STRUCTURAL CERAMIC COMPONENTS BY 3D PRINTING

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Abstract

The Three Dimensional Printing (3DP) Process has been adapted for processing of fine ceramic powders to prepare structural ceramic components. Our preliminary study was designed to reveal those aspects of the 3DP process which must be modified for use with fine ceramic powders. The basic elements of the modified process are to spread submicron alumina powder and print latex binder. Several methods were used to spread thin layers of submicron powders. Green parts are isostatically pressed followed by thermal decomposition prior to sintering to remove the polymer. The fired alumina components are greater than 99.2% dense and have average flexural strength of 324 MPa. This is lower than the best conventionally prepared alumina, but we believe that the strength results will improve as we learn more about the relationship between strength limiting flaws and the 3DP build process.

Introduction

3D printing creates solid objects from a CAD representation by selective binding of ceramic or metal powders with "ink-jet" printing of binder droplets. Earlier work has demonstrated the effectiveness of 3DP as a rapid prototyping tool for investment casting tooling[1~4]. 3DP is, however, a flexible process in which any type of material in the form of powder can be used to create complex shapes. The effort involved in processing new materials systems using 3DP is minimal as compared to other SFF processes. 3DP is one of the few rapid prototyping technologies that involves the deposition of matter during the build process. Powder/binder combinations that are used for conventional powder processing can often be used in 3DP since ink-jets can be adapted to print a variety of binders. In principle, simultaneous control of the component microstructure and macrostructure can also be achieved by varying the amount and composition of binder printed into different locations within a layer. Thus, composition and porosity can be varied from point to point by specification in the original CAD file.

This paper reports on the first use of 3DP for fabrication of structural ceramic parts. It also represents the first use of submicron powder in the 3DP process. Submicron ceramic powders are necessary since the 3DP process produces a porous parts which must be fired to attain full density. The relative particle packing density or "green density" of the unfired part must be sufficiently high in order to sinter to full density when fired [5]. Green densities of at least 60% are often required for ceramics which sinter by solid-state diffusion.

Fine powders pose several challenges for direct application in the 3DP process. First, the current generation of 3DP machines spread dry powder across a piston in thin layers.

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. Simple modifications were made to the conventional spreading method to overcome the difficulties of fine powder. A press-rolling technique was devised for this purpose and using the initial low packing of the fine agglomerates and the load applied to the powder bed by stream rolling the spreader rod, we were able to spread uniform thin layers of fine powder. Uniformity in the microstructure of green samples is necessary to ensure the elimination of defects upon sintering. Isostatic pressing techniques were used to enhance the density before firing. The effects of this post treatment will be discussed.

Laminated building processes have the potential for producing structural parts that are superior to those prepared by other fabrication methods. Powder molding processes involve deformation of powder masses into dies to form complex shapes. The mass typically includes rather large amounts of organic binder to increase plastic flow into the mold, as is done in powder injection molding. The shear history of each volume element of the component is different beacuse of the complex shape of the mold. This results in nonuniform powder packing in the green part and uncontrolled shrinkage and distortion during sintering. Each volume element of a laminated object is, however, prepared in the same way, regardless of shape or dimension. Secondly, binder removal is often accompanied by the formation of defects and adds considerably to the cycle time for component production [6]. Much less binder is required in the 3DP process, since the binder is used only to hold the green part together rather than plasticize the powder mass.

A process to make complex structural ceramic parts without the need for complex tooling will have a great impact on many applications of ceramics. One of the countless possible applications of this technology is the implementation of an accurate testing method for brittle materials. The theta specimen, first proposed by Durelli, Morse and Parks in 1962 is one such example (Figure 1). The special shape of the specimen allows one to test the tensile strength of brittle materials by diametrical compression. The load is transferred to the central bridge due to the outward motion of the ring on the horizontal axis. The test method eliminates the need for complex gripping schemes often required when testing brittle materials. It is a common practice to use 3 or 4 point bending tests for brittle materials for this reason. Theta specimen testing is not often used, however, because of the difficulty in fabricating the complex shape required. The development of 3DP process for fully dense ceramic parts makes the fabrication of theta specimens a trivial matter and a new standard for mechanical testing of brittle materials can be implemented with the help of 3DP technology.

