High green density ceramic components fabricated by the slurry-based 3DP process

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Abstract

The 3DP process has been modified to directly fabricate high green density parts using submicron powder. The slurry-based 3DP process deposits the powder bed by spraying a dispersed slurry of the component material onto a piston. Alumina, silicon nitride, and lead zirconate titanate components with green densities as high as 67% have been fabricated by the slurry-based 3DP process. Solution phase binder systems have proven to be successful for the new process. Substantially improved surface finish over the conventional dry powder-based 3DP process has been demonstrated. Layer heights less than 50 μm can be prepared with this process. Thus, the stepped surface topography commonly observed in solid free form parts is substantially reduced.

Introduction

Structural ceramic components require fine-grained starting powders and high green density in order to achieve near theoretical density after firing. Wet processing techniques such as slip casting and injection molding are commonly used in ceramic forming processes to produce parts that meet these criteria. Structural ceramic components have been fabricated in the past with 3DP using spray-dried powders. These powders are ~50 μm agglomerates of submicron powder. Spray-dried powders were easily spread into uniform layers, but printed components had packing densities less than 35%. Post-processing was required to achieve sufficient density prior to firing.

The slurry-based 3DP process has been developed to overcome the difficulties of spreading fine submicron powder and also to enable layers as thin as 10 μm to be deposited. This paper discusses the slurry-based 3DP process and initial results with different ceramic materials systems. The process is sufficiently generic to be adapted to new materials systems. Our preliminary experiments have been performed on two types of ceramic materials, high purity alumina (several grades of Ceralox HPA) and sintered silicon nitride compositions (HC Stark M11, 6 wt. % Al_2O_3, 6 wt. % Y_2O_3). Firing conditions were 1650°C for 1 hr in air for the alumina samples and 1755°C for 1 hr under 2 psig N_2 for the silicon nitride.

The slurry-based 3DP process

The slurry-based 3DP process was developed to fabricate high green density components from submicron powders using wet processing techniques. Figure 1 shows a schematic of the slurry-based 3DP process. The primary difference from the standard 3DP process

is the manner in which the powder bed is deposited. The powder bed in the slurry-based 3DP process is deposited by spraying a dispersed slurry over the piston and drying. Typical slurry volume fractions are between 30 and 35 vol. %. Binder is then printed into the powder bed to define the shape of the component, and the process is repeated until the component is completed. The powder bed is cohesive, and the part is retrieved by redispersing the unprinted regions in an ultrasonic bath.

