Fabrication of glass-ceramic components via Three Dimensional Printing.

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By
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ABSTRACT

Three Dimensional printing (3DP) is a very flexible solid freeform fabrication technology. The process is used for the manufacture of tooling and functional rapid prototype parts directly from a CAD model. 3DP functions by spreading powder in thin layers and then selectively binding of the powder using a technology similar to ink-jet printing. At the end of the printing session, the powder bed is removed and the loose powder is brushed to reveal the desired green body. This method can be applied towards manufacturing parts in metal, ceramic, metal-ceramic and ceramic-glass composites.

This research is directed towards establishing the processing parameters necessary to fabricate fully dense glass-ceramic parts using 3DP. Glass-ceramics are a class of the ceramic system and are used in many commercial applications. They are formed by the nucleation of a ceramic phase in a glass matrix. The attraction of using 3DP in forming glass-ceramic is the direct densification of the printed green body upon firing without the need for any intermediate processing step like isostatic pressing.

The project started by studying the necessary printing parameters in the ceramic system and used the same parameters for printing on glass-ceramic spray dried powder. The capability to obtain a fully dense glass-ceramic parts directly after firing the green body was proven. The shrinkage in this material system was excessive because of the low packing density of the powder bed.

The efforts were then directed towards the use of powders with high packing density. Plasma sprayed glass powders were chosen, and the printing parameters were optimized to obtain fully dense complex parts. The parts shrinkage upon densifying was reduced significantly as compared to the previous system. Various parts of complex shapes were then manufactured as prototypes using several spherical powder systems.

Formation of a ceramic-glass composite was also explored by using melt infiltration. Alumina preforms were printed, fired then infiltrated using a borosilicate glass called InCeram. The composite was thus formed from fused alumina particles and glass filled pores. Microstructural, porosimetry and mechanical strength studies were performed in order to evaluate the composite. The samples showed high densities and uniform microstructure. The tested parts had high strength which was independent from the printing direction. Complex parts were formed via the 3DP process in this case too.

Thesis Supervisor: Professor Michael Cima
Title: Professor of Material sciences.
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Chapter 1

Introduction

1.1 Three Dimensional printing

1.1.1 Basics
The three dimensional printing process was invented at MIT by a group lead by Prof Ely Sachs and Prof Michael Cima. This process is a flexible manufacturing process that is capable of fabricating parts with unrestricted geometries and various materials. Powdered materials are spread in thin layers, and a computer guided printer head selectively prints a liquid binder material which is capable of joining the powder particle together. This printing process is similar to "ink jet" printing with the major difference of it being capable of printing different kinds of materials (binders or suspensions). The process starts by the creation of a CAD file which is converted to a standard .STL format and then sliced into 2 dimensional thin layers. The file is then down-loaded to the machine which adds thin layers of a chosen powder into a powder bed sitting on the top of a piston and cylinder. As each layer is added, the piston moves downward to accommodate the extra material and then the machine "prints" a binder to form the two dimensional geometry[1..4].

The printed regions form thus one layer of the part, and as more layers are spread and printed a three dimensional solid of complex geometry is created. The binder must always penetrate the two dimensional layer in order to bond to the layer below. This penetration is necessary for the "stitching" of the layers to form a continuous solid in all of the three dimensions. The loose powder in the "unprinted" region is then brushed away and the part can be thus recuperated. The formed "green" part can be post processed using the proper curing or firing schedule at the end of the printing sequence.

Each printing and post processing technique can be different since the materials systems studied are variable,. The material/binder and printing parameters are crucial elements in the formation of a usable part. As the machine and materials systems are under constant change it is hard to describe all the experimental process and it is thus more useful to just underline the basic principle by the schematic description in figure 1.1.
The interesting part of the new generation printers is their capability of accommodating several nozzle heads reducing thus the printing and build up time. This expands the capabilities of 3DP by making it a potential manufacturing process since there is no limit on the powder bed size or printheads that can be used. Our current alpha machine is running with an eight nozzle print head that could be expanded to more than eight if necessary.

Figure 1.1: The Three Dimensional Printing cycle
1.1.2 Materials advantages and disadvantages.

Most of the 3DP disadvantages are more of a practical nature since theoretically the process is capable of creating parts from any kind of material which comes in powder form. These practical difficulties can be solved within a reasonable time frame for many materials systems; But, given the big variety of the materials groups that can be covered, the research effort can become very divergent and versatile. Having this in mind, it is necessary to mention the “common” problems that can be encountered in the fabrication of the part. One of the restrictions of the process at this stage is the need for flowable powders that can be easily spread to get a homogeneous powder bed. This requirement is easily surmountable by pre-processing the powder; but the material system picked can also have some restrictions regarding this subject too. The need of fully dense parts can also be a tough requirement since the printed green part is porous and shrinkage occurs upon densification. The shrinkage can be accounted for in the CAD file and can be reduced after the processing optimization. This problem can thus be solved if we have isotropic shrinkage behavior. The delamination of the printed layers is another difficulty that can be encountered during the printing process. This makes a study of each materials system printing parameters necessary. The delamination/warpage problem can be solved for a given system with the proper understanding of the binder/powder interaction and the binder drying rate[5]. The other major disadvantage which the 3DP process shares with the other RP techniques is the poor surface finish compared to machined surfaces. This problem is being addressed by the use of proportional deflection and various build sequences which help in “smoothing” the surface of the printed part[6,7]

1.1.3 Structural ceramics applications.

Structural ceramics has been attracting a lot of attention lately with the rise in need for high temperature materials parts in the industry. The 3DP technique can play a major role in this area since the ceramic parts are frequently of complex geometry and are usually produced in small to medium quantities. These two conditions make Rapid Prototyping in general and 3DP in particular the manufacturing method of choice.
The structural ceramic parts need to be fully dense in order to be functional. This requirement defines the basic problem that has to be addressed: To achieve full density, the individual ceramic particles in a green preform must fuse together to close all the pores during the sintering stage. The sintering phenomena is driven by solid state diffusion phenomena and is thus a function of the powder surface area. Typically, closely packed submicron powders which possess high surface areas are necessary to obtain complete densification. This packing needs to meet a minimum critical packing density requirement in order to densify and close all the porosity in the green body.

A process that forms shapes starting from powders can accomplish the specified goal by either dry spreading of the powder bed or by aqueous formation of the desired green body (slurry sedimentation, tape casting). These two methods can be approached while using the 3DP technology. However, with the current machine set up, forming complex shapes is limited to only dry powder spreading. Current research is targeting the aqueous powder bed formation approach because of its potential in getting higher green densities[8]. Successes in this research will define the changes that might be introduced to the future 3DP machine set up.

Recently, there has been progress in the fabrication of many structural ceramic parts by 3DP using dry powder. Alumina, zirconia toughened alumina and silicon nitride parts have been produced by the printing on fine and spray dried powder[9]. The use of fine powder was however restricted by the difficulties in powder spreading because of agglomerates formation. This problem caused incomplete spreading of layers and green body defects and inhomogeneities. The spray dried powder had excellent flow-ability and granules were easily spread without major problems in "unprinted" powder removal either.

The printed "green body" was isostatically pressed in a hydrostatic fluid (WIP or CIP) then fired at high temperature to achieve full density by sintering in both the fine and spray dried systems. During compaction the spray dried granules become shattered creating thus the original fine particle conditions necessary for full densification. The main disadvantage of this technique is the need of the pressing step which puts some restrictions on the geometry. This densification process is usually accompanied by large shrinkages because of the initial low powder bed packing density.
1.1.4 Glass-ceramic applications

The range of glass-ceramic compositions is extremely broad and their spectrum of applications is becoming wider with the discovery of new compounds. The printing on glass-ceramic powders can be very similar to the printing on structural ceramic. The only main difference lies in the sintering behavior of the glass ceramic material which does not require high green body density in order to reach full density directly by firing. Glass-ceramics densify usually by a melt sintering process which does not require powder with high surface areas. This fact eliminates the need of isostatic pressing which is the main set-back in the structural ceramic low density green bodies. An in-depth study of this group of materials and the advantages/disadvantages of 3DP in this area will be addressed later in following chapters.

1.1.5 Other 3DP applications.

-Direct fabrication of ceramic molds: 3DP has tremendous advantage in investment casting over any other method in the low to medium size production of parts. It is necessary to create hard tooling in investment casting which is used to injection mold a wax positive. The wax positive is then used for the creation of the ceramic shell by successive dipping in a ceramic slurry. It is usually necessary to dry the ceramic shell after each dip in the slurry and this makes the process slow. On the other hand, 3DP is capable of printing the ceramic shell directly from the computer design without the need for hard tooling or wax positives. The nature of the technique introduced greater flexibility in the design and helped in making mold geometries which were previously impossible[10]. The printing process in this case usually uses colloidal silica as a binder system and the ceramic shell can be of various compositions (alumina, zirconia...). The huge cost reduction offered by 3DP in this area makes the production of few quantities of parts by other techniques economically non-viable. Currently, this application is being commercialized by Soligen[11].

-Components from metal powder: The manufacturing of metal parts from powders is becoming very attractive because of the possibilities for high production rates of complex shapes with better surface finish and good dimensional control. In this area, 3DP is capable of offering rapid solutions to the industry. Stainless steel powders were used in the
printing of parts for the creation of molds used for plastic injection molding. An acrylic latex emulsion has proven easy to print with a good binding characteristics[12]. The green part thus obtained is usually post processed (heat treatment and firing) to obtain a dense metallic part. The advantage of 3DP in this would be the rapidity of the process and the ability to create complex designs with internal cooling passages, proper gate position in injection molds....

-Plastics: The 3DP process can also be used in the fabrication of plastic parts with the use of polymers that come in powder or aqueous form. Printing of biocompatible polymers is performed for many applications in the medical field[13].

1.2 Specific research aims.

This thesis presents various approaches towards the creation of fully dense glass-ceramic components via Three Dimensional printing. Three printed parts are produced by a sequential layer by layer process in which powder are joined by a liquid binder. The attraction of glass-ceramics formation by the 3DP process is the direct transformation of the printed body to a fully dense body in one single firing step. This direct fabrication when combined with the 3DP and CAD technology is capable of creating extremely complex geometries in small time cycles.

The first research aim was to understand the basic parameters effecting the printing of ceramic powders in general then glass-ceramics in specific. This prerequisite research was conducted based on previous expertise established in the 3DP ceramic group as well as current efforts which are being pursued. The research concentrated on establishing a 3DP processing technique capable of producing glass-ceramic composites after achieving a basic understanding of the ceramic green body formation and the parameters effecting the printing.

The first approach was to choose a commercial glass-ceramic composite in a flowable powder form and process it via 3DP. A feldspar/nepheline dental glass-ceramic system was used in order to form fully dense dental crowns. Initial experiments were aimed at examining the capability to obtain fully dense parts even by starting from low packing
density powder beds. Thus an attempt was made to use the dental composite in a spray dried powder form and test the capability to obtain 3DP dense parts. An optimization of this processing approach was conducted in order to be applied to other composites as well.

The second approach was to obtain 3DP dense bodies starting from high packing density beds in order to prove the capability to reduce the shrinkage which occurs upon densification. The materials chosen in this case were commercial glass compositions with good powder flowability and tap density. The aim was to adjust the printing and other parameters in order to optimize a 3DP process capable of producing complex fully dense glass or glass-ceramic shapes using similar material and powder characteristics.

The third approach was to establish a processing technique in order to form 3DP ceramic and glass composites parts by melt infiltration. This method was aimed at reducing drastically the amount of shrinkage necessary to get dense parts by 3DP. An attempt was made to infiltrate 3D printed alumina preforms using a glass matrix in order to form a near net shape 3DP part. The goal was to produce complex parts without the need for post processing and without loosing the good properties of the object like its uniformity and strength.
1.3 Rapid Prototyping

1.3.1 General approach

The term rapid Prototyping has been created to describe a set of new manufacturing methods. These methods rely on different techniques but share the same objective and philosophy: The ability to integrate computer design and product manufacturing in a short time cycle. As the technicalities differed and the approaches diverged new names started to emerge to describe the technology like Solid Freeform Manufacturing (SFF), Desktop Manufacturing, Holoforming, Automated Fabrication... Even though this new industry is relatively very young (1987), it has already established itself in most prototyping facilities and is rapidly moving towards medium to high scale production. So, Rapid Prototyping refers to the various processes that are capable of generating three dimensional solid models from raw materials without human intervention. These processes are in the “additive fabrication” category as the raw material is manipulated so that successive pieces (thin layers) are integrated together to form the desired solid object.