Experimental Procedure

The powder used for this study was Reynolds RC172-DBM alumina, both undoped and MgO doped, with the mean primary particle size of 0.8μm. Through sieving of as-received powder, agglomerates of sizes between 75 and 150 μm were screened to be used in the experiments. The apparent density and the tap density of the selected agglomerates were measured by using the apparatus and the techniques described by J. Lee [7].

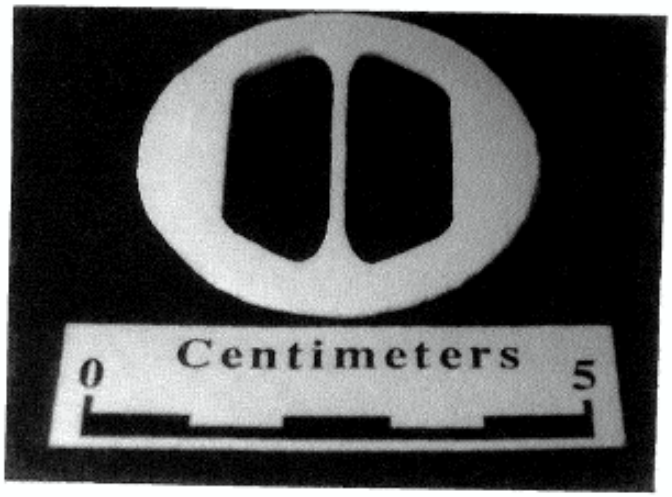

Figure 1. Theta Specimen

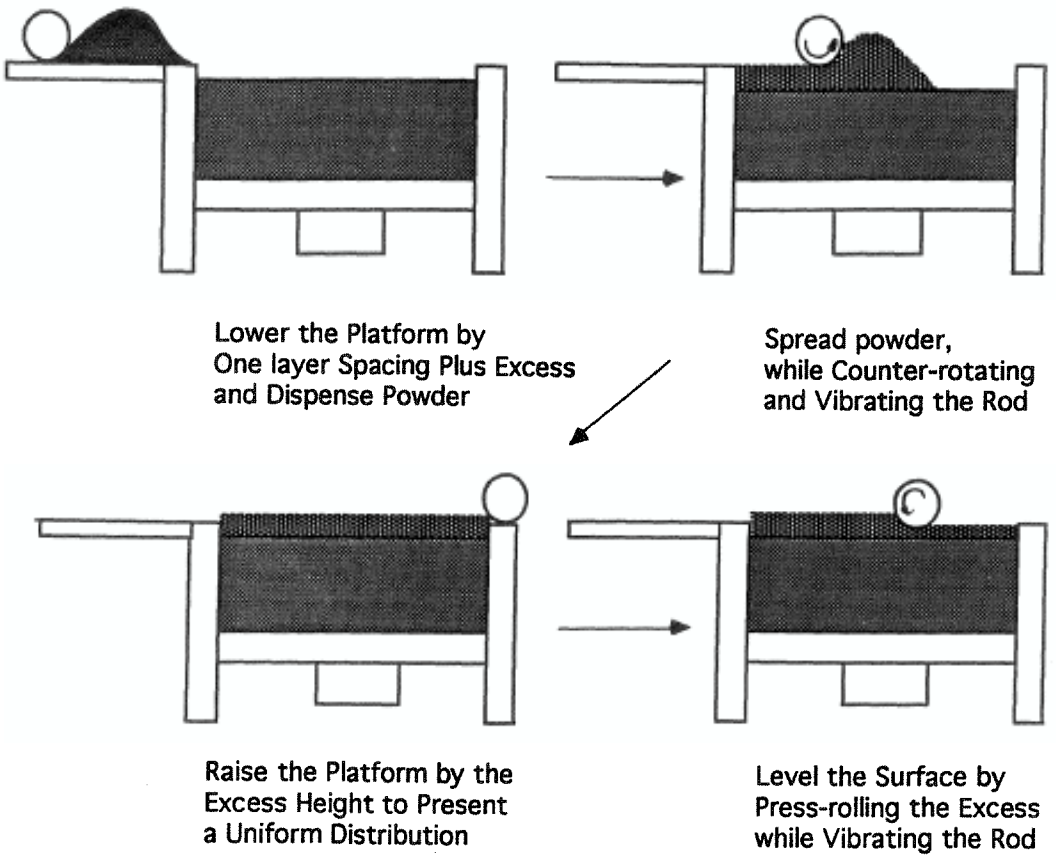

Figure 2. Press-rolling Sequence.

