Structural Ceramic Components by 3D Printing

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Abstract

Several technical challenges exist in adapting Three Dimensional Printing (3DP) to processing of dense ceramic structures. The sintering rate of particulate bodies depends on the sintering mechanism, average powder size, and initial packing density. Fine powders are necessary to ensure appreciable densification rates from powders which sinter by solid state transport. A critical packing density exists for such powders below which densification does not occur. Special build strategies are, therefore, required for 3DP of ceramic structures. We have successfully demonstrated five approaches to produce dense ceramic components by 3DP. First, spray-dried granules of fine ceramic powders are spread in the existing 3DP equipment and bound using a latex binder through an ink-jet print head. The resulting components are then isostatically pressed to raise the green density to a point that the parts will fully densify when fired. A second approach uses glass powders that sinter by a viscous sintering mechanism. Such bodies sinter to full density at all initial green densities. Spray-dried granules of fine glass powders are spread and bound with latex followed by directly sintering to full density. Both of these approaches produce rather large linear shrinkage because of the low overall packing density. Large glass particles have a much higher packing density and produce bodies that sinter to full density because of the rapid viscous sintering. This third technique produces fully dense parts with linear shrinkage of about 15%. The fourth approach involves glass infiltration of porous ceramic bodies. Our results indicate that this technique can produce dense parts with less than 1% linear shrinkage. Finally, the 3DP process has been modified to permit deposition of fine powders as slurries, rather than dry powders. The resulting process considerably increases the bed density and the resulting fine ceramic parts can be sintered to full density without intermediate isopressing.

Introduction

Three Dimensional Printing (3DP) is a rapid prototyping technique to directly manufacture functional parts from different materials systems[1-7]. The 3DP process constructs parts from powder on a point-by-point basis. The powder is spread in thin layers and selectively bonded by ink-jet printing of a binder material. The unbound loose powder is removed after sequential layers have been built to reveal a three dimensional green body. 3DP has been extensively used to make refractory ceramic components for metal casting [2] and is also now being used to make metal parts directly [3]. Polymer parts are also being made with the 3DP process [6,7].

This paper reports on the use of 3DP to fabricate structural ceramic parts. A previous SFF Symposium paper reports on preliminary work to make structural ceramic parts by 3DP [5]. Conventional ceramic part manufacturing involves molding ceramic powders into a desired shape and desifying the shape by sintering. Fine powders aid the sintering process, but pose several challenges for direct use in the 3DP process. The current generation of 3DP machines spread thin layers of dry powder across a piston. Fine powders do not generally flow well enough to spread into defect-free layers. Their high surface area causes increased cohesive strength of the unpacked powder and a decreased flowability.

Most fine ceramic components are sintered to full density by compacting very fine powders (typically less than one micron) and firing at high temperature [8]. Many authors have shown that the nature of the interparticle packing is very important to achieve full density. The particle size and initial density (green density) of the packing, for example, are known to be important factors in sintering kinetics. Fine powders are generally required to achieve significant densification rates for materials that sinter by solid-state diffusion, such as alumina. Fully dense glass parts, however, can be made by sintering glass powders that are many microns in size. Glass sinters by viscous flow of material into the neck between particles. Bruch [9] has shown that significant densification rates are not observed for alumina powders unless the green density is greater than a critical value. The critical density decreases with increasing firing temperature, but high green densities are required to ultimately achieve greater than 99% of full density. This phenomenon depends on the nature of the sintering mechanism. High purity alumina densifies by a solid-state mechanism. Glass powders, however, densify by viscous sintering and can be fully densified from very low green densities

This paper reports on several build strategies that help to overcome the difficulties of building ceramic parts on the current generation of 3DP machines. It also shows that modifications of the current process will be possible that vastly improve the ability of 3DP to produce structural ceramic components. First, spray-dried powder of alumina is used to make a 3DP-derived green body which is isostatically pressed and fired. The pressing step is not required for spray-dried powders of a glass ceramic material since it sinters by viscous flow. The large shrinkage factors of the previous two methods can be avoided by using large glass particles which have high relative tap densities. Very small shrinkage and high density are obtained by infiltrating porous 3DP-derived ceramic bodies with molten glass. Finally, fine powders can be packed to high green densities in the 3DP process by spraying slurries of the powder and drying to form each layer.