The technology has several advantages compared to the other manufacturing methods; it is capable of creating extremely complex shapes even with internal features (virtually any geometry). Many of its derivative processes are practically capable of controlling microstructure and materials mix in a part. Also, it is nearly automated without the need for a manual selection of tools or set ups. The parts are created by the prototyping machine directly from the CAD design in a single manufacturing step independently of their geometry. This single object build style eliminated the problems that can be caused by joining operations. However, the disadvantage of rapid prototyping can be of a major concern as the surface finish of the parts is not totally satisfactory and lamination problems can occur due to the layer by layer build up. The materials restrictions is a drawback which is being constantly surmounted by the expanding research effort. Interestingly, most of these problems are of a practical nature and nothing in the technology itself puts theoretical restrictions on what can be done: Changing some of the controllable parameters like the drying
rate or the layer thickness solves the practical difficulties in many instances without effecting the parts properties.

The Major advantage of solid freeform manufacturing remains in the rapidity of the fabrication process and its full compatibility with the CAD design. The computer data is usually formatted and down loaded directly to the machine which automatically creates the part.

![Diagram showing the process from 3D CAD data to part retrieval](image)

The first step in the process is the creation of a computer aided design (CAD) using a surface (i.e: Autocad) or a solid modeler (i.e: Pro/engineer, I-DEAS). The use of solid modeler is generally preferred since its feature based parametric design approach has greater flexibility and allows rapid design changes. Also, the solid modeling software files can be easily down-loaded to the prototyping machine controllers and are capable of creating assemblies and changing their dimensions [14].

Progress in the software design has allowed the freedom of exploring new options in the design: Computer simulations (heat, stress analysis...) have become standard peripherals to the basic software. It is necessary to create a format that can be downloaded to the machine after the design optimization. Most RP systems use the .STL file format created by 3D systems [15]. The .STL file represents the surface of an object as an array of triangular facets with directed normals that can be stored in an ASCII or binary version. Recently, a new format have been developed which reduced the file sizes and increased accuracy.
especially in the case of complex geometries. This NURBS-based format have reduced the facetting of the parts generated and thus enhanced the part appearance [16]. The next step in the data managing consist of taking the .STL or NURBS file and slicing it into thin layers. The slicing process is the longest process in the data conversion, that is why parallel slicing algorithms have been developed lately[17]. The sliced file is then sent to another computer for layer merging and direct downloading to the RP machine. This design and conversion process is dependent on the software, hardware, file sizes and formats... Many RP technologies have adopted also post processing software that simulate the part build before the actual fabrication.

In general, the applications of the solid freeform fabrication are very widespread since it is possible to create any geometry. The major fields of application will be mentioned only. The first major industries which recognized the importance of RP were the automotive and aerospace industries. The prototypes created are used for visualization, fitting, flow analysis, design analysis, mechanical operation testing, component performance verification, soft tool development and low to medium volume production[18]. These advantages are also important in many industries that rely heavily on complex design and manufacturing like the electronic and plastics industry [19]. It is also obvious that RP is beginning to play a fundamental role in the foundry industry which is the world's sixth largest and most ancient manufacturing method [20]. The prototypes are used in this case as direct molds or as patterns in the casting process. The created parts can be used in sand casting, investment casting, die casting... Also, the creation of masters for electron discharge machining(EDM) by RP methods have become a standard method. This mold/pattern fabrication uses the advantages of silicone moulding, metal spraying and many others
in the manufacturing process. The rapidity of this casting process drastically reduces the
design cycle and the parts can be delivered in a matter of days instead of weeks or months.
Usually, the RP machine create the pattern/mold which can be metal sprayed or silicone moulded prior to the casting.

![Silicone mold](image)

![Pattern plate](image)

The RP pattern can thus be used to create silicon moulds for low production runs (10
to 15 runs). The metal spraying technique can be used for higher volume productions
(5000 to 10,000 runs). A metal spraying gun is used to coat the RP sample prior to embedding in a resin/aluminum mold.

![RP pattern](image)

![Sprayed metal coating](image)

15% resin with 85% aluminum filler are used to create semi-hard mold.

These two processes are becoming popular in the production of rapid tooling and casting parts. The research is now directed towards creating "semi hard" tools directly from the RP process without even needing these easy methods. However, certain kinds of tech-
nologies (stereolithography) will find it very difficult to achieve such a goal and are restricting their research to optimizing surface finish and part accuracy.

1.3.2 Specific technologies

-Stereolithography: This is the name of a process where a laser beam is computer guided in a bath of photosensitive polymer that solidifies through photopolymerization to a certain depth. The beam thus creates a solid cross section of the sliced part which is being build layer by layer. The interaction between the laser beam energy, line width and depth of photopolymerization has been extensively studied by various investigators [21]. This technique was one of the first commercialized RP technologies through different companies in the U. S, Europe and Japan. In the U.S it was distributed by 3D systems Inc. While in Germany, another company (EOS) was producing the European equivalent to the 3D systems machine among other RP machines like a Selective Laser Sintering station[22]. Japanese companies in the mean time created other stereolithography machines like the SOUP[23], Soliform[24] and the Sony. All these machines have different operating conditions and perform divergent tasks but rely on the same basic phenomena. The operating system can be summarized by the schematic in figure 1.2.

Thus the stereolithography part is made with acrylic and epoxy materials (solidified photopolymer). Due to the fact that the part is build in a liquid resin, there is a need to create a support structure that holds the solid fixed during the build. This has created certain complications in the geometrical design, file management and extended the build time. Several software have been developed in this area to automate the support structure design[25]; However, this support automation did not solve the problem of the support removal from the part. The major disadvantage of this technique remains in its incapability of creating non-plastic models. This restriction in the materials choice have made post processing necessary in the rapid tooling and casting area. The use of stereolithography parts in investment casting have been enhanced lately by the introduction of new part build techniques like the “Quickcast” build style introduced by 3D systems and others[26]. The models however need to be “hollow” in order to reduce the pressure on the ceramic mold during the wax expansion. This build up method have also reduced the build
time and the materials consumption. Finally, stereolithography technology have moved from a young to a mature state rapidly, but the insurmountable materials restrictions make this technology limited in its current applications to the creation of plastic parts. Some research is being conducted towards forming silica parts but no major successes have been published yet.

Figure 1.2: The stereolithography machine.
-The Solider process [27]: this relies essentially on the same principle of hardening of photopolymers. The only difference lies in the creation of a mask that allows complete lighting and hardening of the entire surface. The preparation of masks uses the Xerox method. Once the mask is prepared according to the CAD sliced data file, a UV light shines through the transparent spaces and hits a photopolymer bath that hardens instantly. This method allows tension free surfaces and homogeneous bodies since the resin hardens simultaneously on each sliced surface. The non solidified resin is then collected and replaced by a wax that help hold the part upon cooling. At the end of the build, the hardened polymer and the wax are separated in order to get the acrylic part. The wax filling method allows part build without the need for support structure but can create delays which are due to the polymer/wax separation. the solider method has been reported to be quite effective in creating attached assemblies which allow dynamic movements, i.e.: two attached gears that move together. The main disadvantage is the same as in the stereolithography case since this technology only creates plastic parts.

-Laminated Object manufacturing - LOM [28]: The LOM process uses a laser that cuts the contours of the CAD sliced surface in order to create the layer by layer build up. It uses “paper” layers that can be easily cut by the laser beam. Each layer is thus bonded to the stack of layers previously cut by a pressure/heat process: a heated roller moves across the “paper” ribbon while pressing it against the stack. After bonding the additional layer, the laser beam which is guided by the computer sliced file program cuts the contours of the new layer. The material that surrounds the cut section is usually cross hatched into squares in order to facilitate the part removal.

The advantages of this process is its rapidity since you only need to scan the contour and not the whole surface. Stress build up is virtually non-existent since no significant part shrinkage occurs. The main disadvantage is its inability to build thin walls in the vertical (z axis) direction and its poor surface finish. Also, the excess material is wasted and not recyclable[29]. The materials restrictions are less strict in this case since you can obtain thin layers in plastic, ceramics (tape casting) or probably metals which can be cut by laser. So far, the industry has concentrated on special “paper” thin layers which give the final
part a "wood-like" appearance. Some research has been done on tape casted ceramics to form structural ceramic parts[30].

![Diagram of LOM machine](image)

**Figure 1.3: The LOM machine**

-Fused Deposition Modelling -FDM [31]: This is also a layer by layer additive process where the CAD file can be directly down-loaded to the machine. A liquid thermoplastic material is extruded through a small nozzle and deposited into thin layers. The nozzle is guided by the computer sliced file which controls the deposition position [32]. the thermoplastic liquid is kept at one degree above its melting temperature. As the liquid is deposited, it cools and solidifies very rapidly in less than 0.1 seconds[33]. The materials used include a wax filled plastic adhesive material, a tough nylon-like material and investment casting wax. All the materials used are non-toxic, and no excess waste is generated during
the build. The main advantage of this technique is its simple operational needs and low materials cost. The method is being mostly used by the medical industry in the investment casting of orthopaedic implants. Another new applications in the “jewelry” field seem promising. The main disadvantage is the bad surface finish and the materials restrictions. Like many other RP systems, this technique showed successes in building plastic parts. The new research efforts are directed towards getting ceramic prototypes. The following schematic is a representation of part creation using an FDM machine:

![Diagram of FDM machine]

**Figure 1.4:** The FDM machine.

-Selective Laser Sintering -DTM [34]: The SLS process consist of using a laser beam to heat up a powder compact to the point of “sintering”. The technique relies on spreading thin layers of powder and then guiding a laser beam according to a CAD sliced file
through each layer. The temperature of the powder impacted by the beam is raised to the point of sintering (which causes the fusing of the powder particles) forming thus the solid part. The laser power, scan speed and other parameters are determined by the materials in use. In the other areas which are not hit by the laser, the powder remains loose and can brushed off at the end of the build. The main advantage of this technique is its capability to process different kinds of materials. Also, there is no need for a support structure since the loose powder serves as support in this case. The SLS process has been capable of the creation of parts in plastic, wax and other materials that soften upon short laser heating. The process can also be applied to metals and ceramic powders which need to be polymer-coated in order to bond at low heating temperatures (at the softening point of the polymer coating). Usually, the ceramic and metal parts are cured and post processed (fired) to get the desired properties. The main disadvantages of SLS are the poor surface finish and inaccuracies in the part build. These inaccuracies occur because of extra borderline material hardening, non-uniform shrinkage and non-uniform heating which might cause warpage [35]. This warpage behavior can be excessive in many instances since the melting then solidification of the laser scanned layer upon an already sintered underlying layer creates stresses which cause curling/warping of the part. Also, toxic gases emitted from the fusing chamber need to be handled very carefully. The SLS process is described in figure 1.5.
Figure 1.5: The SLS machine
Chapter 2

Study of printing parameters in the structural ceramic system (alumina).

2.1 Basics for printing on ceramics

2.1.1 Powder characteristics.

The powder characteristics are the most contributing factor to the printing behavior of the materials system. Several powder parameters are found to be important in the 3DP process. The most important one is the powder bed packing density which plays a fundamental role in the firing behavior, part shrinkage and green body homogeneity. Fine particles with high packing density are needed to obtain complete densification of the ceramic printed part as mentioned earlier in the first chapter. Typically, a powder bed density of around 60% of theoretical is capable of fully densifying upon firing without any extra steps. Ceramic green bodies with lower packing density than 60% or 50% need to be Isostatically pressed in order to reach this critical density before being fired to full density.

A second important parameter is powder morphology, since the shape and size of the powder effect the firing, homogeneity, flowability, and printed line primitives shape and structure. Another parameter that is important during the printing process is the powder surface tension which, when combined with the binder wetting behavior, will determine the primitives shape and the drying/warpage of the printed region. This drying behavior can cause large stresses in the printed layer which reacts by curling/warping upwards since it is attached to an already dried layer lying underneath it. This phenomena is described in more details in chapter 3 (figure 3.3).

2.1.2 Printing parameters under study.

Various printing parameters can be changed in order to optimize and control the final part performance. These include the binder composition, fluid flow during printing, binder
concentration, and print styles (raster scanning or non-linear checker board scanning). This current research is limited, however, to the study of the effect of binder flow and concentration on the shape of the line primitives in the spray dried alumina system; The effect of the binder/powder bed interaction is also covered in both of the spray dried and fine alumina powder systems. It is important to note here that these two systems were chosen because they possess the particles large surface areas requirement necessary to achieve the full densification of the alumina ceramic.

2.2 Experimental procedure

2.2.1 Materials systems

The two materials systems which were under study varied drastically in powder morphology, powder bed packing and flowability. The first system consisted of fine submicron alumina powder which did not flow well to spread into homogeneous, defect free layers. The powder was Reynolds RC172-DBM alumina both undoped and MgO doped with a mean primary particle size of 0.8 mm. The agglomerate sizes varied between 75 and 150 mm.