The binder used for this study was the Acrysol WS-24 (Rohm and Haas Company, Philadelphia, PA) which is an acrylic copolymer dispersion resin. Three different concentrations of the binder were used for printing, namely 3, 6, 12 wt%.

The 3D printing machine and the process by which the complex shapes are built is described in earlier publications [1~4]. Spreading of the sieved agglomerates was done by using a press-rolling method which is a modification of our conventional spreading technique. Figure 2 shows the schematic of the process. In the first step, the piston is lowered and a layer of loosely, but fairly uniformly packed agglomerates is produced by traversal of a counter-rotating spreader rod over the piston. On the second pass, the piston is raised to expose part of the loosely packed layer. The spreader rod is then forward rotated across the piston to pack the powder rather than shearing away the excess powder. This procedure results in a well packed uniform layer that is ready for printing.

A continuous jet of Acrysol droplets was made by passing the liquid through a 45μm diameter ceramic nozzle vibrated at 60kHz by piezoelectric transducers. The binder flow rate was 1.25cc/min. The printhead was rastered across the piston with a velocity of 1.65m/sec with 178μm spacing between the lines. The layer thickness was 127μm.

The piston containing the powder bed after the entire build operation was removed and heated at 125°C for one hour to remove water from the bed and cure the binder. The printed parts were then separated from the unprinted region by gently brushing away the matrix powder with soft brushes. The retrieved parts were then isostatically pressed either at room temperature or in heated hydraulic fluid. These processes are called cold isostatic pressing (CIP) and warm isostatic pressing (WIP), respectively. The samples were put in a latex bag, evacuated, and sealed before being placed in the chamber of the isostatic press.

Successfully isopressed samples were then placed in a furnace for binder removal at 450° C and then further fired for densification at 1650° C for 4 hours. The bulk densities of the green, isopressed, and fired samples were measured by using an automated mercury porosimeter.(Micromeritics, Norcross, GA). Shrinkages of rectangular samples were measured with micrometers.

Four point bending tests were conducted to find the flexural strength of the fabricated material. Precision grinding of the surface of bending specimens was performed prior to testing in order to measure the intrinsic strength of the material and eliminate effects due to surface defects. Grinding was performed by Bomas Machine Specialties Inc. (Sommerville, MA). The size and the shape of the specimens, and the testing procedures were in strict compliance with the ASTM standard C1161-90.

Results and Discussion

The fine alumina powder used for this study has considerably lower apparent and tap density than other common powders used for 3DP, as shown in Figure 3. Spreading these agglomerates with the conventional spreading sequence resulted in layers that are inhomogeneous and had low particle packing density. Since the uniformity of packing is

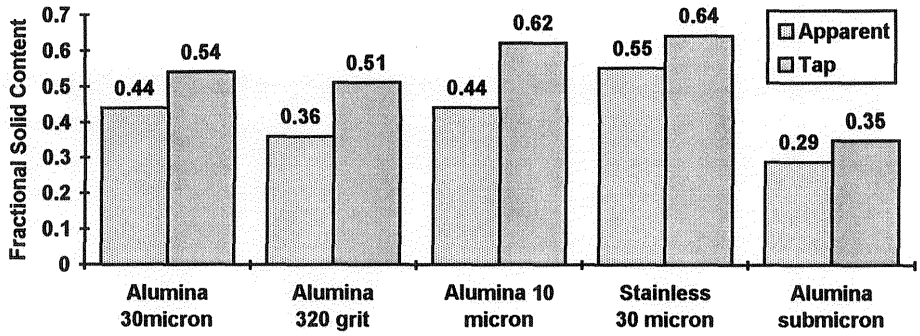

Figure 3. Apparent and tap densities of various powders

crucial for shrinkage control and in preventing the formation of defects in the final component, modifications have been made to the spreading sequence. The press-rolling technique, as described in the previous section has proven to be very effective in creating not only a homogeneous but also well packed layers of dry fine powder. The packing density of the resulting powder bed was 40% which is even higher than the tap density of the material. This phenomena is not observed with any other powders examined in this study. The cohesive strength of the resulting powder bed was quite remarkable and ballistic ejection of particles upon impact of binder droplets was completely eliminated. Ballistic ejection is a common observation for highly flowable powders used in 3DP and must be overcome by increasing the cohesive strength of the powder bed by adding moisture prior to printing [8,9]. The top surface finish was excellent due to the absence of both the ballistic ejection and particle rearrangement caused by capillary force.