Printing on spray dried powder systems

Granulation by spray-drying dramatically improves the flow behavior of fine powder. The net tap density is only marginally improved, however, since the individual granules are porous. Printing on spray-dried powder was conducted using Acrysol WS-24 (Rohm and Haas Company, Philadelphia, PA) which is an acrylic copolymer dispersion. Typically, the spray-dried granules were spherical with an average particle size ranging between 20 and 53μm. Fine alumina powders were spray-dried using polyacrylic acid (PAA) as a dispersant and then printed using a typical binder concentration of 6 vol%. The green 3DP-derived parts were then Warm Isostatically Pressed (WIP) at 40000 psi in

order to obtain the critical density needed for full densification. The pressed alumina parts were fired at 1650° C for 2 hours in air. A feldspar/nepheline glass powder was also spray-dried and used for printing. The printed green body was heated to 450° C to remove the binder, and then fired at 970° C for an hour under vacuum.

The strength of the ceramic parts formed from the spray-dried powder were comparable to those formed by other techniques. The alumina parts had a typical strength of approximately 400 MPa (4-point bending). The green body shrinkage during pressing was approximately 21.5% linear upon pressing, and another 15.2% upon firing. Complex geometries were created in alumina with fired densities of more than 98%. Figure 1 is an example of a complex alumina part in the green form, after CIPing, and after firing.

Material system	Starting powder	Flexural strength MPa
Alumina infiltrated w/ InCeram	Spherical plasma sprayed alumina	205
Alumina	Spray dried alumina	400
Zirconia Toughened Alumina	Spray dried ZTA	475
Silicon nitride	Silicon nitride (press rolled)	570

Table 1: Demonstrated mechanical properties of 3DP-derived materials

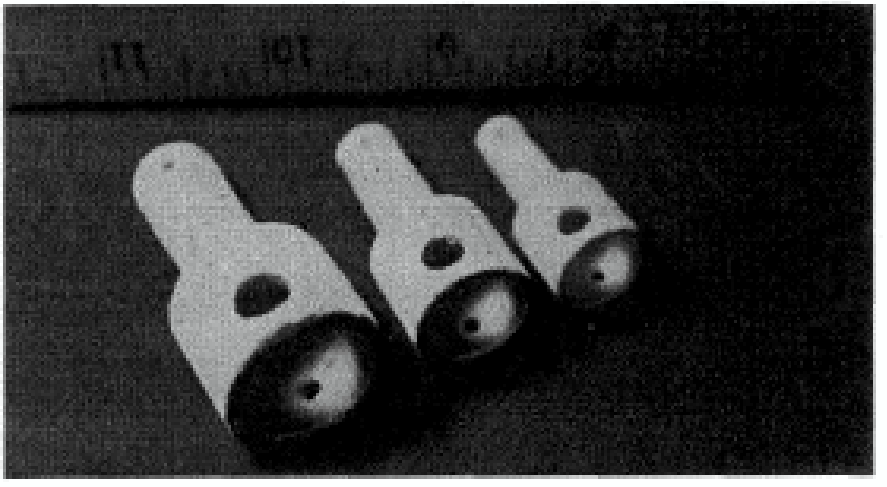

Figure 1: Pre-ignition chamber for diesel engine printed with spray dried alumina. Green body on the left, CIP part in the middle & fully dense on the right side.

The glass ceramic parts were fired to high densities without any intermediate CIP step. This direct fabrication releases possible constraints imposed by CIP on the component topology. These parts typically reached densities of more than 97% of theoretical with an average total linear shrinkage of 34%. A major advantage of the glass-ceramic printed parts is their excellent surface finish, which is similar to smooth glass surfaces.

