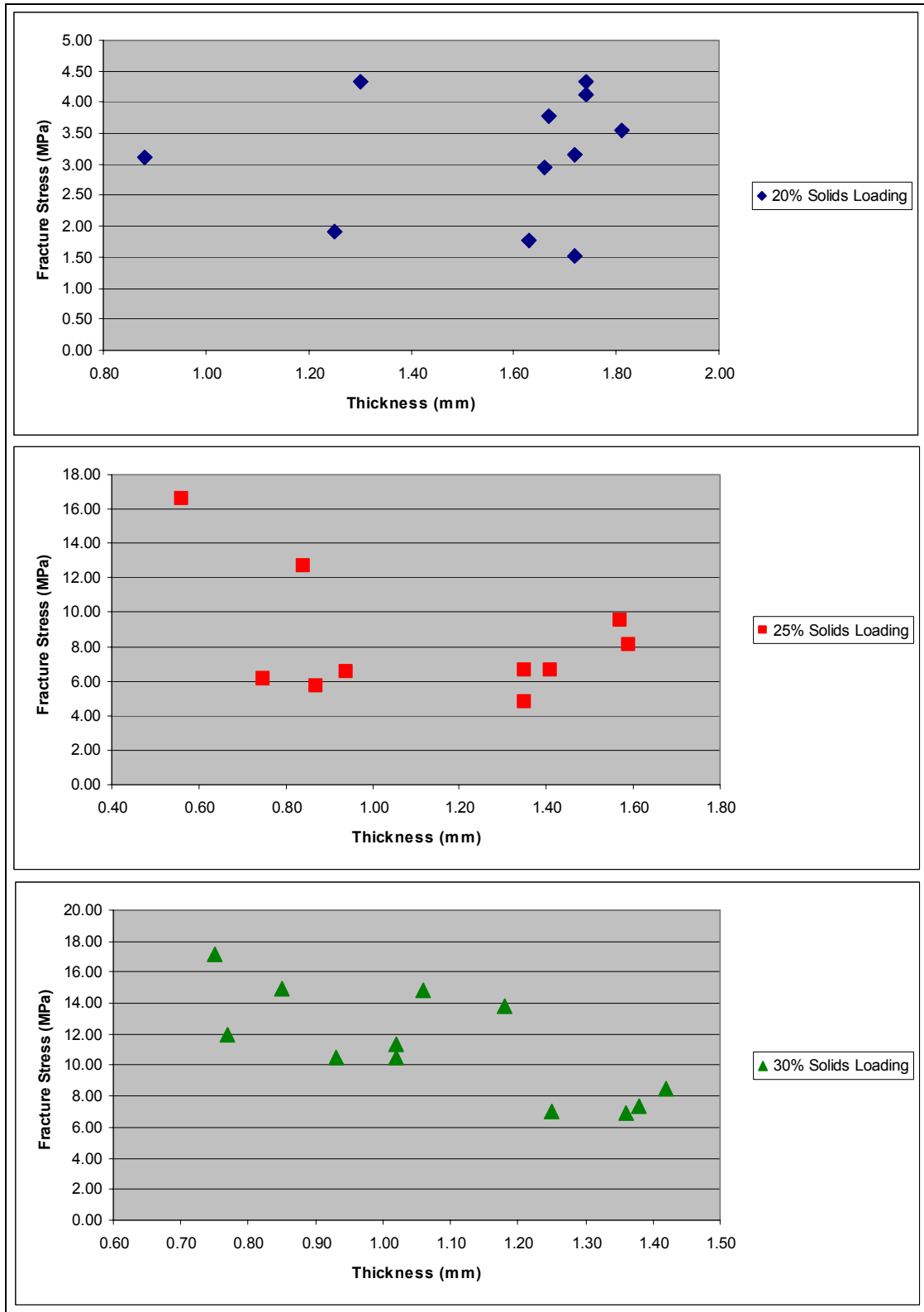


Figure 29. Fracture Stress vs. Thickness at Varying Solids Loads.

