Slurry-Based 3DP and Fine Ceramic Components

M.J. Cima, M. Oliveira, H.R. Wang, E. Sachs, and R. Holman

Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA, 02139.

Abstract

Slurry-based 3Dp\textsuperscript{TM} (S-3Dp\textsuperscript{TM}) is a solid freeform fabrication technique developed at MIT for production of fine ceramic components with complex geometries and fired densities in excess of 99% of theoretical density. Current research involves identification of the factors controlling minimum feature size in S-3Dp\textsuperscript{TM}. The ink-jet printed binder droplet size is the primary factor controlling the minimum feature dimension when deposited on the powder layers. For a given droplet size, however, a balance between spreading of the binder solution on the surface of the S-3Dp\textsuperscript{TM} powderbed and infiltration determine the feature size, while interactions between the polymeric binder and the powder surface (polymer adsorption) control the minimum feature cross-section. Droplet-on-demand printing of the binder solution has been introduced to improve resolution, decreasing the minimum feature width from 300 µm to less than 150 µm.

Introduction

Three Dimensional Printing (3Dp\textsuperscript{TM}) is a Solid Freeform Fabrication (SFF) technique developed at MIT. As with other SFF techniques it is a process based on using sequential 2D slices of an image to build up a 3D component. Presently there are two main approaches to 3Dp\textsuperscript{TM}, traditional 3Dp\textsuperscript{TM} and S-3Dp\textsuperscript{TM}. The difference between the two lies in the method used to form the sequential layers in which the 2D slices are deposited. Previous research has focused on dry powder spreading methods such as shown in Figure 1 where a vibrating roller spreads dry powder from a reservoir over a piston to form a layer. A 2D image of the component cross section is generated from a CAD file, and this image is deposited into the powder layer using inkjet printing. The powder particles are bound together in only the areas where printing occurs. The process is repeated until a complete 3D part is formed within the bed. Powder in the areas where binder is not deposited is excess and provides support to the part being generated.

![Figure 1: Schematic of the traditional (dry-powder) 3Dp\textsuperscript{TM} process.](image)

3Dp\textsuperscript{TM} and S-3Dp\textsuperscript{TM} use the same methods for depositing binder. Each layer is, however, formed in S-3Dp\textsuperscript{TM} by slip casting a slurry of ceramic powder onto a porous substrate which is mounted on a piston. S-3Dp\textsuperscript{TM} has been described in detail by Grau\textsuperscript{1} and is shown schematically in Figure 2. Individual green layers are formed by rastering a jet of ceramic slurry (typically ~30 vol.% ceramic in a water, water-alcohol, or alcohol vehicle) over a porous substrate. The individual jetted beads slip cast and stitch to one another and to the previous layer. The slurry
solids loading, the volumetric flow rate of slurry, the spacing between raster lines, and the cast (green) density of the layer determine the green layer thickness. A drying step removes the excess solvent/dispersing medium. Binder is then printed in a manner that is identical to that used in traditional (dry powder) 3DPTM. Continuous ink-jet printing is practiced by pressurized flow of an electrically grounded solution through a ruby orifice. The resulting stream breaks up into droplets at the Rayleigh frequency by a piezo and is raster scanned across the surface of the powderbed. The stream off droplets can be turned “on” or “off” to define the part edges by charging the droplets and deflecting them into a catcher, as shown in Figure 3. The surrounding green powderbed acts as a support structure for thin sections and overhangs, as in traditional 3DPTM. The binder system currently used is a solution of polyacrylic acid, PAA (MW 60000), from 2 to 5 vol.%, either aqueous or in ethanol. Glycerol is added to the solution to cross link the binder during subsequent curing. The printed green components are contained in the slip cast block of green ceramic (the powderbed) upon completion of the building process. The powderbed is heated to 150°C for an hour in Argon to cure the binder and make it insoluble. The entire block is then submersed in water (or in some cases ethanol), and the un-printed region redisperses, swells, and sloughs off, leaving the printed component. Polyethylene glycol (PEG, MW 400) is added to the ceramic slurry to aid in this redispersion process. Minor sonication removes any residual powder contained in internal structures.

Figure 2: Schematic of the Slurry-Based 3DPTM (S-3DPTM) Process.