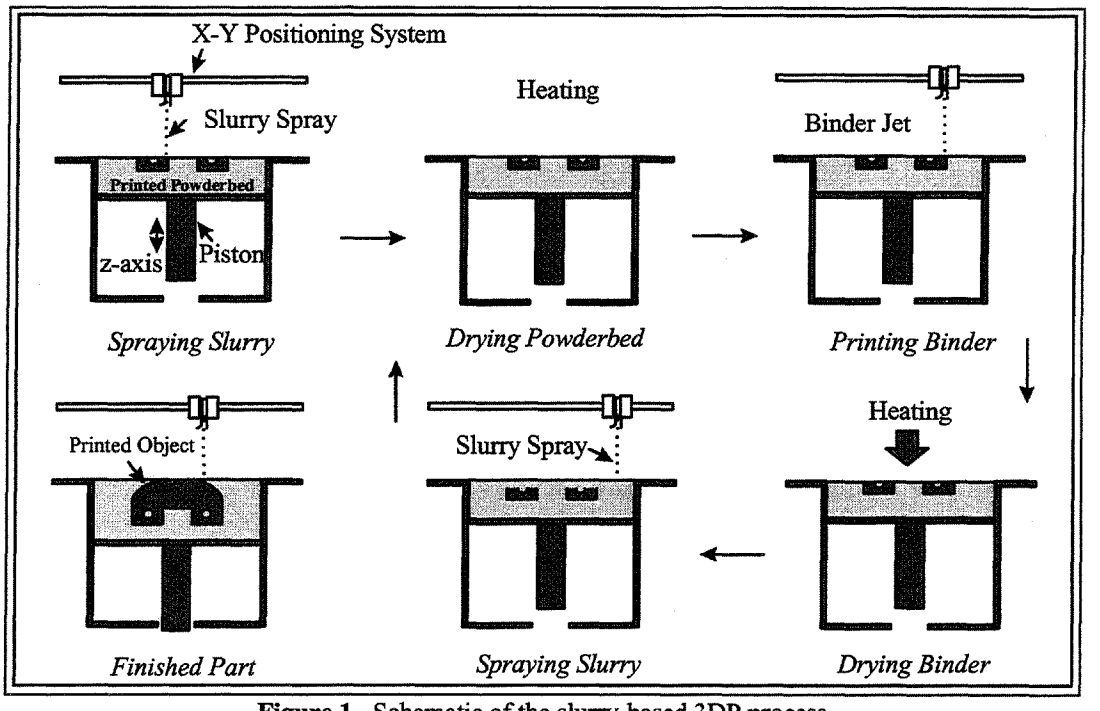


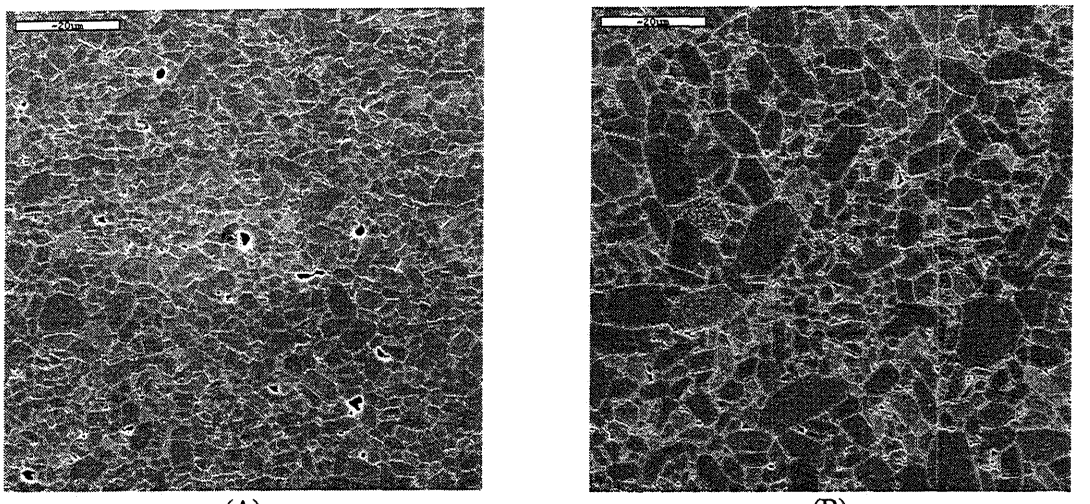
Figure 1. Schematic of the slurry-based 3DP process

Table 1. Densities of alumina powder beds sintered at 1650°C		
Formation Method	**Powder Size**	**Density**
Slurry-Based 3DP	0.5 μm	98.7%
Slurry-Based 3DP	1.0 μm	99.0%
Slip Cast	0.5 μm	99.0%
Slip Cast	1.0 μm	99.2%

Powder bed microstructure

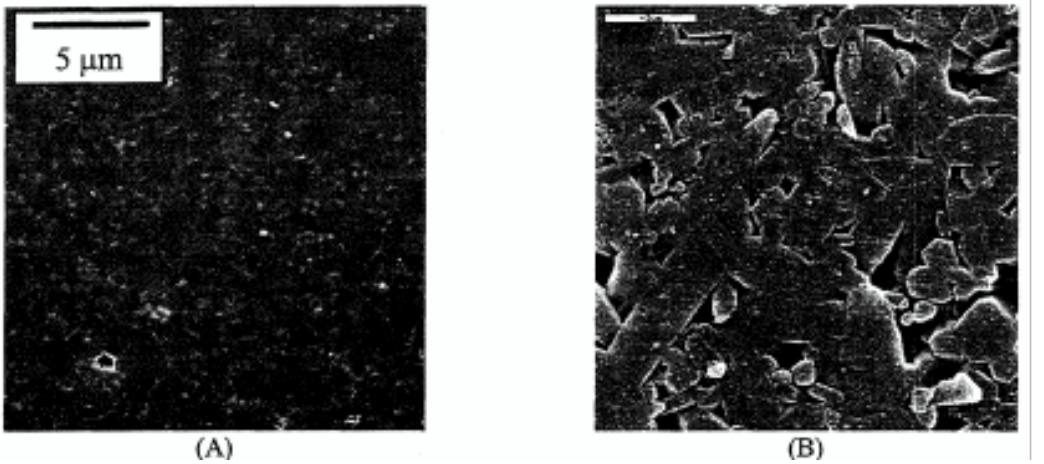
The microstructure of the powder bed is controlled by several variables including stability of the slurry, powder morphology, and the raster variables during the spraying process. Microstructure of powder beds was studied using mercury porosimetry and scanning electron microscopy (SEM). The green densities of powder beds was typically greater than 60% theoretical density and as high as 67%. Mercury porosimetry also indicated that the pore size distribution was uniform with a single population of fine pores. The densities and microstructure of Al_2O_3 powder beds prepared by the slurry-based 3DP process compare favorably with those prepared by slip casting. The densities of sintered