Captive Die Casting

Freeze-tape casting concepts can be applied to develop thick, porous samples of specific sizes. This is accomplished by utilizing captive dies. The freeze casting bed is set up the same as with freeze-tape casting except a doctor blade assembly is not used. Slurry preparation changes slightly, as much less is needed when making only a few samples. Hollow cylindrical dies are placed on the room temperature portion of the casting bed. The ceramic slurry is carefully poured into each die to a desired thickness. A flat weight is placed on each die to prevent the slurry from spreading under the die during the freezing process. The dies are then pulled along the freezing bed at the same rate as the tape casting method. More time is required to completely freeze these samples due to the increase in thickness. Once frozen, the Mylar is cut and the samples, still in their dies, are transferred with the Mylar to the freeze-dryer. The water is allowed to sublimate under vacuum and the green samples are sintered. 8YSZ samples cast with this method are shown in Figure 30 alongside a punched, thick tape cast specimen.



Figure 30. Two Die Cast (Left Half) and a Punched, Thick Freeze-Tape Cast (Right) Sample.

Captive die casting can easily produce uniform, thick samples of porous material. This processing method could be used with any simple shape, given the appropriate die. As displayed in the previous figure, captive die processing can produce very thick samples, magnitudes greater than traditional tape casting. Also, an even thickness is much easier to maintain with the die process, and the edges are much smoother than those resulting from punching. However, the pore structure varies slightly. Due to the constraints on the material from the die, the pores near the walls do not all form in the direction of the cast. This may actually be beneficial, as edge initiated failure may be less disastrous to the die cast sample than with one cut from a tape.

An experiment was conducted to determine how effective this method is for other materials. Stainless steel powder was used to conduct this test. The metal powder was mixed with water, Duramax B-1000 binder, and a small amount of Vanzan in a small container. It was necessary to constantly stir the mixture prior to casting to limit the amount of settling; metal particles do not suspend well in water. After the cast, the samples were freeze-dried and the resulting green samples are displayed in Figure 31.



Figure 31. Captive Die Freeze Cast of Stainless Steel.

Stainless steel is more difficult to sinter than most ceramics. It must be heated in an environment such that it will not oxidize. Two attempts have been made to sinter these. The first sample, sintered in a tube furnace under flowing forming gas, completely oxidized and broke down completely when handled. A second sample was sintered in a furnace under vacuum. This sample appeared to have slight oxidization, but was able to maintain its structure. Future testing will be conducted, with the use of SEM, to determine if these specimens have similar columnar pore structure as freeze-tape cast ceramics. Also, sintering conditions need to be optimized to prevent oxidation.

Infiltration

Infiltration is a method that allows material to be introduced into an existing structure to alter its properties. Freeze-tape cast samples were used to briefly examine the effect of a few infiltration methods. Nitrates (metal salts) can be infiltrated into porous materials in a couple of different ways. They can be dissolved in a solvent and liquid infiltrated, melted directly into the material, or altered to become a citrate and introduced into the pores via capillary pressure or under vacuum. The theoretical capillary pressure of these pores is represented in Figure 32. When trying to infiltrate with a combination of nitrates, such as lanthanum strontium cobalt ferrite (LSCF), the melting method does not work properly. This is because each nitrate has a different melting temperature, so the end result would not necessarily contain the desired combination of elements in any location.