The strength of the green parts varied with the concentration of the Acrysol. Samples printed with 3wt% Acrysol were strong enough to hold their shape, but not enough to be handled casually. Samples with 6wt% binder, however, had adequate strength for both loose powder removal and subsequent handling. Excess polymer from the samples with 12wt% Acrysol was found to segregate at the surface of each layer and is detrimental to the lamination of the layers (Figure 4). The excess binder exhibited other adverse effects on the properties of the samples, as will be discussed later.

The green density of the as-printed samples was found to range from 33 to 36% of alumina's theoretical density which is too low to fire to full density by sintering. As described earlier, we have incorporated an isostatic pressing of these 3DP green bodies to effectively increase the green density without sacrificing our ability to make complex shapes. CIP and WIP at 80°C of the parts were effective in increasing the green density of the samples, as shown in Figure 5. Isostatic pressing dramatically increases the final density of the material. The final density also depends on the binder content as can be shown by comparing the samples with 12wt% and 6wt% binder in the green state. Excess binder between the laminates contributes porosity that can not be removed by sintering. A polished cross section of the higher binder content sample in Figure 6 shows huge cracks between fully dense laminates obviously caused by the presence of excess binder.

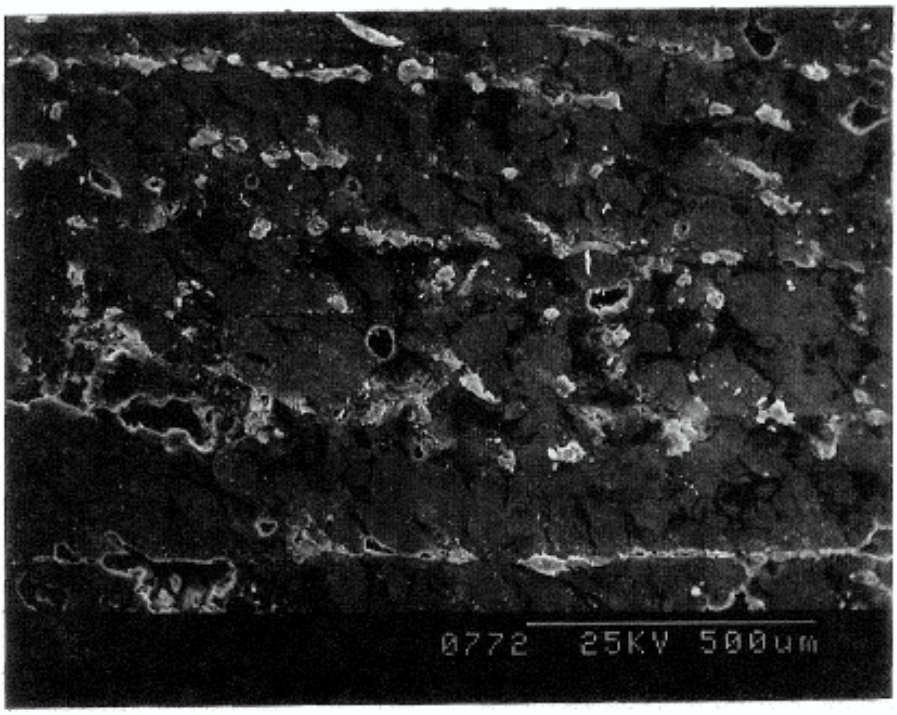

Figure 4. Polished cross section of as-printed part with 12wt% Acrysol.