alumina powder beds are compared in Table 1. Polished cross-sections of sintered alumina and silicon nitride powder beds are shown in Figures 2 and 3, respectively.



(A) (B)

Figure 2. Polished cross-sections of samples sintered at 1650°C. Microstructure of slurry-based 3DP parts (A) are similar to powder beds prepared by slip casting (B). (Scale marker bar is 200 μm).



(A) (B)

Figure 3. Polished section of a sintered silicon nitride part made by 3DP (A). The section shown in (B) has been etched to reveal the structure of the silicon nitride grains.

Powder beds prepared by the slurry-based 3DP process do not contain lamination defects from the layered build process, but can occasionally contain a small number of pores in the 2 to 3 μm range, as shown in Figure 2A. The occurrence of these pores is related to improperly chosen parameters spraying of the powder bed. This dramatically illustrated by comparing surface profiles of sprayed lines separated by varying distance. Figure 4 shows such profiles for silicon nitride suspensions on a very flat slip cast support. The cross sections are perpendicular to the traversal of the spray head. The deposit from each individual line is trapezoidal in cross section and slightly less than approximately 300 μm wide at the top and has a base that is 400 to 500 μm wide. Two sprayed lines separated by less than this distance will overlap to produce a protuberance in the surface as observed in the surface profiles in Figures 4A and B. Larger sprayed line spacing leaves

a small gap as shown in Figure 4C. Also shown in Figure 4 are sections of sintered silicon nitride parts prepared with the corresponding sprayed line spacing. The occurrence of porosity seems to correlate with the production of gaps between individual sprayed lines. These small gaps between lines may not be filled when subsequent layers are deposited.