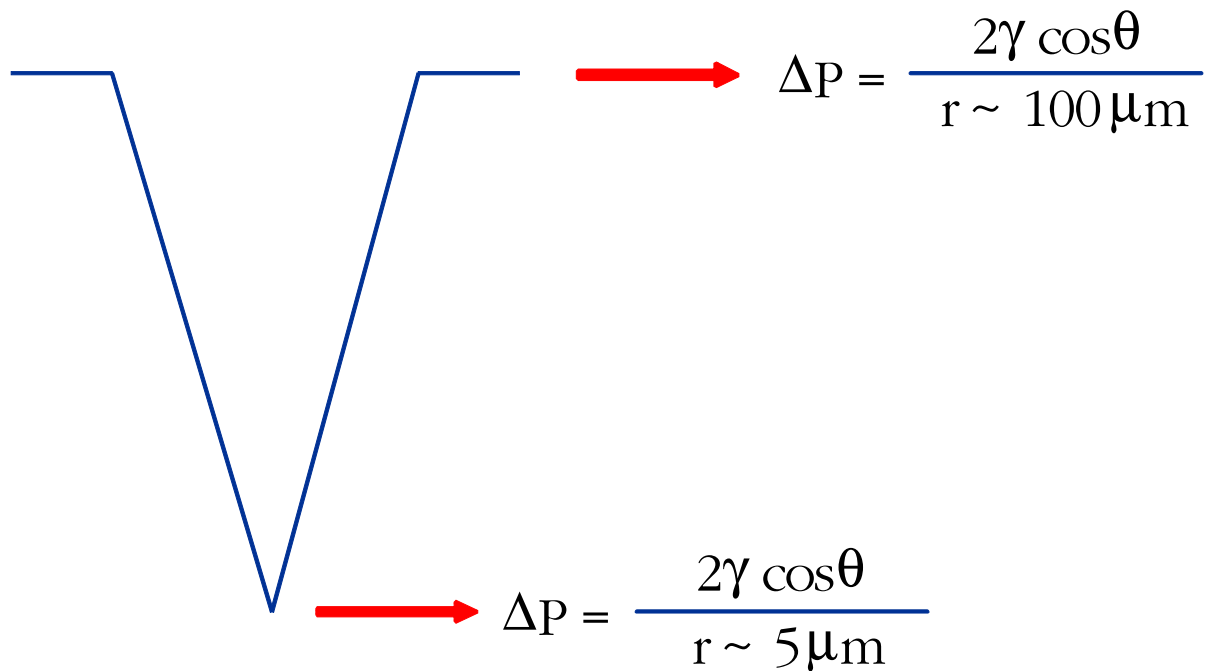


Figure 32. Theoretical Capillary Pressure of Freeze-Tape Cast Pores.

Experimentation can be done to determine the effects of various infiltration techniques on the material, such as changes in electrical conductivity, amount of infiltrated material retained by the structure, and pore blockage. Infiltration was not a vital part of this research, but using samples with large pores makes it easier to do testing with higher viscosity compositions. Once the methods of infiltration are optimized for these specimens, the results can be tailored for materials with smaller pores.

Potential Applications

There exist many possibilities with freeze casting technology. Being able to consistently create materials with predictable porosity can be very beneficial. Also, material choice doesn't have to be limited to ceramics. Metallic powders can be cast

using the same concepts described in this paper. However, making a homogenous mixture with metals in an aqueous solution can be difficult, as the two do not often interact easily. Casting into a die being pulled across the freezing bed is easier than using a doctor blade, as the solids would tend to settle quickly. If a metal was cast with this method and successfully sintered without any oxidation problems, the resulting porous material could be quite useful for various applications.

Fuel Cells

Freeze casting can be useful with incorporated with fuel cell technology. The anode of the fuel cell must be porous enough to allow gas to pass through to the electrolyte, chemically react, and then pass back through the pores. The tortuosity that these exhibit seems to be more suitable for this application than those of traditional pore forming methods; their pore structure is less tortuous than that of freeze casting.

When used for fuel cell applications, the freeze cast material must be attached to the electrolyte by some method. One way of doing this includes freeze casting a small amount of slurry directly onto a sintered electrolyte. A diagram of this process is shown in Figure 33, in which a YSZ slurry is freeze-tape cast onto a prefabricated anode-electrode stack; the sintered result can be infiltrated with cathode material. This undergoes the same sublimation process as a full tape and is then co-sintered. However, the green ceramic will exhibit greater changes than the pre-sintered electrolyte, which may cause the end result to be warped, wrinkled, or cracked.

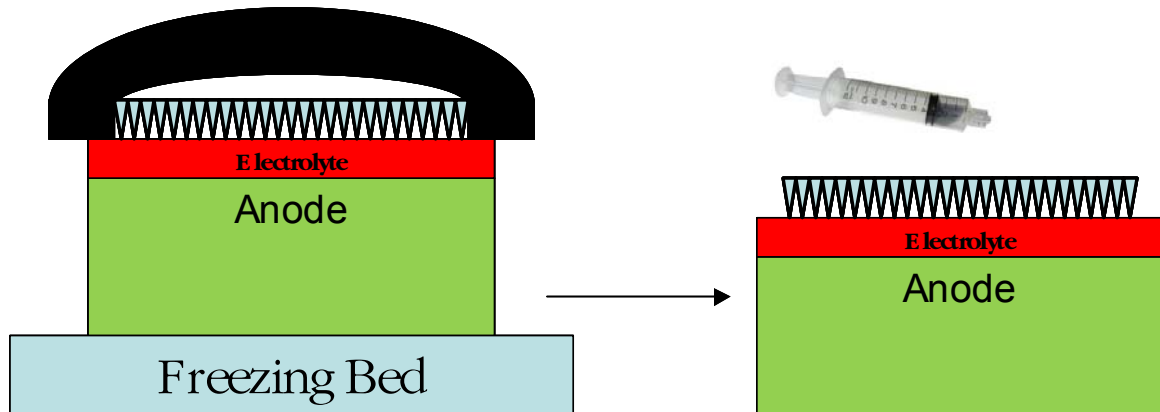


Figure 33. Freeze-Tape Casting Method for SOFC Cathode Infiltration.