The second materials system was alumina spray dried powder. The same submicron powder used above was dispersed in a slurry with 2 wt% poly acrylic acid (PAA). Typically the slurry had a 25 vol% dispersed alumina solids in iodized water. The slurry was mixed using ball milling for 24 hours prior to spray drying. The pH was kept at 4 using small doses of nitric acid in order to get a good dispersion. After spray drying, the powder obtained was spherical with some percentage of “donut-like” irregularities. The flowability was excellent after sieving to less than 67 mm.

2.2.2 Study of line primitives in the fine powder system

Since the fine powder did not flow well, simple modifications to the conventional spreading method were implemented. we were able to obtain thin layers of fine powders by using a press rolling technique which consisted of clockwise rotation of the spreader rod on the powder bed. This rotation mode created pressure that helped in packing the bed
The binder used was 15 vol% Acrysol WS-24 (Rohm and Haas Company, Philadelphia, PA) which is an acrylic copolymer dispersion resin. A continuous jet of Acrysol droplet were printed at a flow rate of 1.25 cc/min with a fast axis velocity of 65 in/sec (printhead speed). The printed liquid is typically passed through a 45 mm ceramic nozzle which is vibrated at 60 KHz using piezoelectric transducers. The Layer thickness was 127 mm. Single primitive lines were printed then cured at 160 °C for two hours prior to removal from the powder bed. Some of the lines were directly studied under the SEM and the rest were immersed in epoxy and optical microscope studies of their cross section was subsequently performed. The powder packing density of the bed was also measured by using a tapping technique [36].

**Figure 2.1:** Press rolling sequence in spreading fine ceramic powders.
2.2.3 Study of line primitives in the spray dried powder system

Various parameters were changed while studying the primitives in this system. The first important one was a change in the powder characteristics: a study of printing on the as sprayed and sieved powder was conducted along another study which used printing on the spray dried powder fired to 450 °C for 4 hours. The binder used in this study was also the Acrysol WS-24, but the binder concentrations were changed from 6 vol% to 15 vol%. A polyethylene glycol (PEG) plasticizer was also added to the 6 vol% Acrysol at a mass percentage of 25 wt% PEG to 75 wt% Acrysol. These various changes were coupled with a variation in the fast axis printing speed which changed the saturation of the printed lines. The flow rate of the binder was kept constant at a rate of 1.25 cc/min. Thus line primitives were printed using two binder concentration, various saturations, plasticizer additions and different powder characteristics. The lines were usually cured in the powder bed at 160 °C for two hours prior to their removal from the bed by carefully sieving the loose powder from the primitives. The lines were then analyzed under the scanning electron microscope (SEM) and a computer software linked to an optical microscope was used to measure their diameter based on a statistical averaging approach. A porosimetry study of a 500 printed lines sample was performed by using a mercury porosimeter (Micrometrics, Norcross, GA). These 500 lines were printed with a 15 vol% Acrysol at a saturation of 60% (Fast axis speed of 65 in/sec with a flow rate of 25 cc/min). The typical layer thickness in this study was 178 mm. The powder bed density was also measured prior to each printing session by spreading a number of layers in the powder bed and measuring their weight.
2.3 Results and Analysis

2.3.1 The fine powder system.

The packing density of the powder bed was typically around 40% and indicated that isostatic pressing prior to firing was necessary to get fully dense parts using this system. The fine powder formed beds that had a high cohesive strength. This behavior is caused by the powder high surface area which is also the reason behind the low flowability during the spreading. Usually, two main factors determine the primitives shape in the 3DP process: the binder/powder capillary energy interaction and the cohesive strength of the bed [37]. The competition between these two effects quantify the degree of rearrangement in the printed region and the binder wicking in the powder. One of the results of the powder bed high cohesive strength was the elimination of the ballistic interaction between binder and powder: The binder droplet tends to displace the powder granules upon impact causing inhomogeneities during printing in the case of other low cohesive energy beds. In addition to this, the primitives did not show any powder rearrangement during printing that might be caused by high capillary action. In fact, the shape of the primitive lines was rectangular rather than spherical which indicated that primitive formation was not driven by rearrangement action. A cross section of the line primitive shows a rectangular to semi-elliptical shape with the larger side being along the fast axis direction (figure 2.2). This larger side varied between 450 to 530 mm while the primitive shorter side was less than 200 mm (figures 2.2 and 2.3). A plausible interpretation of this behavior can be due to the formation of binder droplets on the surface of the bed upon impact. The high cohesive strength of the powder forbids the droplet from displacing or rearranging the alumina granule directly after impact, that's why the droplet tends to spread in the horizontal direction (parallel to the layer). However, due to the porosity of the powder bed, the binder starts to slowly wick inside of the layer forming thus the final primitive rectangular shape (figure 2.4). We can conclude from this that in high cohesive energy beds, the shape of the formed primitives tends to be anisotropic (non-spherical) and it would be expected to be governed by the impact speed and the "wicking" behavior of the binder in the powder bed.
Figure 2.2: Cross section of fine alumina line primitive (perpendicular to fast axis).

Figure 2.3: Fine alumina line primitive (parallel to fast axis).
Figure 2.4: Primitive formation in powder beds with high cohesive energy.
2.3.2 Spray dried powder system

The powder was porous and very flowable in this system. This indicated the low powder bed cohesive energy and its low packing density. The spray dried granule pack closely to occupy around 60% of the powder bed volume. However, the measured packing bed density of the spray dried alumina varied from 32% to 34% depending on the batch. This low packing density was a result of the porosity in the spray dried granule which contain around 50 vol% inter-granular pores. The first observed effects of that were the high powder ejection upon impact of the binder due to ballistic interaction. Another interesting observation was that the powder granule rearrange upon printing to form cylindrical lines. This rearrangement is caused by the capillary interaction between the loose powder bed and the binder. In fact, the printed region showed a typical packing density that is 2% to 3% lower than the loose powder bed density. Thus, capillary action seems to play the major role in this system given that the cohesive energy of the bed is not significant. The line primitive diameter depended on many variables that effected the capillary action as a result of this. The first variable studied was the change of saturation while printing on as sprayed powder. Changing the fast axis speed at a constant flow helps in controlling the saturation of the printing sequence. In table 2.1, the dependence of the average line diameter on saturation is quantified using a statistical average of 25 different lines. We can conclude from this data that the line diameter increases at higher saturations. This behavior was observed upon printing on all the powder that contained PAA even at different binder concentrations. The graph in figure 2.5 is based on the data of table 2.1 and represents the diameter increase with higher saturation (lower axis speed). The concentration of the binder was 6 vol% Acrysol in this particular experiment. One must notice that even though the standard deviation is rather large, the change in line diameter was almost the triple of the deviation if we go from a 60% to an 87% saturation (figures 2.9 & 2.10). This diameter increase with saturation was also observed by “Lauder” while printing on dense faceted alumina powder which did not have pores to absorb the extra binder[37].
Table 2.1: The effect of saturation on primitive line diameter in alumina spray dried powder with PAA.

Changing the powder characteristics by the burn out of the PAA has, however, a direct effect on the line diameter dependence on saturation. The line diameter did not increase with increased saturation upon printing on the powder which contained no PAA. In table 2.1, the data obtained does not show a trend in the line diameter with increased saturation; this can be more obvious if we look at the resulting graph in figure 2.6. One thing to notice in this case is that the parts printed with this powder (no PAA) did not warp during the build up. On the other hand, printing on the powder with PAA caused warpage that disrupted the part build (see figure 3.3 for a description of warpage).

Table 2.2: The effect of saturation on line diameter in alumina spray dried with no PAA.
Figure 2.5: Effect of saturation on line diameter using alumina spray dried powder containing PAA
Figure 2.6: Effect of saturation on line diameter on alumina spray dried without PAA
Thus, the PAA presence in the spray dried granule is changing the drying behavior during the printing. The granules which contain PAA were not absorbing the printed binder and the drying was rather slow. In the case of PAA burn-out, the powder seemed to absorb the binder at a fast rate reducing thus the warpage that is due to slow binder evaporation. The difference between the two kinds of powder was more detectable when a study of the binder wetting behavior was conducted. In fact, the SEM analysis showed that the Acrysol binder tends to wet the powder with no PAA, and the binder seems to coat the granules after printing (fig 2.7). On the other hand, the Acrysol tended to stay on the intergranular necks in the case of the powder with PAA without "wetting" or even partially "coating" the granules (fig 2.8). As a result of this, the fired powder absorbed the Acrysol and the change of saturation did not effect the line diameter as the extra water in the binder was sucked to the inside of the porous powder. The non-fired powder (with PAA) did not absorb the extra water of the increased saturation and this lead to an increased line diameter. The addition of the PEG plasticizer to both powders did not change the line diameter interaction with saturation: the line diameter increased with increased saturation only in the case of non-fired powder as expected (see tables 2.3 and 2.4).

<table>
<thead>
<tr>
<th>Speed in/sec</th>
<th>65</th>
<th>52</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg line diameter</td>
<td>252.4</td>
<td>301.2</td>
<td>328.0</td>
</tr>
<tr>
<td>Micrometer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>St deviation</td>
<td>19.7</td>
<td>30.4</td>
<td>22.7</td>
</tr>
<tr>
<td>Saturation</td>
<td>60</td>
<td>76</td>
<td>97</td>
</tr>
</tbody>
</table>

Table 2.3: Line diameter increase with increased saturation while printing Acrysol with PEG on non-fired spray dried alumina (with PAA).
<table>
<thead>
<tr>
<th>Speed in/sec</th>
<th>65</th>
<th>52</th>
<th>35</th>
</tr>
</thead>
<tbody>
<tr>
<td>Avg line diameter Micrometer</td>
<td>263.8</td>
<td>262.0</td>
<td>277.1</td>
</tr>
<tr>
<td>St deviation</td>
<td>17.0</td>
<td>18.9</td>
<td>20.4</td>
</tr>
<tr>
<td>Saturation</td>
<td>60</td>
<td>76</td>
<td>97</td>
</tr>
</tbody>
</table>

**Table 2.4:** No increase in line diameter with saturation while printing Acrysol with PEG on fired alumina spray dried (without PAA).

The presence of the plasticizer increases the plastic flow capabilities of the printed region. This helped in reducing the warpage of the printed layer under the same generated drying stresses when the polymer is added.

![Image](image.png)

**Figure 2.7:** Acrysol wetting of granule with no PAA (15 vol%)
Figure 2.8: Acrysol non-wetting behavior with granule containing PAA. The Acrysol stays at the inter-granular necks (15 vol%).
Figure 2.9: Line printed with 6 vol% Acrysol on alumina spray dried containing PAA at a 60% saturation.

Figure 2.10: Line printed with 6 vol% Acrysol on alumina spray dried containing PAA at 87% saturation
The last parameter studied was the effect of increased binder concentration on primitives. The addition of binder tended to decrease the diameter of the line primitive as more rearrangement occurred. When the binder concentration was increased from 6 vol% to 15 vol%, the lines shrunk by around 50 μm. The excess of binder printed on the spray dried which contained PAA, accumulated on the necks and created more inter-granular stresses that increased capillary rearrangement. The data presented in figure 2.11 clearly shows the average diameter line shrinkage with more Acrysol concentration.

Figure 2.11: Effect of binder concentration on line diameter of spray dried alumina containing PAA.
Chapter 3

Glass-ceramic system: Printing on spray dried dental powder.

3.1 Objective

3.1.1 General goal

One of the main objectives of this research is to prove the capability to form fully dense glass-ceramic parts via 3DP. Glass-ceramics densify via a viscous liquid sintering process. The advantage of this sintering procedure lies in the fact that non-fine ceramic powders can be sintered to full density. In the case of the other solid state sintering process. It is necessary to have fine powder with primary particle size of <2 mm in order to achieve full densification. It is also for this reason that it is possible to use large powder granules that can fully densify in one firing step. This sintering behavior combined with flexibility of 3DP allows the creation of virtually any complex shape required: All the geometrical restrictions which are due to the cold/hot isostatic pressing step are eliminated. In addition to this, the nature of the process allows for printing on various forms of powders besides spray dried, like coarse or spherical, and reaching full density (see chapter 4).

The sintering properties of the glass-ceramics group open the possibility of producing dense ceramic parts by directly firing even the low density green bodies. This idea pushed the research towards demonstrating the capability of 3DP in printing then forming a dense part in one firing step. The success of the work is the first experimental proof of this outlined concept.

3.1.2 3DP as an alternative technique.