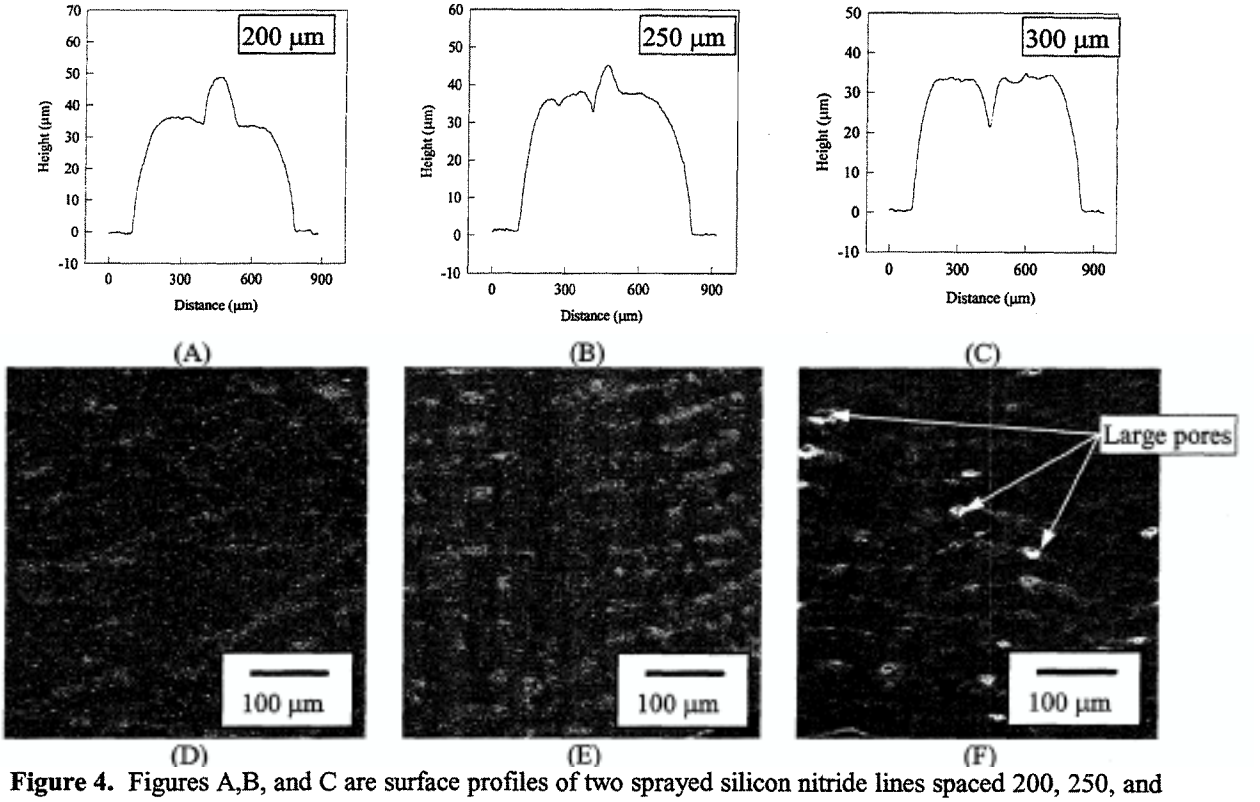


Figure 4. Figures A,B, and C are surface profiles of two sprayed silicon nitride lines spaced 200, 250, and 300 μm, respectively, apart on a slip cast bottom layer. Separation of sprayed lines by 300 μm or greater leads to a gap between the sprayed lines. Figures D, E, and F show the corresponding silicon nitride powder beds prepared with sprayed line spacing of 200, 250, and 300 μm, respectively, after sintering. The large pores in the microstructure coincide with conditions where the gap forms between two sprayed lines.

Binder selection and interactions

The binder systems used for the slurry-based 3DP process must meet several requirements. First of all, the binder needs to penetrate the powder bed and have sufficient strength to survive the part retrieval process. Secondly, the binder must be insoluble prior to redispersing the unprinted powder bed. The intrinsic properties of the binder are also critical to its performance in ink-jet printing and binder-powder interaction. Important intrinsic properties include surface tension, viscosity, conductivity, pH and chemical stability. Resolution of the printed part in the 3DP process mainly depends on binder-jet performance and binder-powder bed interaction. Low surface tension binder has high penetration rate and penetration depth, but it spreads more easily, reducing printing resolution as compared to high surface tension binder.

Three types of commercially available binder systems were examined- polymeric particle suspended binder (latex), wax emulsion binder, and homogenous solution phase binder systems. Latex binders do not infiltrate into the powder bed even if the individual polymer particles have smaller particle size than the mean pore size of the power bed. It is believed that the polymer particles tend to coalesce and form a surface film on the powder bed. The smallest particle size of polymeric particles examined was 14 nm in the Estek 1200 polyester latex as determined by dynamic light scattering technique. Even this latex forms a surface film. Wax emulsion binder also forms a surface film when it is printed onto the powder bed. However, during drying, the wax surface film easily melts and penetrates into the powder bed. Low melting point waxes such as carnauba wax and paraffin are preferred since they must melt to infiltrate the powder bed. Solution phase binders easily penetrate into the powder bed as long as the molecular weight of the binder is less than ~5,000. Solution phase binders must be cured at elevated temperature to strengthen the part and to make the binder insoluble in water.

Joncryl 52 is a water-based solution phase binder that has been used effectively. It is a styrene-acrylic copolymer with molecular weight 1800 and viscosity of 2.8 cps for a 10 volume % solution. Binder burn-out from the part is easily achieved during the firing cycle, and binder residue is not significant in the sintered component. Furfuryl alcohol resin has also been used as a solution phase binder. Furfuryl resin can be diluted in acetone to yield a low viscosity, low surface tension binder. These solution phase binders offer the ability to control both surface tension and viscosity. Penetration behavior of three different binder systems is summarized in Figure 5.