An alternate method would be to apply the electrolyte to either a green or sintered anode. This would be done by creating an electrolyte slurry with an organic solvent and spraying it uniformly over the base (small pores) side of the anode. The electrolyte would be allowed to dry and then the combination would be co-sintered. This may also produce flaws since the porous material will have different sintering behavior than the solid electrolyte.

Other Applications

Freeze cast materials have a high potential to be used in filtration applications. Through various testing, it has been determined that materials can be cast fairly thick while retaining the same pore structure as that of thinner specimens. However, as thickness is increased it becomes harder to cast uniform tapes. At this point it may be necessary to utilize a captive die of specified dimensions that can be pulled along the freezing bed. Thick specimens could be used to filter liquids and could filter particulates from air.

CONCLUSIONS

Summary of Results

The 3D morphology study gave insight into the formation of the porous structure during freeze casting. As the tape freezes, rows of ice crystals are formed along the length of the tape, giving it its resultant graded pore structure. Small ice crystals form initially at the base of the tape while larger crystals grow whilst progressing upward through the thickness. The SEM images aided in the determination that the pores are not shaped as perfect cones while the ice crystals form.

As solids content is varied, the structure of the cast tape changes dramatically. Lower concentrations of solids produce brittle, yet very porous, tapes. Solids content less than 20% were too fragile to test and were deemed unsuitable for real world application. Similarly, solids loadings exceeding 40% failed to form a liquid, homogeneous slurry and were thus incapable of being cast. This is not necessarily the case for all materials; it is simply what was discovered with the NiO/8YSZ mixture. The structure becomes much more stable as solids load is increased, but porosity greatly decreases, limiting its potential for applications requiring ease of flow.

The density of a 40% solids loaded tape is comparatively larger than that of 20% and 30%, which based on the obtained SEM images seems completely reasonable. Changes in casting temperature did not greatly affect the density of the 40% solids. On the other hand, densities increased for both 20% and 30% solids loads as casting temperature was increased. It appears that $-30\text{ }^{\circ}\text{C}$ is the ideal casting temperature for the

current setup. Further insight was achieved by examining the 90° orientations of samples cast at varying temperatures. A pore tilt, away from the casting direction, was experienced and increased as freezing temperatures decreased.

A majority of the 3YSZ samples used in the concentric ring-on-ring compressive tests experienced high strength failure. The lower solids concentrations were not able to withstand high stresses. Thickness appeared to only be a factor with 30% solids loading; it decreased in failure stress as thickness increased. The other two solids concentrations produced fairly linear results with no slope, with the exception of a few extraneous data points. It appears that samples not exceeding one-millimeter in thickness can withstand the highest stresses.

Using a combination of the experimental results, optimization can be explored. Depending on the intended application, it appears that pore sizes can be changed and tilted for filtration, and/or structural strut sizes can be increased and densified for higher strength purposes.

Considerations for Future Work

There are many factors that go into perfecting a process such as this. Results can be optimized, but a large amount of time would be necessary. The Transport Characteristics section briefly introduced some future work. The following is a compilation of other considerations that could be helpful in determining additional benefits of this casting method.

Equipment

As mentioned in a previous section, the freezing bed is only capable of maintaining subcooling temperatures approximately half that of the refrigeration unit, in Centigrade; a -80 C input temperature yields approximately -40 C freezing bed temperature. The casting temperature was measured with a thermocouple and recorded for each tape. However, when the insulation is removed from the aluminum bed, it immediately starts to gain heat. The temperature also increases as the room temperature slurry is cast over it. Thus there is a difference in freezing temperature on either end of the tape, causing variations in freezing rate throughout the tape.

Since the tapes produced by freeze casting are small to account for the limited dimensions of the freeze-dryer, it seems that a small tape caster could be used. The caster would only have to be a few feet long and could have an insulating cover that would be suspended a few millimeters above the slurry as it is being cast. The decreased size and added insulation would help to maintain freezing temperatures and reduce convective heat transfer. However, with freeze-casting being a practice that is not widely used, manufacture costs may be rather high.