An alternative approach in the shaping of glass-ceramics can have an important impact. Glass-ceramics are prepared by mixing and batching the proper compositions of raw materials, melting the compound to form a homogeneous liquid and then cooling is usually performed. Once the glass is melted and ready for delivery, many shaping techniques can be used to get the desirable part. These include spinning, rolling and casting.
Other techniques include glass-ceramic powder pressing followed by sintering. Each technique offers some advantages and some drawbacks depending on the glass viscosity and on the part geometry. In this respect, 3DP can have a leading advantage since the process is independent of the geometry and viscosity given that the shaping takes place at room temperature. The 3DP process is very promising in the formation of complex shapes that are hard to manufacture by different techniques. It can be also of major use in the fabrication of low to medium size production parts which might be difficult to fabricate by regular methods. In these two areas, the use of the 3DP process can be economically justifiable and advantageous. The main disadvantages of the process can be the shrinkage which occurs upon part densification and sintering, and the restriction on the raw materials which must be in powder form.

3.1.3 Properties of the demonstration material system

It was advantageous to use an already commercial glass-ceramic material in the fabrication of a dense 3DP parts. Given the widespread use of ceramics as dental restorative material, a dental ceramic was chosen to prove the capability of applying the 3DP process to a specific material system. The system consisted of a nepheline/feldspar composition which was used in the CAD-CAM techniques for the formation of dental restorations. The heat treatment for this specific composition was optimized and the mechanical strength was shown to be satisfactory. A detailed study of the sintering schedules and microstructural analysis were also available[38]. All the materials parameters being optimized, the research focused on the 3DP shaping technique with the objective of creating fully dense printed parts.
3.2 Glass-ceramics: Definition and applications.

Glass-ceramic materials are polycrystalline solids prepared by the controlled crystallization of glasses. The difference between a glass and a crystal phase lies in the ordering of the atomic cell. Solid crystals possess a long range ordered atomic cell structure which allows the formation of grain boundaries and which can have anisotropic properties. Glasses on the other hand do not show an ordered atomic structure but can have some order in the near neighbors cell structure (short range order). This order disappears as soon as we go beyond the near-atom neighbors distance. The glass phase is a metastable thermodynamic phase which occurs at the glass transition temperature as the glass melt is cooling down. The formation of glass-ceramics starts by the melting then cooling of the glass material. Upon cooling the liquid reaches high viscosity in a short time and thus impedes the formation of the crystal nucleus and their growth.

The main advantage of glass-ceramics lies in their capability to be shaped while in the glass phase prior to their transformation to a glass-ceramic composite. This facilitates their fabrication process without loosing the good properties of ceramic materials. In general, glass-ceramics can be shaped using powder packing techniques (pressing and molding) or melt shaping techniques (casting). The powder packing techniques consist of pressing or forming a glass powder batch in a desired shape prior to firing it to get a dense glass part. The melt techniques rely on shaping the glass while in its liquid melt phase prior to cooling to form a solid glass part. The choice of the proper fabrication method depends on the glass melting temperature, its viscosity and other properties. However, it is necessary to perform the proper heat treatment to get a controlled nucleation and growth of crystals in the glass part regardless of the fabrication method.

The nucleation can be homogeneous or heterogeneous depending on the composition and atomic structure. Homogeneous nucleation depends on the temperature, short range atomic diffusion, and the free energy change at the critical radius of the nucleus[39]. Another nucleation mechanism can be initiated by the presence of impurities and is called heterogeneous. Useful heterogeneous nucleation can be accomplished by the introduction of small amounts of dispersed metallic nuclei which behave as nucleation sites. A subgroup of the homogeneous or heterogeneous nucleation occurs when a homogeneous liq-
uid phase separates into two immiscible phases upon cooling. This immiscibility is observed on the microscopical scale where one of the metastable phases can act as a nucleating site. The binary Al₂O₃ - SiO₂ system presents examples of such a system where the liquid separates into two immiscible liquids one rich in alumina and the other abundant with silica. The alumina rich phase crystallizes and creates nucleation sites readily (homogeneous). Further heat treatment allows crystal growth after nucleation and can be controlled by varying the temperature and time schedules[40]. The addition of some oxides like titania which do not act like glass modifiers can enhance the nucleation of the immiscible glass phases and helps in forming the controlled crystallization (heterogeneous). These different nucleation mechanisms and the various methods and compositions available have created the necessary conditions that made glass-ceramics a known distinct materials group.

Historically, the first attempts to create a matrix of both a crystalline and a glass phase were done by the French chemist Reamur more than 200 years ago[41]. However, the important technological discoveries in this area did not appear until the mid of the current century when the glass-ceramic technology evolved into a commercial industry. Glass-ceramic have become a necessity in many fields because of their mechanical, thermal and electrical properties. Other advantages are due to their good optical properties and high chemical resistance. The properties of these materials depend on both their composition and microstructure; The huge amount of compositional variations and the ability to control crystallization have made many useful combinations possible. The range of glass-ceramics has become very broad and includes many systems like the Lithium-silicate, Magnesium-silicate, Alumino-silicate and Fluo-silicate. The good mechanical strength of glass-ceramics at high temperatures is important in many commercial applications like heat exchangers, kitchen ware, stove hot plates and guided missiles (table 3.1). Their chemical strength combined with mechanical strength made them of use in construction materials, grinding equipment, pipings for corrosive elements. The very low thermal expansion of certain glass-ceramics and their light transmission capabilities helped in developing new optical instruments and laser devices (table 3.2). Their dielectric properties enhanced their use in microelectronics. Also, the bio-compatibility of many glass-ceramic combina-
tions made them a class of bio-ceramics. In this field, glass-ceramics are frequently used in the dental industry and in orthopedics (bone replacement)[42].

<table>
<thead>
<tr>
<th>Material</th>
<th>MOR (MN/m²)</th>
<th>MOR (lb/in²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glasses</td>
<td>55-70</td>
<td>8000-10000</td>
</tr>
<tr>
<td>Glass-ceramics</td>
<td>70-350</td>
<td>10000-50000</td>
</tr>
<tr>
<td>Electrical porcelain</td>
<td>80-140</td>
<td>12000-20000</td>
</tr>
<tr>
<td>(glazed)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>High alumina</td>
<td>200-350</td>
<td>30000-50000</td>
</tr>
</tbody>
</table>

Table 3.1: Modulus of Rupture values for glass-ceramics and other materials (0.5 cm diameter rods in 3-point bending)


<table>
<thead>
<tr>
<th>Crystal Phase</th>
<th>Thermal expansion coeff. (1/C)</th>
<th>Temperature range (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O-Al₂O₃-SiO₂</td>
<td>-86 * 10⁻⁷</td>
<td>20-700</td>
</tr>
<tr>
<td>Al₂O₃-TiO₂</td>
<td>-19 * 10⁻⁷</td>
<td>20-1000</td>
</tr>
<tr>
<td>2MgO-@Al₂O₃-5SiO₂</td>
<td>26 * 10⁻⁷</td>
<td>25-700</td>
</tr>
<tr>
<td>Li₂O-Al₂O₃-4SiO₂</td>
<td>9 * 10⁻⁷</td>
<td>20-1000</td>
</tr>
</tbody>
</table>

Table 3.2: Thermal expansion coefficients of crystal types present in glass-ceramics

3.3 Experimental procedure

3.3.1 Powder characteristics.

The material was received in powder form and was supplied by a German company (Mark 4, produced by Vita Zahnfabrik, Bad Sackingen, Germany). The powder is composed mainly of nepheline (80 wt%) and of feldspar (20 wt%). It comes in a homogeneous glass form with a particle size varying from 3 to 7 mm. Other batches of similar compositions were mixed in-house then ball milled for two days to obtain similar powder characteristics to the Mark 4 powder. This particular composition was chosen because it maximized the fracture strength of the final part. It was also found that nucleating the material at 900 °C for 4 hours followed by crystal growth at 1000 °C for 2 hours created the optimal mechanical properties and microstructure[38].

3.3.2 Spray drying

The need for flowable powder which are easy to spread using 3DP pushed towards forming spherically shaped powders. One of the practical methods to accomplish that was through spray drying the powder after dispersing it in a slurry form. After optimizing the dispersion parameters, 25 vol% glass-ceramic powder were mixed with iodized water to form a slurry. Polyvinyl alcohol-PVA(Aldrich chemicals, MW = 9000 - 10000) was the binder used since it helped in the formation of a low viscosity slurry. The 2 wt% binder helped in forming fine dispersed powders since the long polymer chain surrounded the powder particles and created an electric double layer that separated the particulates through electric repulsion. Small amounts of nitric acid were added in order to keep the slurry pH between 4 and 4.5. The slurry was then mixed by ball milling for 24 hours and was finally ready for spray drying. The dispersed mixture was fed to the spray dryer at a rate of 1.2 cc/min and at outlet temperature of around 300 °C. This resulted in the formation of spray dried particles which varied in size from 67 mm to 15 mm in diameter.

3.3.3 Printing parameters

Printing on the resulting spray dried powder was then performed under various conditions. Several printing trials involved printing with 6 vol% Acrysol on as-prepared pow-
der. Another printing procedure was performed by printing 6 vol% and 15 vol% Acrysol on fired spray dried granules. These powders were fired to 450 °C for 4 hours prior to printing to obtain complete burnout of the PVA binder. After being able to print several parts, a study of the line primitives was performed using SEM analysis and line width optical measuring software. Along with varying the binder concentration from 15 vol% to 6 vol% Acrysol, the saturation of the printed lines was also changed by changing the fast axis printing speed in a range varying between 65 in/sec to 45 in/sec. The binder flow was kept constant at 1.2 cc/min in all the experiments with all the other standard machine parameters (spreading, piezo-electric frequency...).

3.3.4 Firing

The part in the powder bed is heated to 160 °C for 2 hours at the end of the printing process in order to cure the binder and obtain good green strength in the printed part. The printed region is then separated from the unprinted loose powder bed by brushing. The resulting part is embedded in a coarse alumina powder bed and put inside a crucible. The first step in firing consists of vaporizing the Acrysol binder prior to vacuum sintering. This "debinding" is accomplished by heating the crucible to 450 °C for 4 hours inside a small furnace at atmospheric pressure followed by partial sintering at 750 °C for 2.5 hours to regain some of the lost green strength. The crucible is then moved to a high temperature vacuum furnace called Centorr (Centorr Assoc, Suncook, N.H) where the final firing starts under a vacuum of 2*10-5 torr. Various firing schedules were thus conducted at different temperatures and times with keeping a constant heating rate of 5 °C/min.
Figure 3.1: Chart of experimental steps needed for the formation of fully dense glass-ceramic parts using spray dried powder.
3.4 Results and analysis

3.4.1 Powder characteristics.

The spray dried powder contained 2 wt% PVA binder and varied in size from 73 μm to 15 μm. The small number of bigger chunks that were observed disappeared after sieving the powder prior to printing (fig 3.2). The powder bed packing density was measured and varied between 29 wt% and 31 wt% of the materials theoretical density (depending on the batch used). The printed parts usually exhibited a packing density of 2 wt% less than the measured bed density. The particles have mostly a sphere-like shape with some irregularities (donut-like shape). Its excellent flowability resulted in a uniform and homogeneous powder bed after spreading.

Figure 3.2: Dental glass ceramic powder after spray drying.
3.4.2 Printing parameters effects.

The first printing trial was performed on as-received powder which contains polyvinyl alcohol-PVA. An excessive amount of warpage was observed upon printing the first layer. The spray dried granules seemed to partially disintegrate upon printing and this lead to a large amount of rearrangement within a layer. This excessive shrinkage during the drying of the binder has caused high stresses in the layer. The shrinkage also occur upon spreading and printing the second layer, and put a stress on the already dried first layer. Because of this stress, the first layer responds by warping because of this stress. Upon spreading the third layer, the curvature in the previous two layers disturb the homogeneity of the new layer and printing becomes impossible. This phenomena is best described in the following graph:

![Graph showing stress formation and shrinkage effects during printing](image)

a/ Stress formation during first layer printing.  
b/ Shrinkage effect of first layer after drying.  
c/ Printing of second layer also creates stress.  
d/ Curling & warpage occur after the drying of the second layer.

*Figure 3.3: Warpage during printing on spray dried powder containing PVA*

The excessive rearrangement during printing is due to the hydrophilic properties of the PVA binder. Polyvinyl alcohol absorbs water during printing and the granules disintegrate because of high water concentration in their pores. The disintegrated particles create
smaller powder chunks which are lighter and more susceptible to capillary stresses. These smaller chunks rearrange more effectively under the same capillary stress and cause the warpage of the part. The SEM analysis of the printed region revealed some disintegrated particles as shown in figure 3.4. Granules which did not contain PVA did not exhibit disintegration upon printing as can be seen in figure 3.5.