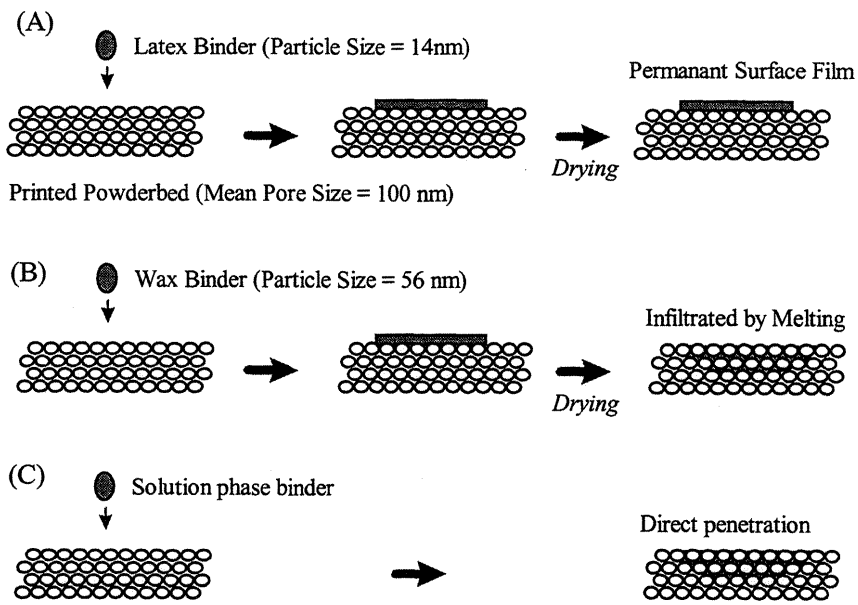


Figure 5. Schematic picture showing penetration behavior of three different binder systems.

Another important aspect of the binder system is the wetting behavior difference between the binder printed region and the unprinted region of the powder bed. Lamination defects

and surface roughness are observed when the wetting behavior differs substantially between the binder printed and unprinted regions. This wetting behavior difference depends on properties of binder materials. Aqueous slurries do not wet regions of the powder bed printed with wax emulsions due to the hydrophobic nature of the wax. Alcohol-based or aqueous-alcohol mixed slurries have a much lower contact angle and wet the binder printed regions more uniformly. Addition of a wetting agent into aqueous slurry also improves the wetting characteristics and consequently gives rise to better printed microstructure as shown in Figure 6. Triton X-100 surfactant decreases the contact angle of 35 v/o alumina slurry on paraffin substrate from 98° to 45° while maintaining a well-dispersed suspension state in the slurry.