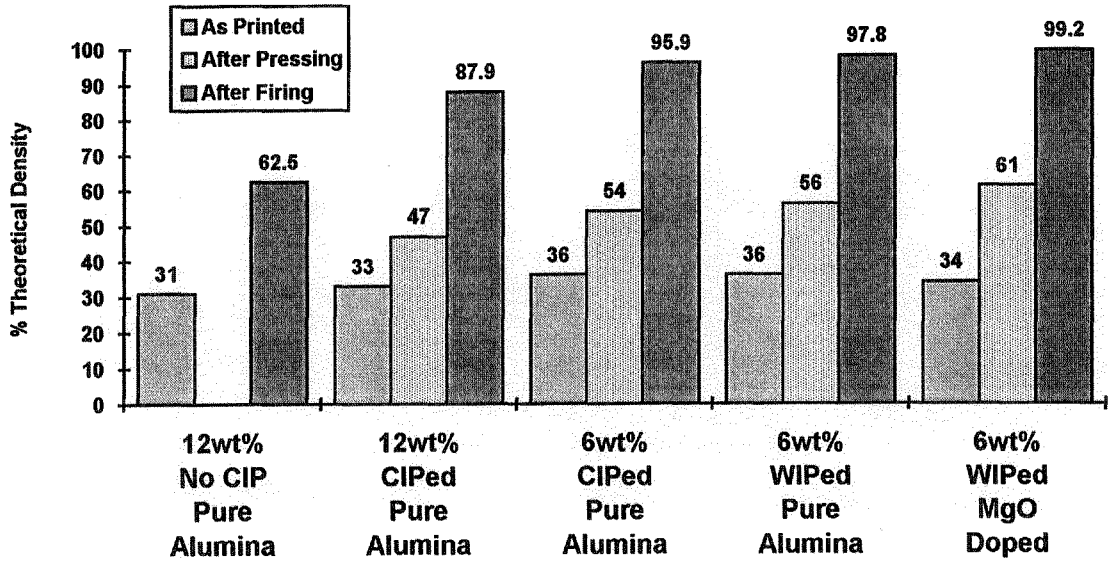

Figure 5. Bulk densities of parts at each stages.

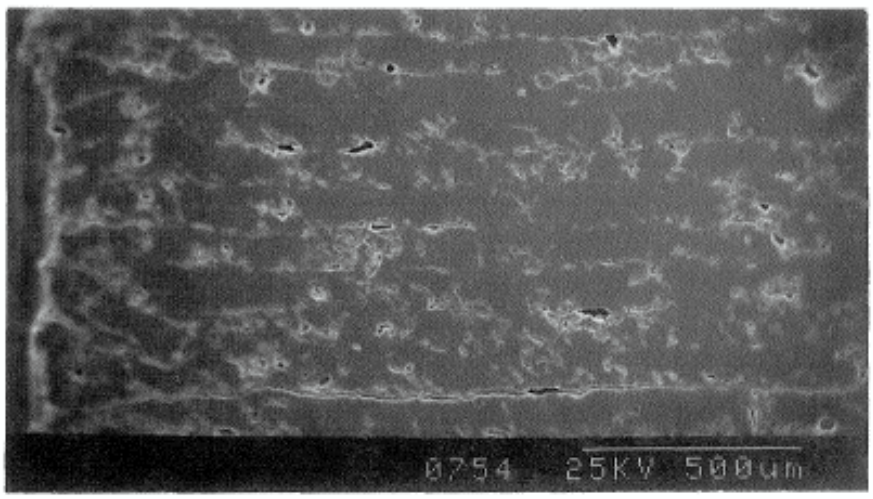

Figure 6. Polished cross section of CIP and fired sample with 12wt% Acrysol (Undoped)

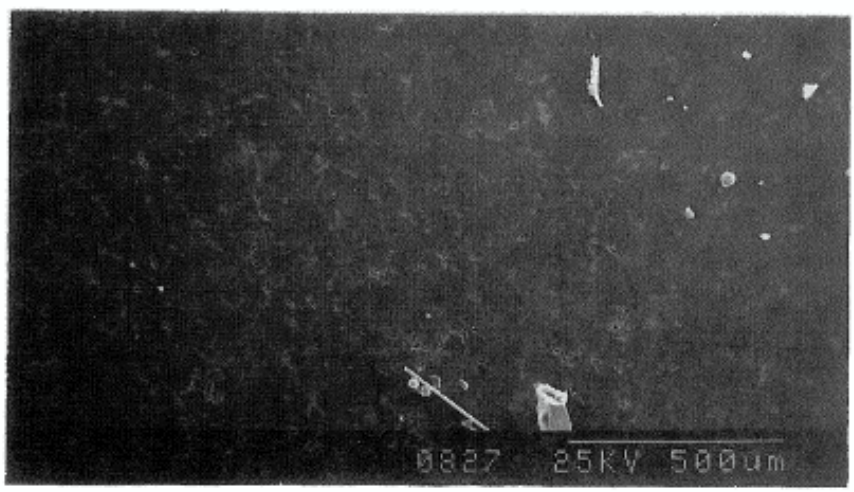

Figure 7. Polished cross section of WIP and fired sample with 6wt% Acrysol (Undoped)