Figure 3.4: Spray dried granule containing PVA after disintegration due to water absorption during printing.
Figure 3.5: Spray dried granules without PVA did not show disintegrated parts upon printing with 15 vol% Acrysol.

Since this problem was caused by the PVA water absorption, the obvious possible solution was in the burn out of the PVA binder prior to printing. The powder was thus heated to 450 °C in order to vaporize the binder. Having these initial powder characteristics several printings were performed using different binder concentrations. Study of the effect of saturation on line primitives at different binder concentrations did not reveal much variation due to binder absorption of the porous spray dried powder. In fact, the line diameter did not show a significant change upon a change in saturation (fig 3.6). This observation was also seen upon printing on alumina spray dried powder which did not contain binder (fig 2.6). In fact the powder seem to absorb most of the printed binder since little amounts of binder are left at the necks. Microstructural analysis using the SEM showed a very small amount of Acrysol at the neck, even at 15 vol% concentrations. A
comparison between the binder presence at necks in the case of alumina as opposed to the glass-ceramic case reveals the extent of powder absorption in the latter (fig 3.7 & fig 3.8). It is also noticeable that this excess in absorption allowed the use of more binder concentrations in the printing without any warpage during the green part formation. There seems to be a direct link between the amount of binder at the bridges and the stresses in the printed region: the more the binder at the necks the more likely that larger amounts of stresses are going to be generated.

Figure 3.6: The effect of saturation on line diameter in glass-ceramic primitives printed with 6 vol% Acrysol (no significant trend is observed).
Figure 3.7: Acrysol at neck in primitive printed with 15 vol% (glass-ceramic).

Figure 3.8: Acrysol at neck in primitive printed with 6 vol% (alumina).
On the other hand, the effect of Acrysol concentration increase is significant to some extent in the line primitives behavior. The addition of binder concentration (vol%) seems to cause smaller line diameters. This effect is very effective in the case of non-fired powder where the binder stays mostly on the necks; while in the case of fired powder this is less important since the printed binder is mostly absorbed by the porous powder (compare figure 3.9 to figure 2.11). The 9 vol% excess binder decreased the lines diameters of the spray dried alumina (containing PAA) by more than 40 to 50 μm (figure 2.11). The same 9 vol% excess merely decreased the lines diameters in the absorbing glass-ceramic granules by around 20 μm (figure 3.9). Thus, the increase in binder generally leads to an increase in capillary arrangement in the line primitives because of the excess in Acrysol at the bridges. This excess puts extra stress on the powder granule and the result is smaller line diameters especially in the case of low packing density powder bed (flowable spray dried powder).

It was concluded that printing with 15 vol% Acrysol on fired glass ceramic powder (after PVA burnout) gave excellent green body strength with no observed warpage during the build. Several bars and gears were printed using this technique. A picture of one of the printed gears is shown in figure 3.10.
Figure 3.9: Effect of printed binder concentration on line diameter (larger concentration results in smaller diameters).
Figure 3.10: Gear printed with 6 vol% Acrysol on glass-ceramic dental powder (green body).
3.4.3 Firing and densification.

It was necessary to study the extent of densification of the low packing density green body by firing it at an optimized schedule to obtain the lowest porosity. The firing step was crucial in this case since the desired goal was to directly create fully dense parts from the low density powder beds. The liquid phase sintering of the glass-ceramic is capable in theory of drastically reducing the porosity, but closing the last pores of the printed body needed to be addressed on the practical level.

The first objective was to determine the proper temperature/time schedule necessary to obtain full density parts. Two paths were followed to achieve this: the high-temperature/short-time schedule and the low-temperature/long-times one. In both cases higher temperature and longer times lead to the melting of the sample: In figure 3.11 the sample most to the left is an example of excessive glass melting of the printed bar. On the other hand, lower temperatures combined with short times can yield to excessive porosity in the sample: The bar second to the right is an example of such a case (low density). Two sintering schedules were optimized which resulted in fully dense parts: Sintering at 1030 °C for 6 minutes or sintering at 970 °C for 65 minutes (see table 3.3).

The next problem which needed to be solved was to reduce the amount of warpage that was observed after firing. This warpage was due to the formation of heat gradients through the sample during firing and to the in-homogeneous heat transfer from the various directions inside of the crucible. The solution was reached by eliminating the thermal fluctuations after embedding the sample in a coarse alumina powder bed. The alumina powder homogenized the heat transfer without interfering with the sample shrinkage during firing. Fully dense non-warped parts were thus created after reducing significantly the firing heat anisotropies.

One of the important advantages of glass-ceramic systems is the smoothening of the rough printed surface upon firing. The glass flow during sintering reduces drastically the porosity and in-homogeneity at the surface and gives an excellent surface finish close to that of smooth glass surfaces. This surface finish improvement is temperature/time dependent and can be controlled during the firing step. This is another reason that makes the fab-
rification of glass-ceramics by 3DP very attractive since surface finish is a main issue in Rapid Prototyping.

However, the use of low packing density powder beds lead to large shrinkages which make dimensional control more difficult. This problem can be reduced drastically by using higher packing density beds, and this solution will be the topic of chapter 4. Thus, the main disadvantage of using spray dried porous powders remains in the excessive shrinkages observed upon densification. Fully dense samples showed volumetric shrinkages of around 67% while the linear shrinkage was around 33%. These observations make dimensional control hard to predict as the shrinkages might show non-linear behavior depending on the part dimensions. Also, the densification behavior is dependent on the spray dried powder batch which might be of different packing density (function of spray drying conditions). A more detailed study into part shrinkage needs to be addressed if this specific process is going to be applied commercially. Once such a research is finalized, the part shrinkage behavior can be accommodated for in the CAD design prior to printing and the problem can be solved.
<table>
<thead>
<tr>
<th>sample#</th>
<th>temp (°C)</th>
<th>time (min)</th>
<th>observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1150</td>
<td>10</td>
<td>melt</td>
</tr>
<tr>
<td>2</td>
<td>1050</td>
<td>5</td>
<td>melt</td>
</tr>
<tr>
<td>3</td>
<td>950</td>
<td>5</td>
<td>porous</td>
</tr>
<tr>
<td>4</td>
<td>1000</td>
<td>5</td>
<td>porous</td>
</tr>
<tr>
<td>5</td>
<td>1025</td>
<td>5</td>
<td>porous</td>
</tr>
<tr>
<td>6</td>
<td>1040</td>
<td>5</td>
<td>melt</td>
</tr>
<tr>
<td>7</td>
<td>1030</td>
<td>5</td>
<td>excellent</td>
</tr>
<tr>
<td>8</td>
<td>1030</td>
<td>6</td>
<td>96% dense good SF</td>
</tr>
<tr>
<td>9</td>
<td>750 (3hr)/1030</td>
<td>6</td>
<td>94 % dense no warpage</td>
</tr>
<tr>
<td>10</td>
<td>970</td>
<td>30</td>
<td>~75%</td>
</tr>
<tr>
<td>11</td>
<td>970</td>
<td>45</td>
<td>94% No warpage</td>
</tr>
<tr>
<td>12</td>
<td>970</td>
<td>65</td>
<td>97% No warpage</td>
</tr>
</tbody>
</table>

Table 3.3: Firing schedule experiments for dental glass-ceramic 3DP parts.
Figure 3.11: 3DP glass-ceramic bars fired under different conditions
Figure 3.12: Cross section of a fully dense glass-ceramic part.
Chapter 4

Fabrication of dense parts from plasma sprayed powder.

4.1 Materials and powder characteristics

It was necessary to look for powder granules that are dense and flowable in order to improve the powder bed density. These two conditions were satisfied by using plasma sprayed powder. The plasma melted and rapidly solidified powders are becoming a commercial need because of their spherical form (good flow), controllable particle size and narrow distribution (for homogeneous processing). The plasma spraying process can be applied to any composition as long as its constituents are available in powder form [43]. The constituent agglomerates are usually melted using a plasma flame then cooled rapidly in a quenching gas atmosphere. The melting of these agglomerates creates spherical drops that solidify homogeneously upon quenching due to their small size.

This technique can be used in producing any glass-ceramic or glass composition that may be needed by the 3DP process. The advantages of using this method to create glass-ceramic powder is its ability to produce many suitable compositions in a relatively simple and low cost process. In contrast to many commercial plasma sprayed powders, the glass-ceramic low melting temperatures make their production by plasma melt spraying easy and cheap, in contrast to many commercial plasma sprayed powders.

In applying 3DP to fabricate glass-ceramic part, these powder characteristics offer the most advantageous solution in terms of part homogeneity and low shrinkage percentage. Therefore, it was necessary to choose commercially available powder systems that also fit the easy-flow criteria. The first material system used was a soda-lime glass system. The second system was an alumino-silicate glass which was also commercially available in a spherical powder form. It is interesting to note that the chosen compositions were arbitrary since the main objective was to represent the capability of applying 3DP to fabricate fully dense glass or glass-ceramic parts by printing on plasma sprayed spherical powder.

The soda-lime and the alumino-silicate powders were both purchased from Potters Industries Inc (PA, USA). Their compositions puts them in the category of regular com-
mercial glass systems. Table 4.1 summarizes the various used components with their percentage as reported by the producing company. These powders are usually produced in very large batches of more 500 to 1000 lb. This high production rate helps in reducing the powder cost to less than $2 / lb.

The presence of Al2O3 improves the glass by decreasing devitrification and increasing durability in the soda-lime system. The MgO is used in small amounts to control the setting rate during the processing of the glass. The Na2O3 component is added to enhance the meltability of the soda-lime while the CaO is introduced to significantly reduce the chemical vulnerability [40].

CaO improves chemical durability and decreases viscosity while MgO increases the tensile strength in the alumino-silicate system. The B2O3 helps in the glass processing by favorably effecting the temperature course of the viscosity curve [44]. These glasses have usually a higher softening temperature and lower thermal expansion coefficient than the soda-lime glasses since they have a higher alumina content. The alumino-silicate glasses are generally used in glass fibres applications as well as in glass-metal high temperature seals[45]. In addition to this, they are used in other glass high temperature applications like combustion tubes, high pressure steam boilers, discharge lamps, household cooking, high temperature glass filters. The alumino-silicate system has also the capacity to transform the glass into a glass-ceramic system by small additions of TiO2 impurities. The titanium dioxide induces the separation of a secondary amorphous phase on cooling the glass, thus forming nucleation sites (heterogeneous microimmiscibility of glass-ceramics) [40].

The compositions of these two glass systems determine the characteristics of the glass as well as its manufacturability. The two compositions are well within the range of what is called the A-glass (soda-lime) and the E-glass (alumino-silicate). The two specially designed commercial designations are used in many applications which vary depending on small deviations in the general compositions.
<table>
<thead>
<tr>
<th>Composition%</th>
<th>Soda-Lime glass</th>
<th>Alumino-Silicate glass</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>72.5</td>
<td>52.5</td>
</tr>
<tr>
<td>Na₂O</td>
<td>13.7</td>
<td>0.3</td>
</tr>
<tr>
<td>CaO</td>
<td>9.8</td>
<td>22.5</td>
</tr>
<tr>
<td>MgO</td>
<td>3.3</td>
<td>1.2</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.4</td>
<td>14.5</td>
</tr>
<tr>
<td>FeO/Fe₂O₃</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>0.0</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Table 4.1: Compositions of the soda-lime and alumino-silicate glass system as reported by the manufacturer.
4.2 Experimental procedure

It was necessary to study the powder morphology before starting the printing parameters optimization. SEM analysis of the powder was carried on the soda-lime powder in order to see the particles shape, size, distribution and to compare it with reported results from the manufacturer. Also, measurement of the powder bed density was done to try to predict the shrinkage behavior of the part after densification.

Several powder size distribution were used. Four different powder and materials characteristics were used as listed in table 4.2. In all the printing sessions, 20 vol% Acrysol was the binder of choice. The fast axis speed was kept at 1.5 m/s and the binder flow rate was also constant at 0.8 cc/min. Heating of the powder bed layers during printing was also made possible by the use of infra red lamps which were suspended on the top of the bed.

<table>
<thead>
<tr>
<th>Powder type</th>
<th>Particle size distribution (µm)</th>
<th>Particle size mean (µm)</th>
<th>Powder bed density%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime #1</td>
<td>65-73</td>
<td>66</td>
<td>61%</td>
</tr>
<tr>
<td>Soda-lime #2</td>
<td>20-71</td>
<td>49</td>
<td>59</td>
</tr>
<tr>
<td>Soda-lime #3</td>
<td>35-61</td>
<td>35</td>
<td>57</td>
</tr>
<tr>
<td>Alumino-silicate #4</td>
<td>9-43</td>
<td>26</td>
<td>53</td>
</tr>
</tbody>
</table>

Table 4.2: Glass powder systems used in various printing sessions.