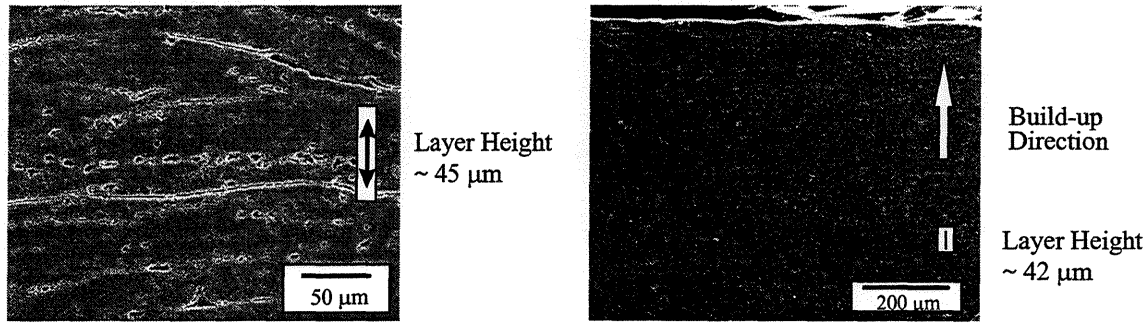


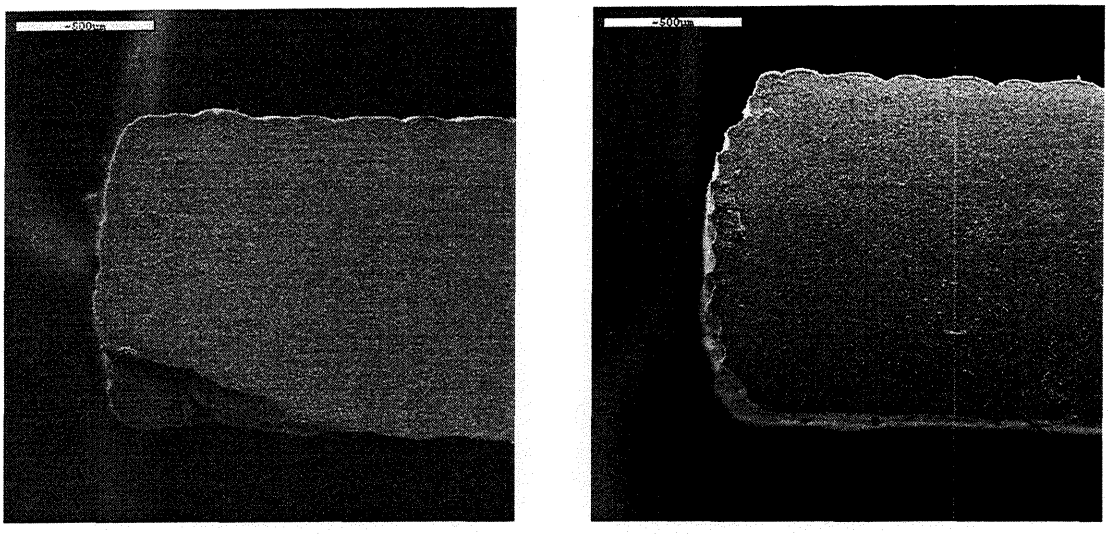
Figure 6. Cross sectional microstructures of sintered powder bed prepared with and without wetting agent in the slurry are shown in (A) and (B), respectively. Lamination defects are observed in (A) due to the wetting behavior of the slurry on binder printed regions.

Printed parts and surface finish

The effect of the amount of binder deposited on the microstructure of the printed part was studied in detail by varying binder flow rate, line spacing, print speed, and layer height. Single line primitives of binder printed into slurry-based 3DP powder beds have a semi-circular cross section compared to circular primitives that are observed for the standard 3DP process. The surface finish was found to be improved by printing with smaller layer heights. Figure 7 shows cross sections of alumina parts printed with 10 weight % Joncryl 52 solution. The edge of the part printed with 50 μm layers has a smoother surface finish compared to the part printed with 100 μm layers. Single line primitives with this binder are on the order of 150 μm thick. The surface finish begins to degrade and the edge of the part has a saw-toothed appearance as the layer thickness approaches the thickness of a single primitive.

Surface finish is also dependent upon the surface tension and viscosity of the binder system. Furfuryl resin binder has both low viscosity and surface tension (~23 dynes/cm) since it is diluted in acetone. Parts printed with furfuryl resin binder display the best surface finish among the binder systems. Figure 8 displays a cross section of an alumina part printed with furfuryl resin. The angled surface does not display stair-stepping that is

typical in most SFF processes, but printing resolution is substantially reduced due to significant spreading of the printed binder.



(A) (B)

Figure 7. Cross sections of alumina parts printed displaying the effect of layer height on the surface finish of the parts. Parts with 50 μm layer height (A) has smoother surface finish than parts printed with 100 μm layer height (B). Binder concentration is identical for both parts. (Scale marker bar is 500 μm)

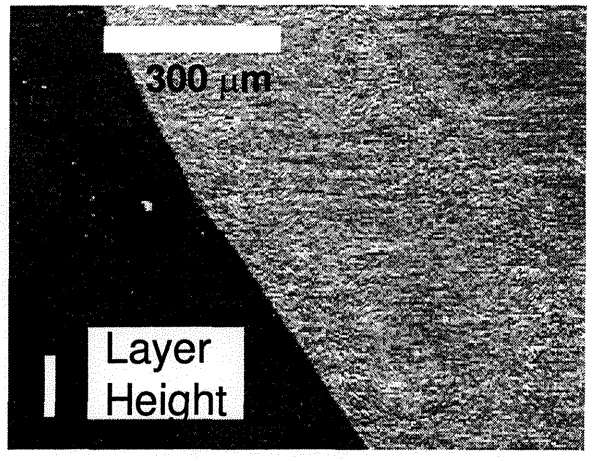


Figure 8. Cross section of alumina part printed with furfuryl resin binder. Angled surfaces do not display stair-stepping.