Melt infiltrated alumina/glass composites

Molten glass will spontaneously wick into oxide ceramic bodies because of its low contact angle on these surfaces. Thus, porous ceramic bodies can be fully infiltrated simply by contact with molten glass. This technique has been used to prepare dental ceramic components with little dimensional change from that of the initial porous body [10]. 3D Printing on alumina powder was performed to form melt infiltrated glass/alumina composites. Three different forms of alumina powder granules were used; spray-dried alumina, coarse platelet alumina and dense spherical alumina (Table 2).

Material	**Binder**	**Density of preform prior to infiltration**
30 μm spherical alumina	20 vol% Acrysol	48%
30 μm coarse, platelet alumina	6 vol% Acrysol	36%
<53 μm spray dried alumina	6 vol% Acrysol	58%

Table 2: Alumina powders for In/Ceram infiltration

Acrysol was also used as the binder to form the green body. The alumina preform was then fired at 1600° C to insure that it was strong enough so as to not deform during infiltration. The preform was then removed to a gold-platinum crucible and placed on the top of a proper amount of boro-silicate glass powder called In-Ceram™ (Vita Zahnfabrick, BadSackingen, Germany). The alumina preform and the glass powder were fired to 1100° C for 4 hours at atmospheric pressure in order to achieve complete glass infiltration of the preform. The density of the infiltrated parts was measured using low pressure mercury porosimetry and SEM microstructure analysis was conducted on different complex-shaped parts to study the uniformity of the infiltration. 4-point bending test was performed on bars printed along two different printing directions (fast axis and slow axis) to measure the strength of the composite. Helium hermiticity testing and thermal conductivity measurements were also performed.

The spherical alumina/InCeram and the coarse alumina/InCeram composites exhibited a total shrinkage of less than 1.5% during the transformation from a green to a fully dense body. The spray-dried alumina/InCeram composite shrank linearly by around 19% during the sintering stage of the preform because of the alumina sintering of the inter-granular pores of the grains. The density of the composites was typically in the range of 93% and 99% of the calculated theoretical density. Microstructural analysis showed that the infiltration was uniform regardless of the part geometry. The SEM picture in Figure 2 is a typical microstructure where the dark areas are the alumina granules and the glass appears light gray. The defects appears as spherical pull-outs which are an artifact of

polishing and grinding. The helium infiltration test showed that the printed composite parts were also hermetic. The MOR results for the composite bars had an average of approximately 200 MPa regardless of the printing direction. The strongest bars had an MOR similar to the strength observed in 4-point bending tests of pressed and infiltrated alumina/InCeram bars [11].

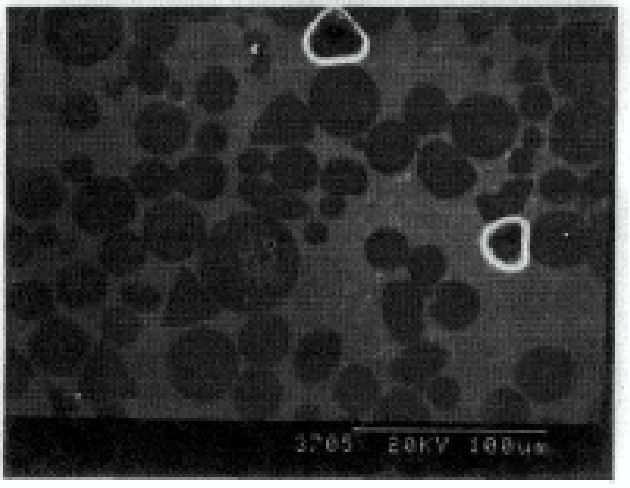

Figure 2. SEM of polished cross-section of a part made out of alumina/InCeram.

Spherical glass powders

Plasma sprayed glass powders were also used to 3D Print complex shapes. These powders have rather high tap densities because of their large size. Secondly, they easily densify by viscous sintering even with large particle size. Soda-lime and alumino-silicate powders of various particle sizes (Table 3) were spread in layers of 120 μm or 170 μm and printed with 20 vol% Acrysol. These large particles are highly flowable. Thus, the slight friction between the wet printed region and the material being spread was enough to cause noticeable slipping of the partially built component. This problem was easily solved by installing infra-red lamps so that each layer could be dried before spreading the next layer.