Many variables were changed in the various printing sessions. Obviously, the use of different powder systems created differences in the powder bed densities. The second major parameter of interest was the layer thickness which changed from 120 or 150 mm to 170 mm. Also, in the case of the finer powder alumino-silicate system (26 mm grain size), preheating the powder for few minutes using microwaves prior to spreading proved necessary in order to avoid defects. In addition to this, the use of infra-red heating lamps changed the drying rate during printing and effected the green body formation.

Printing rectangular bars using different conditions was usually performed prior to final part fabrication. This approach helped in optimizing the printing and sintering
parameters before creating complex parts. A total of 8 printing experiments were performed to study the effect of layer thickness, bed density and IR heating on the printing behavior. The dependence of saturation% on layer thickness and powder bed density seemed to have an important effect on the part build up. Thus it was necessary to calculate the saturation% for the various systems according to the following conventional formula

\[
\text{Saturation} \% = \frac{\text{Conversion constant} \times \text{binder flow rate}}{(1 - \text{powder bed density}) \times \text{velocity} \times \text{line spacing} \times \text{layer thickness}}
\]

where the velocity is the fast axis speed (m/sec), powder bed density is the packing density function, the conversion constant depended on the units used and the line spacing was kept constant at 200 mm in all the experiments. Table 4.3 provides a description of the various printing parameters used for these experiments. Interestingly, the amount of experiments needed to optimize the process was relatively limited in comparison to the number of systems used because of the good powder flowability and their high packing density.

The as-printed bars were then heated to 450 °C for 5 hours at atmospheric pressure to accomplish the Acrysol binder burn-out. The first three bars printed with the soda-lime #1 system were sintered in a vacuum furnace (Centorr Assoc., Suncook, N.H). All the other sintering experiments were performed in a regular Nytech furnace at atmospheric pressure. Various firing schedules were conducted at different temperatures and times in order to optimize the densification of the bars. Low density porosity measurements were then conducted on some of the samples to determine the amount of porosity left. In the first five sintering schedule, the soda lime (#1) bars were placed in an alumina crucible with no coarse powder support. All the other firing experiments were performed using coarse alumina or zirconia as a support powder. The printed parts were usually totally embedded in the coarse powder during both the binder burn-out and the final firing. The dimensions of the bar were exactly measured using calibers before and after densification in order to observe the shrinkage behavior. After optimizing the printing parameters, several complex
parts were designed, printed and fired using different parameters. A more detailed description of the formation of these complex parts will be covered in a separate section.

<table>
<thead>
<tr>
<th>Powder system</th>
<th>Layer thickness (µm)</th>
<th>Saturation%</th>
<th>Drying conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime #1</td>
<td>170</td>
<td>67%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #1</td>
<td>120</td>
<td>94%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #1</td>
<td>120</td>
<td>94%</td>
<td>IR heating</td>
</tr>
<tr>
<td>Soda-lime #2</td>
<td>170</td>
<td>63%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #3</td>
<td>120</td>
<td>86%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #3</td>
<td>120</td>
<td>86%</td>
<td>IR heating</td>
</tr>
<tr>
<td>Alumino-silicate #4</td>
<td>150</td>
<td>63%</td>
<td>No heating</td>
</tr>
<tr>
<td>Alumino-silicate #4</td>
<td>150</td>
<td>63%</td>
<td>Powder preheating &amp; IR heating</td>
</tr>
</tbody>
</table>

Table 4.3: Glass bars printed under different conditions.

<table>
<thead>
<tr>
<th>Powder system</th>
<th>Layer thickness (µm)</th>
<th>Saturation%</th>
<th>Drying conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soda-lime #1</td>
<td>170</td>
<td>67%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #1</td>
<td>120</td>
<td>94%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #1</td>
<td>120</td>
<td>94%</td>
<td>IR heating</td>
</tr>
<tr>
<td>Soda-lime #2</td>
<td>170</td>
<td>63%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #3</td>
<td>120</td>
<td>86%</td>
<td>No heating</td>
</tr>
<tr>
<td>Soda-lime #3</td>
<td>120</td>
<td>86%</td>
<td>IR heating</td>
</tr>
<tr>
<td>Alumino-silicate #4</td>
<td>150</td>
<td>63%</td>
<td>No heating</td>
</tr>
<tr>
<td>Alumino-silicate #4</td>
<td>150</td>
<td>63%</td>
<td>Powder preheating &amp; IR heating</td>
</tr>
</tbody>
</table>

Table 4.4: Optimal printing conditions for plasma sprayed glass systems.
4.3 Results

4.3.1 Powder morphology

The SEM study of the non-printed soda-lime #1 revealed its powder characteristics. First, the powder granule with no major observed non-spherical defects (figure 4.1). The second important factor was that the granule size distribution was homogeneous and consistent with the manufacturer’s reported data (figure 4.2). It is these two properties that were the reasons behind the high powder bed packing density and the excellent powder flowability. This powder geometry minimized inter granule friction and increased thus flowability.

![Soda-lime (#1) plasma sprayed granule.](image)

**Figure 4.1:** Soda-lime (#1) plasma sprayed granule.
4.3.2 Printing parameters effect.

The most promising observation associated with printing on plasma sprayed glass was the absence of warpage during the build. In addition to this, no powder ejection was observed upon the binder droplet impact on the powder bed. This printing behavior can be due to various factors related to the powder morphology and the binder/granule interaction. The high packing density of the bed and the high density of the granules hinder the movement of the glass spheres and reduce the bed response to the Acrysol ballistic action. Also, the printed primitive capillary rearrangement upon drying is limited by the low capillary stresses generated and the inability to significantly increase the packing density. The weakness of the capillary action is expected since the granules are fully dense and the only existent pores behind the driving force are the ineffective large inter-granular pores.

Printing on fine powder is generally difficult because fine powder does not easily spread. The fine powders tend to form agglomerates which introduce defects and voids in the spread layer. The formation of agglomerates was extremely enhanced by the absorbed
moisture from the atmosphere in the case of the alumino-silicate fine powder system (26 µm). Printing on the as received powder proved to be ineffective for this reason. Preheating the fine powder for few minutes before spreading reduced significantly the agglomeration and solved the problem.

One of the main difficulties encountered was the printed layer position shift upon spreading. The high friction of the rolling bar with the wet printed region result in the displacement of the printed layer. This behavior was excessive in the systems where the saturation was generally higher than 75%. In the low saturation systems (around 65%) the layer shift was not significant. This problem was solved by reducing the moisture in the top wet layer by using infra red heating lamp. The drying of the printed layer prior to spreading reduced the roller-bar/wet-powder friction and restored the accuracy of the green part build. Heating was necessary for this reason in the high saturation printing experiments according to the results in table 4.4.

In general, the Acrysol was concentrated on the inter-granular necks of the printed primitive. No major binder/powder wetting was observed as can be seen in the typical binder formation at the neck of figure 4.3.

Figure 4.3: Acrysol at the intra-granular necks in the soda lime system (#1).
Overall, printing on all of the chosen four materials systems was successful after optimizing the various parameters. Also, printing on 120 mm thin powder layers using the plasma sprayed powder enhanced the capability to build accurate glass-ceramic parts. The absence of warpage and ejection allowed the use of high concentrations of binder (20 vol%), and the green body strength was thus pretty satisfactory.

4.3.3 Firing and shrinkage behavior

Large pores were observed on the surface of the densified parts upon firing under vacuum and this resulted in a defective body. The presence of small amounts of binder, evaporated under low pressure and high temperature conditions, was most probably behind the bubbles formation which created the big pores. Firing under atmospheric pressure solved this problem without negatively effecting the densification of the part.

Various temperature/time firing schedules were performed in order to optimize the density of the soda lime system. According to the results presented in table 4.5 the best firing temperature was 780 °C with an optimal time of 4 or 5 hours. The measured parts density at these firing schedules revealed very high densities of more than 98% of the theoretical density. This firing temperature, being higher than the soda lime softening temperature (Tg=735 °C), have caused some part deformation due to melt sintering lumping. This effect was reduced significantly upon using alumina or zirconia as a coarse support powder.

Similarly to all the other melt sintering experiments, warpage behavior was observed upon firing with no support powder. The bars which were fired warped upward and this indicated that the warpage behavior was not caused by a deformation related to melting like “slumping”. This warpage was due to heat transfer variations in the different locations of the body. The introduction of the alumina support powder reduced the heat variations upon firing and solved the warpage problem. Typically, the part was totally embedded in the coarse alumina or zirconia powder in order to reduce the part deformation and to get homogeneous isotropic heat transfer at the firing temperature.

The firing schedule for the alumino-silicate system was also optimized. Only two experiments were necessary to obtain the optimal densification. The first firing tempera-
ture was 900 °C for 4 hours and proved to be excessive. The second firing temperature chosen was 880 °C for 4 hours and resulted in full body densification without excessive melting. Interestingly, in both the soda lime and the alumino silicate systems the best firing temperature seem to be around 40 °C higher than the materials softening point.

Having high powder bed density combined with minimal powder displacement upon printing (low ejection) created the optimal conditions for low shrinkage after firing. The measured linear shrinkage for the soda-lime #1 system was typically around 14% which is approximately equivalent to a 37% volumetric shrinkage. Since the bed density was 61% and the final part density was typically higher than 98%, it can be deduced that the measured shrinkage was consistent with the density measurements.

The measured linear shrinkage was 18% (around 45% volumetric shrinkage) in the alumino-silicate system. It was expected to obtain a slightly larger linear shrinkage than that observed previously in the soda lime system since the powder bed density was lower in this case (54%). It can be deduced from this shrinkage data that the part densification was almost complete in this system also.

Finally, the use of plasma sprayed powder proved to be successful in the formation of glass or glass-ceramic 3DP parts. First, powder ejection upon binder impact was not observed, warpage during printing was minimal and all the powder spreading difficulties were easily solved by powder preheating or by heating the printed region using infra red lamps. The objective to reduce the shrinkage was successful given that the shrinkage data obtained from the 3DP printed parts were comparable to those found in other optimal powder processing methods.

It was necessary to demonstrate the 3DP process advantages in the formation of complex shapes based on these resulting successes. In this respect, it was natural to prove the capability of 3DP in fabricating complex parts at a fast rate after having optimized all the parameters needed.
<table>
<thead>
<tr>
<th>Sample#</th>
<th>Firing temp</th>
<th>Time/ Pressure</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>640</td>
<td>35 min/ vacuum</td>
<td>Bubble formation</td>
</tr>
<tr>
<td>2</td>
<td>690</td>
<td>35 min/ vacuum</td>
<td>Bubble formation</td>
</tr>
<tr>
<td>3</td>
<td>750</td>
<td>35 min/ vacuum</td>
<td>Bubble formation</td>
</tr>
<tr>
<td>4</td>
<td>740</td>
<td>2 hr/ atm</td>
<td>Porosity</td>
</tr>
<tr>
<td>5</td>
<td>780</td>
<td>2 hr/ atm</td>
<td>densification/ warping</td>
</tr>
<tr>
<td>6</td>
<td>780</td>
<td>3 hr/ atm</td>
<td>Good density/ warping</td>
</tr>
<tr>
<td>7</td>
<td>780</td>
<td>4 hr/ atm</td>
<td>98.5% warping</td>
</tr>
<tr>
<td>8</td>
<td>780</td>
<td>4 hr / atm</td>
<td>no warping/ embedded in coarse alumina bed</td>
</tr>
<tr>
<td>9</td>
<td>780</td>
<td>5 hr / atm</td>
<td>no warping/ embedded in coarse alumina bed</td>
</tr>
</tbody>
</table>

Table 4.5: Firing schedule for the soda lime #1 system.
4.4 3DP parts from plasma sprayed powder.

4.4.1 Fully dense printed gear.

Five gears were printed with 20 vol% Acrysol on soda lime #1 powder. The gears where then fired to full density while embedded in alumina coarse powder. The gears shrunk isotropically with no deformation in the final part. This was the first printed complex part.

![Figure 4.4: Fully dense (right) and green as printed gear (left).](image-url)
4.4.2 Printed catheters used in the medical industry.

These catheters are used for medical tube fitting and were printed with both the alumino-silicate (#4) and the soda lime systems (#1 & #3). In the parts printed with small openings of less than 500 mm, the open orifice closed after firing due to the part shrinkage and the melt sintering process. The parts with relatively larger openings (around 1mm) densified without closing the tube orifices (figures 4.5).

Figure 4.5: Dense and green catheters printed with alumino silicate & soda-lime.
4.4.3 Pre-ignition chamber component for Diesel engine.