Parts have been printed with three ceramic materials systems to date: alumina, silicon nitride, and lead zirconate titanate (PZT). Two simple silicon nitride parts are shown in Figure 9 and a bisque fired cross section of one such silicon nitride part is shown in Figure 10. The sample remains porous upon bisque firing and does not shrink. The mounting material is observed to creep into the pores near the surface of the bisque fired sample and is the cause of the different contrast near the sample surface. The bisque fired

section is used to estimate the dimensional accuracy of the slurry based 3DP process. This is a fifty layer part which consists of a flat base with middle section of which rises above the base. The middle section is nine lines wide. A Joncryl 52 solution is used as the binder with a 300 μm line spacing. The binder flow rate is such that this spacing results in a part that is 3.4 wt. % binder. Also, the spcaing is such that the edge lines of the middle section are printed 2700 μm apart. Measurements of the binder spreading in silicon nitride powder beds reveals that individual lines of printed binder are on average 342 μm wide. The expected middle section width is, therefore, 2700 μm plus 342 μm or 3042 μm. The measured value is 3110 μm with an absolute error of 68 μm or 2%. More work is needed to refine the process planning rules to account for such systematic errors.

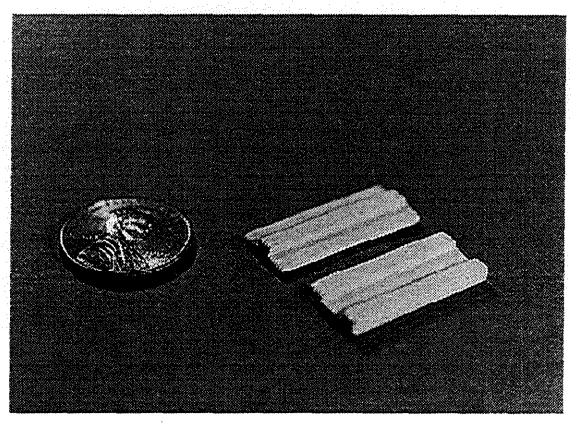


Figure 9. Two simple silicon nitride parts used for dimensional testing.

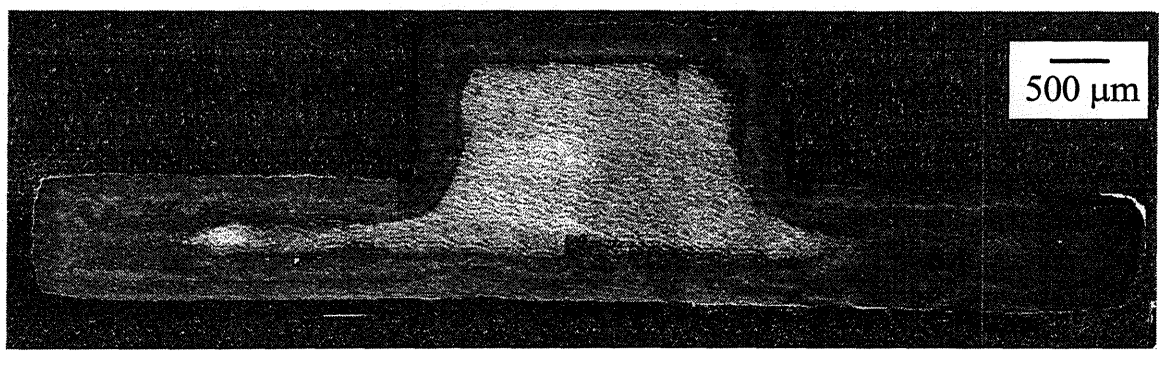


Figure 10. A cross section of a bisque fired silicon nitride part shown in Figure 9. The material with different contrast near the surface of the sample is the result of mounting material only partially permeating the porous sample.

Conclusions

The slurry-based 3DP process has been used successfully to prepare high green density components with fine-grained ceramics. Improved surface finish is possible by controlling the properties of the binder system and reducing the layer height. The process is generic and can be readily adapted for new materials systems by optimizing the stability of the slurry. Our future work will be to refine the process planning so as to more precisely control the final component dimensions.