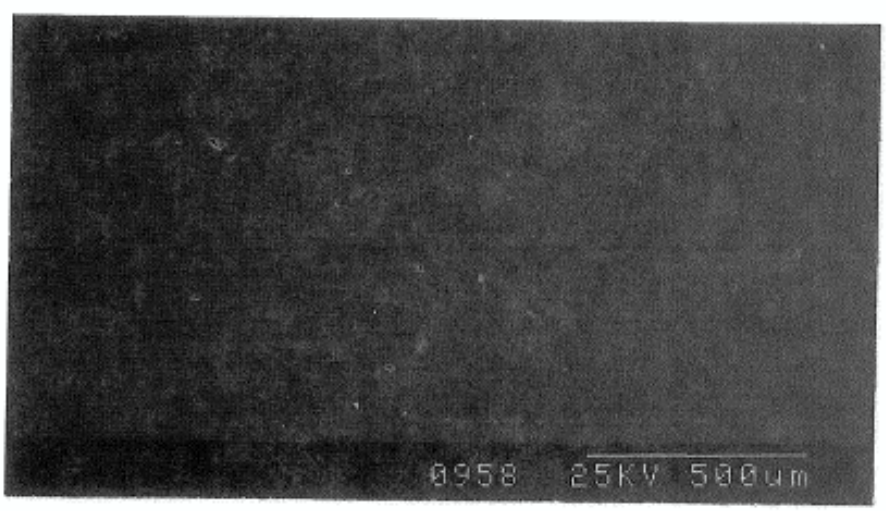

Figure 8. Polished cross section of WIP and fired sample with 6wt% Acrysol(MgO doped)

Density measurements on the samples with same binder content but different isopressing technique also show interesting behavior. Warm isostatic pressing is carried out above the glass transition temperature (46°C) of the Acrysol binder. Thus, the polymer viscosity decreases and results in redistribution of the binder while the pressure induced densification is in progress. The final densities of the subsequently fired parts have shown average value of 98% of the theoretical density of alumina. Figure 7 shows the cross section of a sample produced by WIP and sintering at 1650°C. No defects associated with lamination are apparent in the micrograph.

The results with the MgO doped alumina powder have shown the effectiveness of its role as the grain growth inhibitor and resulted in parts with 99.2% density. Figure 8 shows the MgO doped sample fabricated by the identical conditions as the above mentioned undoped samples.

Sintering shrinkages in different directions were also found to be strongly dependent on process parameters. As shown in Figure 9, the excess polymer present in between the laminates in the case with the 12wt% Acrysol caused more shrinkage in the direction normal to the build plane and thus caused very anisotropic shrinkage. Reduction in the anisotropy was achieved by the elimination of the excess binder content as shown in the case for 6wt% Acrysol. Further improvements and near isotropic shrinkage was obtained by implementing the WIP technique in conjunction with the reduction in binder content.

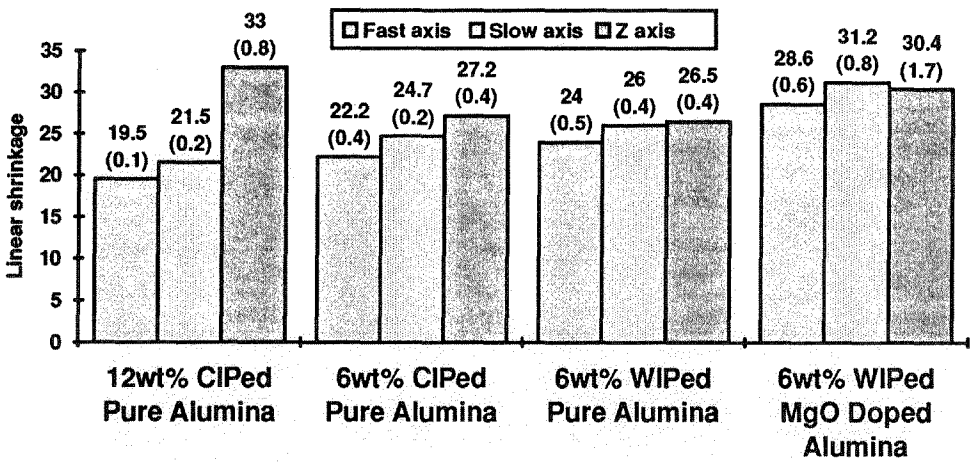

Figure 9. Total linear shrinkage in different directions. (Numbers inside the parentheses indicate the standard deviation of the shrinkage data)