The chambers were printed with the soda lime (#1) powder and fired to full density at the optimized schedule. The parts were embedded in zirconia powder upon firing in order to get rid of deformation. One part was fired with no support powder and deformed significantly at the used firing temperature. A very small amount of "slumping" was observed due to melt sintering as the small opening on the sides deformed from a circular to a slightly elliptical shape (very small change).

Figure 4.6: Pre-Ignition chambers for diesel engine in the green (right) and dense form (left).
4.4.4 Rocker arm part with fitted ball

A small rocker arm part was printed with a ball that exactly fit inside of the arm’s empty space. These components were printed using the soda lime (#2) powder. The ball/arm assembly was then fired while embedded in alumina powder. The final part was a dense rocker arm with a small ball that was capable of turning inside of it. This part is a perfect example where complex shapes and assemblies can be made by 3DP in a single step without the need to cut the parts in half for fitting and avoiding thus the undesirable trimming lines.

Figure 4.7: Rocker arm with ball assembly.
4.4.5 The "Theta" part

The theta specimen possess a special shape which allows one to test the tensile strength of brittle materials by diametrical compression. This test method eliminates the need for complex gripping schemes needed for testing brittle materials. The theta specimen is not however used because of the difficulty in fabricating the complex shape. 3DP can offer a solution because of its capability to fabricate dense parts independently of the geometry.

Figure 4.8: The theta specimen.
Chapter 5

Study of glass infiltration in alumina printed parts

5.1 General description and goals

5.1.1 Objective

The final objective of the research targeted the formation of dense ceramic/glass composites with a minimal amount of shrinkage. A way of achieving this goal was to use glass infiltration in the porous printed preform to get densification. This approach was capable of reducing drastically the amount of shrinkage since no major sintering occurs and the high density is achieved by infiltration. The only disadvantage of this technique lies in the fact that the functional parts can not operate at temperatures that are higher than the melting temperature of the infiltrating glass. The success of this method demonstrates the capability of 3DP to form ceramic/glass composites without major shrinkage in what can be described as a near-net shaping process.

5.1.2 Melt infiltration technique

This is a relatively new technique that is similar to the infiltration process in the metal-matrix composite domain. The technique offers an alternative method to the formation of near-net shape fully dense part via infiltration of glass in a ceramic preform. The advantage of ceramic/glass composites is their environmental resistance, good thermal properties combined with good strength. The melt infiltration is a pressureless process which is directly driven by the capillary forces of the system. It can described as the penetration of a fluid into a porous solid or packed powder bed and this makes it analogous to other more familiar processes like slip casting and filtration. It is necessary to cover the basic phenomena and the various conditions that govern the process before going into the specific process used. The requirements to form a successful ceramic matrix include many variables like the time of infiltration, infiltration temperature, melt preform wetting interaction and chemical interaction, powder morphology and melt viscosity. A simple model derived by Washburn which assumes the preform to be similar to a bundle of parallel capillaries,
can give a useful insight into the parameters that control the infiltration [46]. Other more complex approaches can be also used in case a need for precise optimal predictions [47]. The Washburn model predicts the infiltration depth (x) as a function of time (t), viscosity (h), wetting angle(θ), surface tension(γ), and capillary diameter(D).

\[ x^2 = \frac{\gamma Dt \cos(\theta)}{4 \eta} \]

The simplicity of this equation disregards the irregularities in the preform voids but gives a good rough approximation to the possible experimental manipulations that might be performed to optimize the infiltration of our specific system. The first parameter that is of concern here is the melt viscosity at the infiltration temperature which is proportional to the infiltration time. Any change in the melt temperature directly effect the infiltration depth and time especially in the case where the viscosity is exponentially dependent on the temperature. It is expected that the infiltration will be faster in the case of coarser powder morphologies since the infiltration time is inversely proportional to the capillary radius. However, The capillary pressure can be to high and can significantly rearrange and break the preform when the powder particles are to fine. Thus a compromise in the particle size should be found in order to obtain short time infiltrations without disturbing the preform.

The low viscosities that are required makes it necessary to operate at an infiltration temperature that is higher than the melting point of the matrix. This conditions puts another restrictions on the infiltration as it is necessary not to have chemical reactions occurring between the preform materials and the infiltrant and it is also obvious that the preform should be stable at the processing temperature. Even though all these conditions seem very restricting, there is a large amount of material systems that can form a melt infiltrated composite, especially the infiltration of ceramics with glassy melts.

5.1.3 Various infiltration processes

Most of infiltration processes are driven by capillary action of a porous body on a low viscosity material usually in the melted form. Infiltrating vapors, liquids or suspensions
has been a useful technique in producing composites of various characteristics. The processes that take advantage of infiltration can vary drastically going from chemical vapor infiltration to reaction bonding of ceramic matrix. A brief survey of the most important infiltration methods will be presented before describing the studied glass/alumina infiltration one.

A widely used technique in this area is chemical vapor infiltration (CVI). This well established technique consists of infiltrating a preform with a mixture of gases that react to form a ceramic compound that deposit on the preform material. By choosing the proper gas mixtures many ceramics can be deposited to form the part [48]. This densification process is usually done in big batches that typically lasts a few days. Densities in the range of 80% to 90% is achievable using this process.

Polymer infiltration and pyrolysis can also be used to get dense ceramic composite parts. Usually, a preform can be infiltrated with liquid polymers, molten or in solution, that are pyrolyzed to leave a ceramic deposit [49]. The most important examples of this process is the infiltration and pyrolysis of polycarbosilanes to form SiC matrix and polysilazanes to form silicon nitride parts.

Preforms are also infiltrated using sols that can be subsequently gelled by drying. These sol-gels are then sintered at low temperatures relatively to powder compacts. This technique is constrained by the high cost of the sol-gels and the need for repeated infiltration/sintering steps. Many ceramics matrices can be produced through this route like alumina, zirconia and silica [50].

The porous body can be infiltrated with a liquid or slurry that react after deposition with another gas or liquid to form a ceramic matrix by reaction bonding [51]. A typical example of this would be preforms that are infiltrated with silicon powder slurries which, after drying, are sintered in nitrogen to form silicon nitride. In fact, active research in this area is being addressed by the 3DP project, were silicon printed parts are infiltrated then fired under nitrogen atmosphere to form a silicon nitride fully dense part.
5.2 Experimental procedure

5.2.1 Materials systems

All the infiltration were done using a glass composite of proprietary composition. The glass is called Inceram and was supplied by a German company (Vita Zahnfabrik, Bad Sackingen, Germany). A rough analysis of the glass was performed using EDAX to get an idea about the major components of the infiltrated melt. The preforms were all printed with alumina powder using Acrysol as a binder. However, the powder morphology was changed in order to obtain the optimal ceramic/glass composite. The first powder used was spray dried alumina which had a particle size range between 20 mm and 67 mm. The powder was spray dried using PAA which was burn-out prior to printing by heating the granule for 450 °C for 4 hours. The second material system was regular coarse alumina powder which had a particle size range less than 49 mm (sieved to -325 mesh size) and was provided by Norton Company (Waltham MA). The third system was a spherical alumina powder which was plasma sprayed by a Japanese company (Showadenko corporation) and distributed in North America by the ICD group (Lyndhurst, NJ). These spheres had average granule diameter of 30 mm.

5.2.2 Infiltration

Several parts of each alumina powder morphology were printed with a 15 vol% Acrysol concentration. The first parts put under study were small cubic forms which had a rectangular hole in their top section (fig 5.1 & fig 5.2). The top of the cube which covered the hole was printed using two layers of around 500 mm thickness. These two layers formed thus a bridge like form which will be referred to as the thin section of the part. Other parts were also printed and infiltrated using different geometries like regular bars and rectangular forms with controlled internal holes that can be used as heat exchangers. The parts were heated to 450 °C for 4 hours to burn out the binder then fired at 1600 °C for 4 hours at atmospheric pressure in order to increase the preform strength. The fired alumina components were then transferred to a gold/platinum crucible which contained the proper amount of “Inceram” powder evenly spread under the preform part. The infiltrant/
preform were fired to 1100 °C for 4 hours under atmospheric pressure then removed from the furnace.

5.2.3 Microscopic analysis and porosity measurement

The surface of the infiltrated composites were studied under the scanning electron microscope (SEM). The infiltrated “cubic” samples of the various powder morphologies were cut, polished and gold coated in order to study the sample uniformities at several positions under the SEM. Electron microscope analysis of the fracture surface of broken spherical alumina infiltrated bars was also conducted. Both low and high magnification SEM photos were taken of several samples and the results will be discussed later in this chapter. In addition to the microstructural study, porosity measurement of the fired preforms, the infiltrated composite and the pure infiltrant were performed in order to measure the densification behavior. The mercury porosimetry was first performed on pure “Inceram” after melting the powder at 1100 °C for hours to get a 500 g solid sample. Two sets of samples prepared using the spherical, coarse and spray dried alumina powder were then fabricated. The first set was made of fired parts which were put in the porosimeter prior to infiltration. In this case, both low and high pressure porosimetry measurements were conducted. The second set was infiltrated at different times with different Inceram amounts and the obtained composite parts were then subject to low pressure porosimetry measurement.

5.2.4 Mechanical testing set up

It was necessary to conduct a mechanical testing study in order to obtain data on the composite strength and its dependence on the process. Two sets of rectangular bars of 12 specimen each were printed using 20 vol% Acrysol. The first set consisted of bars which were printed along the fast axis printing direction while the second set had the bars main axis parallel to the slow axis direction (fig 5.3). After the usual firing procedure, the bars were infiltrated at different times in batches that contained 3 to 4 bars. The two sets were then send to Bomas Machine Specialties (Sommerville, MA) to obtain type A MIL-SID 1942 bend bars (1.5 *2.0*25 mm) in order to perform modulus of rupture tests. The bars were then tested in four point bending flexural test in a self aligning test fixture at a cross-
head speed of 0.2 mm/min. this testing was done using an Instron electro mechanical testing system (Instron corp., Canton, MA). The test bars inner span was 20 mm with a depth of 1.5 mm and a width of 2.0 mm.

Figure 5.1: Alumina printed “cubic” part after infiltration with Inceram glass.
Figure 5.2: Schematic of part infiltration sequence
Figure 5.3: Alumina bars printed along different printing directions for mechanical testing.
5.3 Results and analysis

5.3.1 Uniformity and surface smoothness

The SEM analysis of the surface of the infiltrated spray dried powder revealed a smooth glass-like finish which was slightly disturbed by the curvature of the granule. The presence of the glass phase in between the alumina spray dried reduces significantly the surface roughness of the usually obtained 3DP parts. The SEM photographs were taken at several locations of the “cubic” part (fig 5.2) and the high magnification picture in figure 5.4 shows the glass spray dried interaction at the surface. Even though this picture was taken from the thick region area of the part, it revealed the typical surface microstructure encountered throughout the sample. In figure 5.5, the low magnification picture of the “thin section” bridge shows the good surface finish obtained even at the thin sections.

On the other hand, the analysis of the cut and polished sample of the same material system showed a uniform sample with some defects. Interestingly, the infiltration of the spray dried powder seemed to be homogeneous throughout the part, since both the thick and thin section showed a very similar microstructure. In figure 5.6 one can see the thin 500 mm bridge totally infiltrated with the Inceram glass (white) while the spray dried granule were evenly distributed across the bridge width. This microstructure did not change in the other areas as can be observed from figure 5.8. In this particular sample, a lot of defects appeared due to the grinding. The typical high magnification picture of one of the defects showed that the defect cut through the spray dried particle, the fact that indicated that this was indeed a polishing pull-out (fig 5.7).

The coarse alumina infiltrated parts showed similar microstructure with the exception that the alumina granule were not spherical but of random form. The infiltration was homogeneous across the sample even at the thin section (fig 5.9). The grinding defects in this case were less abundant as can be seen in figure 5.10 (taken at the thick cross section). The alumina powder (dark) are evenly distributed in the glass matrix (white) in the high magnification pictures of figures 5.11 & 5.12.

The infiltrated spherical alumina preform gave the least defects upon grinding. In this case also, the defects are caused by the pull-out of the spherical alumina granule (dark)
from the glass matrix (white). The nearly spherical defect forms is a clear evidence that the cause of the irregularities is not the existence of pores after the infiltration in figures 5.13 and 5.14. Thus, as in the other systems, the samples prepared from this powder were very uniform with less grinding defects and good surface finish.