Glass composition	Particle size distribution (μm)	Particle size mean (μm)	Powder bed density (%)
Soda-lime	65-73	66	61%
Soda-lime	20-71	49	59%
Soda-lime	35-61	35	57%
Alumino-silicate	9-43	26	53%

Table 3: Plasma sprayed glass powder used in printing.

The plasma sprayed powders offer the most advantageous solution in the fabrication of glass-ceramic via 3DP because of their excellent flowability and high packing density. The 3DP parts created using these powders densified directly upon firing from green to fully dense form. The part shrinkage was low and similar to the data obtained from other ceramic powder processing techniques. The measured shrinkage data varied depending on the powder packing density of the used powder (Table 4).

Material System	Powder bed density	Shrinkage during CIP	Shrinkage during firing	Overall volumetric shrinkage	Linear shrinkage
Fine powder alumina	42%	18%	38%	56%	25.1%
Spray dried alumina	32%	28%	38%	66%	31.6%
Spray dried glass ceramic	32%	N/A	67%	67%	31.6%
Dense glass ceramic powder	62%	N/A	38%	38%	14.7%
Glass infiltrated alumina	48%	N/A	1%	1%	0.7%
Spray deposited alumina	49.2%	N/A	49.8%	49.8%	20.26%

Table 4. Shrinkage of the various materials systems.

The soda-lime powder had a tap density 61% of theoretical and sintered to 99.2% dense with a total linear shrinkage of only 12%. Other soda-lime and alumina silicate powder systems had a packing density between 50% and 60% of theoretical and densified fully with linear shrinkage in the range 14%-18% (depending on the powder). Several complex fully dense parts have been created using 3DP (Figures 3 and 4). It is important to note also that no topological constraints are imposed on fabricating glass-ceramic components using the plasma sprayed powder since no intermediate isopressing step is needed. Figure 4, for example, is a small rocker arm with an independent sphere of glass within it. The simple assembly was designed and simultaneously built by 3DP and then fired.

Figure 3: Pre-ignition chamber printed with soda-lime glass. Green body on the right and fully dense part on the left side of the frame.

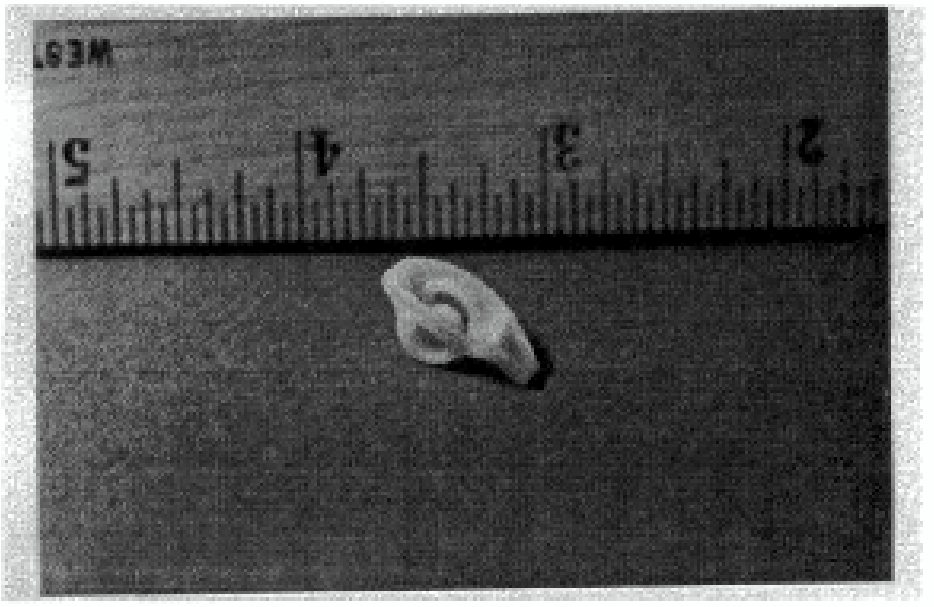

Figure 4. Rocker arm made with soda-lime glass. A small sphere is contained within the rocker arm. This sphere is too large to be placed with the rocker arm. It was constructed at the same time as the rocker arm using the 3DP process.