Optimization of the amount of binder and the isopressing technique have allowed us to obtain a near fully dense pure alumina parts with 3DP. Although our current practice of wet-bag isostatic pressing does limit the topologies which can be pressed, alternative procedures are being investigated for isopressing of more complex parts. They include the dipping of the 3DP parts in a latex solution for forming a protective coating, and an *in situ* bagging technique of the samples by printing excess binder only at the edges of the part.

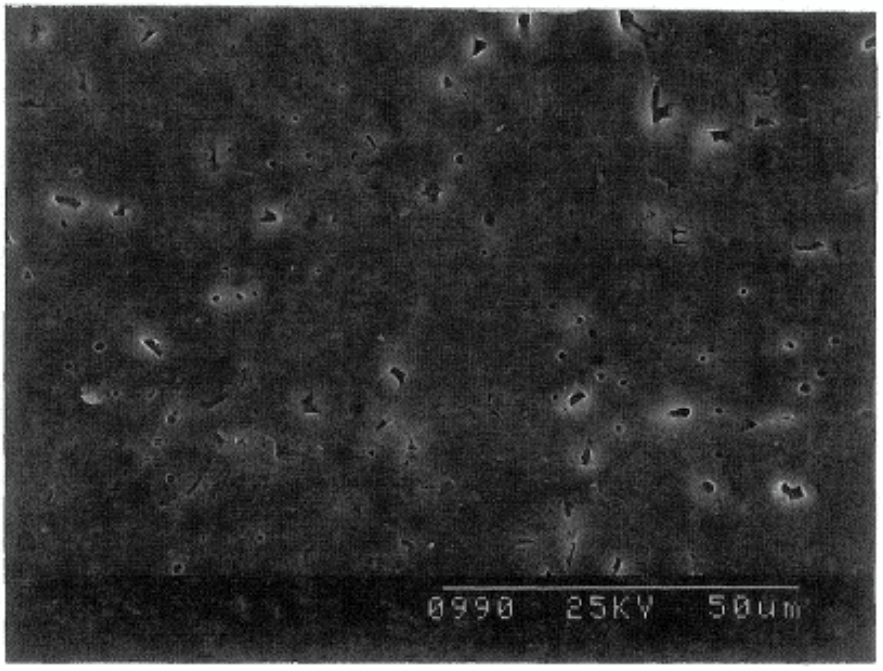

Figure 10. Thermally etched cross section of undoped sample. (6wt% binder, WIPed)