5.3.2 Densification and shrinkage
The glass density was measured twice (after melting) and revealed a density of 3.58 g/cc and 3.59 g/cc which was within experimental error of the reported theoretical density of 3.60 g/cc. The composition of the InCeram is described in table 5.2. The density of the preform alumina varied with the powder morphology (after firing). The Coarse powder system had a density of 35% while the spherical system showed a 48% density. The spray dried fired preform had a density of 58%, and showed the least density after infiltration (without optimization). Assuming this density, the theoretical density of each materials system was calculated accordingly by using this straightforward approach:

\[
\text{Theoretical density } = \frac{\text{preform density} \times \text{theoretical alumina density}}{1 - \text{preform density}} \times \text{theoretical Inceram density}
\]

The three materials system had thus different theoretical densities since the alumina percentage was different in each case. The spray dried powder system had a theoretical density of 3.75 g/cc while the spherical powder system had a 3.77 g/cc. The first samples measured were infiltrated without optimization of the process and revealed a relatively low density. These two samples were build using spray dried powder preform and showed a density of 79% and 83%. After optimizing the infiltration and predicting the amount of infiltrant needed, spherical alumina preforms were infiltrated then used for porosity measurement. Various samples infiltrated in different batches showed densities that varied from 93% to 101%. It is important in this case to take into account the assumption that we made in calculating the theoretical density and the error that might be due to the porosity measurement. However, these high densities were consistent with the absence of pores as seen in the SEM analysis (fig 5.13 & 5.14).
The shrinkage using this kind of infiltration was minimal and the only measured shrinkage occurred after the firing of the preform. In most cases the linear shrinkage was around 1%, but some part expansion occurred during the infiltration and was usually less than 0.5% (linear). Combining the shrinkage and expansion effects together, the parts had a low shrinkage percentage of less than 1%. These results makes the process a near net-shape fabrication technique. It is interesting to note here that the shrinkage behavior is slightly dependent on the materials system used and on the firing, and this factor can be an issue in case high part accuracy is needed.

Figure 5.4: The glass/spray dried granule interaction at the surface of the composite
Figure 5.5: The surface microstructure at the thin section of the composite.

Figure 5.6: Microstructure of the thin section in the polished spray dried sample.
Figure 5.7: Thin section in the spray dried alumina system.

Figure 5.8: Microstructure of the thick section in the polished spray dried sample.
**Figure 5.9:** Thin section in the coarse alumina system.

**Figure 5.10:** Thick section in the coarse alumina system.
Figure 5.11: Microstructure of the thick section at medium magnification

Figure 5.12: Microstructure of the coarse alumina system at high magnification.
Figure 5.13: Microstructure of the spherical alumina system.

Figure 5.14: Low magnification SEM of the spherical alumina system.
5.3.3 Mechanical properties

Two sets of bars printed along the fast printing axis and the slow axis were tested. Graphs of the Modulus Of Rupture results for the slow and fast axis are presented in figures 5.15 and 5.16. The bars printed along the fast axis showed a slight difference in the average strength than the ones printed along the slow axis (table 5.1). However, this difference was within the statistical error of the 4-pt bending test. The average strengths for the fast axis set and the slow axis one were 199 MPa and 205 MPa respectively. This slight difference indicates that the printing direction does not play a major role in determining the strength of the parts which are isotropic. On the other hand, the strength results were lower than those of regular structural ceramic components which usually can go up to 300 to 400 MPa. Thus the Inceram/alumina composites are in the category of medium strength components which include many glass-ceramic components.

Typically, the strength of alumina-glass composites increase with increased alumina content. This strength also depends on the particle size in the case of medium to high alumina volume fractions. This particle size dependence disappears at lower alumina fractions of less than 30%. The strength usually increases with smaller particle size and higher packing density. Interestingly, the strength dependence on alumina fraction is a function of particle size too. The smaller particle size (5 to 12 mm) composites showed an extensive strength dependence on alumina fraction while the larger grain sizes (40 mm) showed only a slight strength change with alumina packing [52].

In general, the fracture toughness of glass-alumina composites is in the range of 3.5 to 4.0 MPa/m2 and are slightly dependent on alumina volume fractions. The SEM of the fracture surface obtained from our samples revealed the existence of grain pullouts (fig 5.17 & 5.18). The toughness of the system is also effected by the internal stresses created because of the thermal expansion mismatch between the alumina skeleton and the Inceram [53].
Figure 5.15: Modulus Of Rupture results for bars printed along the fast and slow direction.
<table>
<thead>
<tr>
<th>Direction</th>
<th>Average (MPa)</th>
<th>St dev</th>
<th>Highest</th>
<th>Lowest</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fast axis</td>
<td>199</td>
<td>12.71</td>
<td>213.3</td>
<td>175.8</td>
</tr>
<tr>
<td>Slow axis</td>
<td>205.23</td>
<td>16.43</td>
<td>233.6</td>
<td>178.6</td>
</tr>
</tbody>
</table>

Table 5.1: MOR results of the infiltrated bars printed along the fast and slow axis.

<table>
<thead>
<tr>
<th>Oxide</th>
<th>Mol%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_3$</td>
<td>31</td>
</tr>
<tr>
<td>B$_2$O$_3$</td>
<td>23</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>17</td>
</tr>
<tr>
<td>La$_2$O$_3$</td>
<td>13</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>7</td>
</tr>
<tr>
<td>CaO</td>
<td>5</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>3</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 5.2: Composition of InCeram glass
Figure 5.16: Fracture surface of spherical alumina/Inceram bar.

Figure 5.17: Pullout present on the alumina/Inceram part fracture surface.
5.4 Summary of advantages.

The main disadvantages of this composite is its relatively medium operating temperature. That is why the components have to be used at temperature below the softening point of the glass infiltrant. The other disadvantage is the incapability of using the infiltrated parts in jobs that require high strength like in structural ceramics applications.

On the other hand, the composite showed very good homogeneity and isotropy with respect to its microstructure and strength. The printing process did not play a major role in effecting the MOR results since parts build using the common pressing technique showed similar behavior. The maximum strength obtained using the 3DP bars was only 2 to 5 MPa lower than the maximum obtained using the pressing/sintering technique.

Also, the minimum amount of shrinkage obtained (<1%) is essential in the formation of accurate near-net shape parts which require minimum finishing. This makes the melt infiltration technique a very attractive option to use in combination with the 3DP process. In comparison with the many other techniques that start with powder as a raw material to obtain a dense part, the infiltration is the optimal solution in reducing shrinkage. In fact, the shrinkage percentages differ depending on the initial powder bed packing density and on the heat treatment (sintering or infiltration) as can be seen in table 5.3.

The other crucial advantage that the melt infiltration process introduces to the 3DP parts characteristics is the capability to obtain excellent surface finishes that makes them comparable to glassy surfaces. This finish combined with the easiness of the process makes this composites one of the best options on the rapid prototyping market in terms of good surface finish. In order to obtain good results in this area, it is necessary to exactly predict the amount of glass infiltrant needed to form a controlled excess glass layer at the part surface.

Finally, the ability of 3DP to form very complex parts in a short time period can be combined with the fast infiltration process in order to manufacture parts in very short production cycles.
<table>
<thead>
<tr>
<th>Material System</th>
<th>Powder Bed Density%</th>
<th>Shrinkage during CIP</th>
<th>Shrinkage during Firing</th>
<th>Overall Shrinkage: volumetric</th>
<th>Linear shrinkage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fine powder alumina</td>
<td>42%</td>
<td>18%</td>
<td>38%</td>
<td>56%</td>
<td>28%</td>
</tr>
<tr>
<td>Spray dried alumina</td>
<td>32%</td>
<td>28%</td>
<td>38%</td>
<td>66%</td>
<td>31%</td>
</tr>
<tr>
<td>Bimodal metal powder</td>
<td>70%</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>&lt;1%</td>
</tr>
<tr>
<td>Spray dried Glass-ceramic</td>
<td>32%</td>
<td>N/A</td>
<td>67%</td>
<td>67%</td>
<td>33%</td>
</tr>
<tr>
<td>Fully dense Glass-ceramic powder</td>
<td>62%</td>
<td>N/A</td>
<td>38%</td>
<td>38%</td>
<td>14%</td>
</tr>
<tr>
<td>Alumina infiltrated with Ince-ram</td>
<td>48%</td>
<td>N/A</td>
<td>1%</td>
<td>1%</td>
<td>0.7%</td>
</tr>
</tbody>
</table>

Table 5.3: Shrinkage percentage data for various materials systems used in 3DP to obtain fully dense parts.
Chapter 6

Conclusion

The introduction of Three Dimensional Printing as a new prototyping and manufacturing technique in the glass-ceramic and glass industries can be of major importance especially in the case of complex geometries and short term production cycles. Several techniques were developed starting from various powder systems which were optimized to use the 3DP process in parts fabrication.

The advantages of glass and glass-ceramics lie in their liquid phase sintering behavior which does not require the use of fine powders with high packing densities in order to densify fully. Most glass-ceramics are formed while in their glass phase before being processed to their glass-ceramic form. The good glass-ceramic properties are a result of this transformation from pure glass to a glass-ceramic composite without losing the advantage of the easy glass forming during the shaping step. The attraction of 3DP remains, however, in its capability of rapidly creating any complex part independently of the properties of the composite which can put restrictions on its shaping and fabrication (i.e: glass viscosity).

The first important need was the optimization of the printing parameters in the various powder systems. The presence of binder in the grains caused warpage due to particle disintegration or to the high printed binder content which created large intra-granular stresses in the case of spray dried powders. This problem was solved by performing binder burn-out prior to printing on these porous spray dried powder. The use of low Acrysol concentrations with the addition of plasticizers helped in reducing the warpage significantly. The printing behavior depended on the saturation in the case of dense spherical or coarse powders. Usually, 15 vol% to 20 vol% Acrysol were printed on the 7 mils layers (around 67% saturation). Infra red lamp drying was necessary to avoid defects during printing when the saturation was typically higher than 80% like in the case of printing on thin layers.

A study of the printed line primitives was also conducted in order to understand the effect of various parameters on the part build. The primitives microstructure was depen-
dent on many parameters like the powder morphology, saturation and binder volume percent. The line primitives were rectangular in shape with no excessive capillary rearrangement in the case of high cohesive strength beds (fine powder). On the other hand, printing on spray dried powder beds showed a different behavior since the bed's capillary strength was higher than its cohesive strength. The lines were thus cylindrical due to capillary rearrangement which was more obvious at higher binder concentrations. The lines diameter increased with lower Acrysol percentages when printing on spray dried powder beds as the intra-granular stresses are reduced and the capillary arrangement becomes weaker. The saturation changes did not significantly effect the line diameters when printing on spray dried powders after binder burn-out since the inter-granular pores absorbed the excess moisture. However, the line diameter increased with saturation when printing on green spray dried powder due to PAA binder coating of the granule.

The research then moved towards fabricating glass-ceramic parts after studying the effect of the various printing parameters. The first glass-ceramic system used was the nepheline/feldspar dental glass ceramic. Printing on spray dried powder was successful by performing binder burn-out prior to printing. Up to 15 vol% Acrysol was printed with no part warpage being observed during printing. The printed samples were fired directly from their green form after optimizing the right firing parameters. Fully dense glass-ceramic parts were thus obtained with an excellent surface finish. The major disadvantage of this system was the excessive amount of shrinkage observed due to the low powder bed packing density of the spray dried granule. The 35% linear shrinkage (68% volumetric) reduced the capability to obtain accurate 3DP glass-ceramic parts.

The next system targeted reducing 3DP glass parts shrinkage by using high packing density beds. Soda-lime and alumino-silicate plasma sprayed powders were chosen to demonstrate the capability of fabricating dense parts with low shrinkages. The used powders possessed many different particle size distribution ranging from a 26 mm to a 66 mm average granule diameter. Printing 20 vol% Acrysol on these several powder systems helped in forming strong green bodies. Various complex parts were printed and fired directly to full density at an optimized temperature/time schedule. The amount of linear shrinkage was low and ranged between 12% and 18% depending on the initial powder bed packing density. The use of plasma sprayed powders proved to be successful in the forma-
tion of glass or glass-ceramic parts since dense complex parts were directly formed with a shrinkage data comparable to other optimal powder processing method.

The last approach aimed at creating ceramic/glass composite 3DP parts at a minimal amount of shrinkage. A melt infiltration process was used in combination with 3DP to fab-
ricate near net-shape dense parts. Printing on alumina formed porous green bodies which were fired to get strong alumina preforms. These preforms were then infiltrated using a borosilicate glass leading to a dense alumina/glass composite. The printed and infiltrated parts exhibited very low linear shrinkages (<2%) without showing non-uniformities in the infiltration at different geometrical locations. The strength of the fabricated composite was good since 4-point bending test Modulus Of Rupture results were in the range of 200 MPa regardless of the printing direction. A similar strength was exhibited by the same compos-
ite which was prepared by a pressing and infiltration technique.
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