For each tape that is cast, the rate at which the carrier is pulled is manually adjusted. However, the current setup uses adjustments related to percentage of maximum power. Prior each cast, this is set to approximately 20% of power, turned on, and visually adjusted to pull at around 1 mm/sec. This method is by no means accurate. It would be ideal to get a computer controlled motor with which the casting rate could be input. This would greatly assist in achieving consistency among tapes.

Sintering

An appropriate suggestion for processing would be to conduct a full study with the purpose of optimizing the sintering cycle. It would be best to start with a specific ceramic material, solids load, and casting temperature. This would then go through a series of tests in both the TGA and dilatometer to determine the best conditions to achieve the desired density, grain growth, and sample shrinkage. If necessary, various additives could be used to change the results, such as altering coefficient of thermal expansion with aluminum titanate. The resulting sintering cycle should then be able to be used for all solids loads and casting temperatures used with that material. However, the study would have to be repeated for every type of ceramic material that would be cast, as particle size and sintering behavior would vary.

Crystal Growth

Though a study was done to determine the effect of varying freezing temperatures, there was little time to explore the actual formation of ice crystals. The ice crystals appear to grow differently with increased freezing rate. It would be interesting to measure the unidirectional crystals throughout a thickness of tape while still frozen. However, this would be quite difficult as a test specimen would have to be transferred quickly to a microscope capable of maintaining temperatures below 0 C and have high magnification.

An alternate method would be to do a series of transient heat transfer analyses to determine the temperature of the slurry at any given time. Crystal growth rates could

then be established based on the temperature changes. However, achieving an accurate result would be difficult. The pulling rate would have to be used in conjunction with the conduction of the freezing bed and the convection from the air in order to make a proper calculation. Additionally, as ice crystals form there is no longer consistency within the material. Sections of ice and cooled ceramic, with differing thermal properties, form throughout the tape, which would have to be incorporated in order to reduce error. However, since the tapes tend to freeze fairly rapidly, assuming the tape is a consistent material may be reasonable.

Transport Characteristics

Glass encapsulation techniques and a thermogravimetric analysis (TGA) fixturing support have been fabricated to support future testing and modeling validation; some samples were prepared along with a test rig for the TGA. This test rig, shown in Figure 34, rests atop a balanced rod within the TGA machine. One of the sections of removed material is large enough for a glass-coated specimen to rest on, while the other slots of removed material allow gas to flow over the porous YSZ surface. The TGA is then set up with the desired temperature profile, much like a furnace, and is run under the aforementioned forming gas. The TGA program then determines the rate of weight loss, which can be used to accurately determine the amount of reduction.

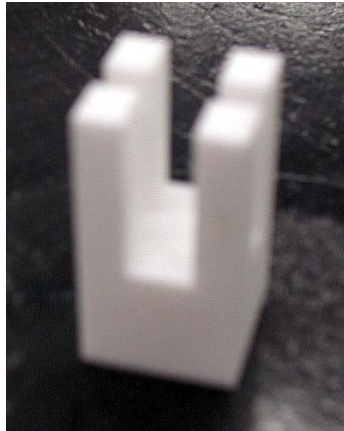


Figure 34. Flow Experiment TGA Test Attachment.

This type of experimentation could then be used with traditional pore forming methods to determine how well the gas is transported through the pores. The results from this would be very interesting. It would be a great future experiment to conduct. This could greatly assist in determining the potential of these samples to be used in filtering applications.

Further Morphology Studies

The four viewing angles of the freeze cast specimens are helpful in understanding the 3D structure that results from the process. However, there are other methods that can be utilized to visually inspect the structure in its entirety. One such method is the use of Magnetic Resonance Microscopy (MRM). This method is similar to using a microscope, but is able to non-invasively take images at different thicknesses. The images can then be compiled in a computer program and a 3D image results. However, MRM machinery with high resolution (up to $\sim 20\ \mu\text{m}$) is required to accurately map samples containing such small pores. This machinery may not be readily available.

Another device that can be used is an optical microscope. Using this microscope effectively to create a 3D image would be quite difficult and time consuming, but it can be more desired if cost is an issue. First, the sample would have to be mounted in a suspension, such as a hardened epoxy. The sample would then have to be polished so that the top of the sample was just slightly exposed. At this point, the sample would be placed in the optical microscope and scanned into a computer program. Once this is completed, the sample would again have to be polished down by a specified thickness. This would have to be conducted with precision in order to achieve an accurate end result. The sample would then be scanned again and this process would continue until the bottom of the sample was reached. The images that were gathered would then have to be compiled, making sure that each image is placed in the proper orientation.

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