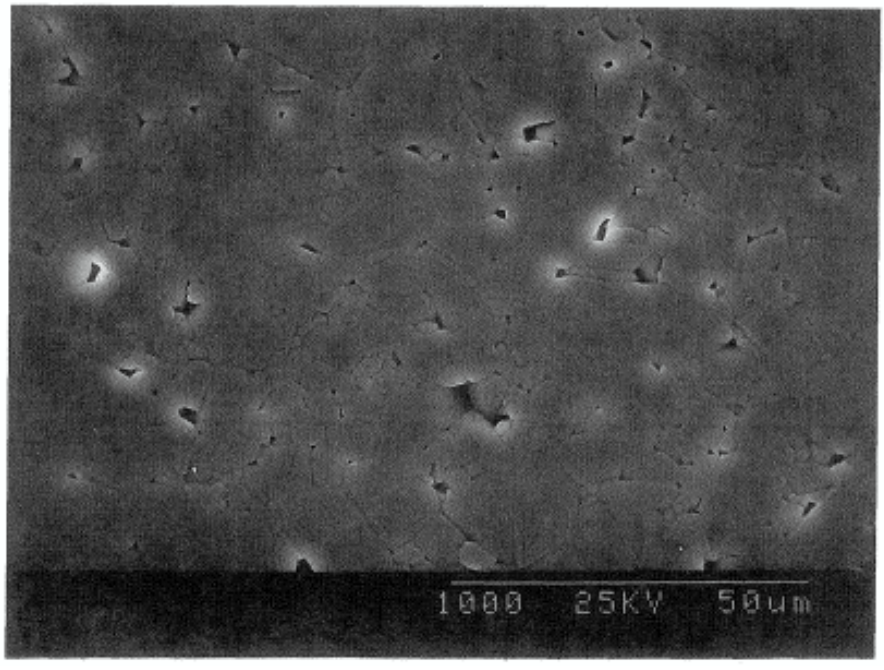

Figure 11. Thermally etched cross section ,MgO doped sample.(6wt% binder, WIPed)

The WIP procedure has also demonstrated effectiveness in improving the green density of other powder systems. In a preliminary experiments, WIPing parts made from printing Acrysol on a powder bed of spray dried alumina have resulted in a fully dense fired part. Further investigation with this system is also being conducted.

The mean flexural strengths of the 3D printed bars upon four point bending was 231.6MPa and 324MPa for undoped and MgO doped samples, respectively. MgO normally is added as an alumina grain growth inhibitor. Absence of MgO caused obvious signs of discontinuous grain growth which accounts for the 1.5% residual porosity and the relatively low strength in the case of undoped samples. (Figure 10) Samples with MgO-doped alumina powders do not exhibit discontinuous grain growth, as shown in Figure 11. Although conventionally prepared alumina has a slightly higher flexural strength of 350 to 450MPa, [10] we view our results as very promising since the microstructure of our samples exibit signs of slight under-sintering. Optimization of the sintering schedule is under investigation and promises to yield improved properties.

Conclusions

Fine powders coupled with appropriate modifications in the powder spreading mechanism allowed us to fabricate the first near fully dense ceramic parts by 3D printing. The parts also benefited from the absence of particle movement during the printing cycle, thus drastically improving the surface finish of their top surfaces. The amount of binder printed into each layer has been found to play an important role in formation of defects between laminates and shrinkage anisotropy. The WIP method was also effective for enhancing the final density of the parts, as well as, in eliminating the interlaminar defects. Flexural strengths of the bend bars have shown 324MPa and higher upon four point bending tests. MgO-doped alumina powder brought improvements in the strength of the material by inhibiting the abnormal grain growth during firing which increased the final density of the component and decreased the grain size. Sintering schedules are being studied to further improve properties. Successful completion of these investigations will enable us to manufacture complex ceramic parts for structural applications directly by 3D printing.

Acknowledgments

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References

1. Sachs E., M. J. Cima, J. Cornie, "Three Dimensional Printing: Rapid Tooling and Prototypes Directly from a CAD Model.", CIRP Annals, vol. 39/1, p.210-204, 1990

2. Sachs E., et al, "Three Dimensional Printing: Ceramic Tooling and Parts Directly From a CAD Model.", Nat. Conf. on Rapid Prototyping, p. 35-37, 1990

3. Sachs E. et al, "Three Dimensional Printing: Ceramic Shells and Cores for Casting and Other Applications.", 2nd Int. Conf. on Rapid Prototyping, p.39-53, 1991

4. Ashley S., "Rapid Mold-Making For Investment Casting.", *Mechanical Engineering*, 1992, vol. 114, no.11, p.49-51

5. Brunch C. A.,*Am. Ceram. Soc. Bull.*, vol. 41, no.12, p.799, 1962

6. Lewis J. A., M. J. Cima, *J. of Am. Ceram. Soc.*,vol. 73, no.9, p.2702-2707, 1990

7. Lee J., "Powder Layer Generation for Three Dimensional Printing" S.M. Thesis, Dept. of Mechanical Engineering, Massachusetts Institute of Technology, June 1992

8. Lauder A. M. J. Cima, E. Sachs, and T. Fan, "Three Dimensional Printing: Surface Finish and Microstructure of Rapid Prototyped Components"; in Proceedings, Synthesis and Processing of Ceramics: Scientific Issues, Boston, MA,1991

9. Fan T., A. Lauder, E. Sachs, M. J. Cima, "The Surface Finish in Three Dimensional Printing," presented at the 3rd Int. Conf. on Rapid Prototyping, 1992

10. Schwartz M., Ed., "Handbook of Structural Ceramics", McGraw-Hill, 1992