Spray-deposition of fine powders

High density fine ceramic powder beds were created by spraying isopropanol-based alumina slurries on a substrate. The amount of powder deposited per spray was kept under the critical cracking thickness in order to make crack free powder bed. Each spraying step was followed by a short (~1 min) infra-red drying cycle. The high density powder bed was printed with PMMA/acetone solution to define the shape of the desired

component. Printed components were subsequently retrieved from the powder bed by washing in water. The printed parts were sintered at 1650° C for 2 hours.

The green density of the powder bed prepared by spraying isopropanol/alumina slurry was measured by the porosimeter as 49.2%. The powder bed, as well as the rectangular printed bars, densified to 99% upon firing at 1650° C for 2 hours. The green part shrank by 20.26% upon densification. The cross-sections of the fired parts (Figure 5) do not show any lamination defects.

We envision a simple modification of the current 3DP machine so as to incorporate spray deposited layers. Such a system is currently being installed on one of the machines at MIT.

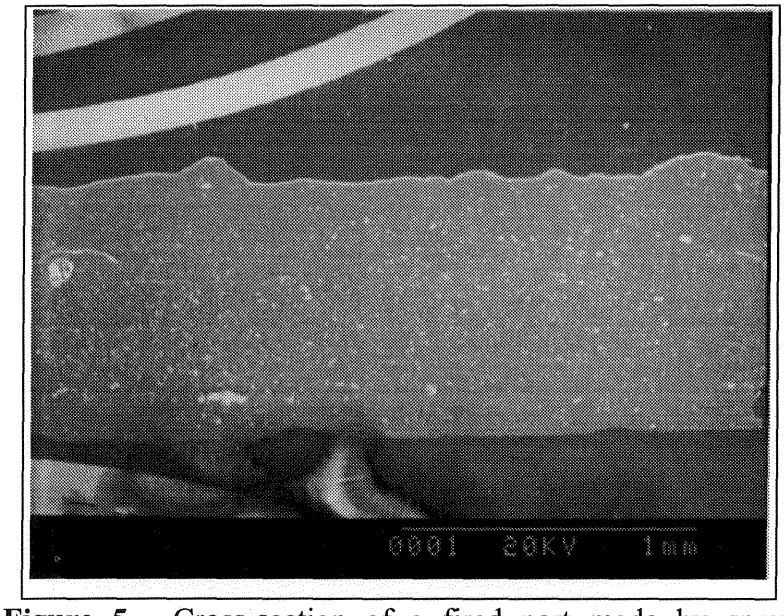

Figure 5. Cross-section of a fired part made by spray-deposition technique.

Concluding remarks

Powder-based SFF processes, such as 3DP, replace the forming step in conventional powder manufacturing processes. Thus, post processing steps, such as sintering or infiltration, must still be practiced when using an SFF process to make components. The effectiveness of post processing toward producing high density parts is intimately related to the nature of the green microstructure and to the materials being processed. Some processing strategies are easier than others to implement in 3DP. Indeed, direct use of fine ceramic powders seems to require significant modification of existing 3DP machines so that slurries can be accommodated. Fine powders can be used in the form of spray-dried granules, but only if large shrinkages are acceptable. Glass parts or glass infiltrated parts seem to be most amenable to direct use by the 3DP process. High density glass components can be made with little effort.

Modification of 3DP machines for optimum performance in a given application is not surprising. Efficient and reliable materials handling equipment, such as layer spreading equipment and ink jet print heads, is subject to the nature of the materials being used. That is, this equipment functions best for only a narrow range of materials properties. Fortunately, there are many design options for each of these subsystems. Each subsystem approach requires testing for its impact on post processing, control strategies, interaction with other subsystems, and reliability testing. This has become a major focus area in 3DP research. Fortunately for us, it is also a very rich area for interesting engineering problems and materials processing phenomena.

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