Figure 3: Schematic of continuos jet print-head turned “Off”
Line merging is a new layer forming method that avoids inter-line defects and reduces the line ridges (roughness at the top surface of the bed) seen in rastered powderbeds, while offering the potential for higher production rates. These failings of the conventional jet rastering layer forming method required that a more continuous slurry spreading process be developed to minimize or eliminate the line ridge defects. In the new line merging approach, the nozzle path of conventional jet rastering is maintained, but the inter-arrival time is reduced dramatically through machine design, and the slurry chemistry is adjusted to slow the rate of slip casting. Thus, the jet rastering approach is made to approximate a continuous deposition process, as follows: If the inter-arrival time is reduced enough, line N+1 is deposited before line N is fully slip cast, and the curvatures of the wet lines merge seamlessly together into a uniform “wet front” which advances steadily across the powderbed, as seen in Figure 4. Polito\(^2\) implemented this approach and showed that the resulting powderbed had significantly reduced line ridge and inter-line defects.

![Figure 4: Schematic diagram of line merging concept](image)

Printing style can affect printed part definition. The conventional print style is to raster the binder nozzle across the powderbed surface. Alternatively, a vector approach can be used where the outline of the part is first traced with the binder stream then the interior of the part is printed with the raster-type method. Vector printing the parts in this manner requires a much lower droplet frequency and more control on the placement of each individual drop than CJ printing could offer. Drop on Demand (DoD) printing provides this by generating each drop with a specific electronic waveform applied to a piezo. The waveform expands then contracts the hollow cylindrical piezo around a steel tube carrying the binder, creating one droplet. DoD printing generates droplets in the range of 1kHz while CJ printing operates at 25-60kHz. Figures 5(a) and 5(b) show the difference in droplet placement between raster-style printing and vector-style printing.

![Figure 5: Comparison of drop placement in a) raster style and b) vector style printing](image)
Surface Roughness

The roughness of the top surface of printed parts originates from the layer forming method. Each deposited line of slurry slip casts before the next is deposited and naturally form a rounded shape with conventional slurry jet rastering. This process results in “ridges” along the width of the completed layer which transfer to the printed part. Slurry line merging, described above, attempts to overcome this problem. Figure 6 compares images of two powderbeds as well as laser profilometry measurements made of the beds².

![Cross Section Profile: No Merging](image1.png)

![Cross Section Profile: With Merging](image2.png)

**Figure 6:** Top: Image of conventional (left) and merged (right) alumina powderbed. Bottom: Profilometry measurement of conventional (left) and merged (right) bed.

The roughness on the vertical sidewalls of a printed is controlled by binder droplet registration and by the shape of the binder primitive. Droplet registration depends on the capabilities of the machine used as well as the stability of the binder stream. The binder primitive is the shape that a single printed line (or droplet) of binder creates in a powderbed and is shown in Figure 7. The aspect ratio of the primitive, the ratio of the width to depth, is controlled by binder adsorption to the particles as well as the liquid infiltration behavior of the binder. A lower aspect ratio primitive allows for lower sidewall surface roughness. The height of each layer and the amount of binder printed must be set to values where the layer height is in the approximate proportion shown in Figure 7³.
Figure 7: Cross section of binder primitive formed with CJ printing in an alumina powderbed. Hatched lines show proportion of layer height to binder primitive to reduce sidewall roughness.

The roughness of the bottom surface of printed parts can be represented by the image shown in Figure 8(b). Bottom surfaces exhibit low roughness. This can be attributed to the large amount of overlapping of binder primitives that occurs within layers of printed parts.

Figures 8: Images showing a) sidewall and b) bottom surface roughness. Images are of S-3DP™ MR2 components.

Layer Height

The controlling parameters for the height of a jetted layer of slurry are the slurry flow rate, nozzle diameter, raster line spacing, nozzle raster speed, and the packing fraction of the slip cast. Presently, the smallest layer height achieved with S-3DP™ is 13 µm, using an alumina slurry.5 The maximum layer height is set by the Critical Saturation Thickness (CST) and is discussed in detail by Grau1. The CST defines the maximum thickness that powderbed can be 100% saturated with liquid before cracking of that layer occurs due to drying stresses. The surface tension and pore size both affect the value of the CST, with larger pores and lower surface tension increasing the CST.

Line Width by CJ and DOD Printing

Large area AC plasma display panels (PDP) usually employ a barrier rib structure to separate the sub-pixels of red, blue and green colors. To achieve high image quality, the barrier ribs must have high dimensional accuracy. S-3DP™ offers the potential of producing large size components while retaining high dimensional accuracy. Uniform ribs have been produced by CJ printing using a binder nozzle size of 30 µm and alumina as the material system to demonstrate the capability of S-3DP™. The rib width of 300 µm shown in Figure 9 was obtained after sintering, while the green rib width was about 330 µm. This is still larger than the required
width for PDPs but the rib width can be reduced further by increasing the printhead velocity and by decreasing the size of binder printing nozzle and binder flowing rate. Another method to reduce the printing line width is S-3DP™-DoD printing. The minimum line width presently achieved with DoD printing in alumina with an average droplet size of 40 µm is 150 µm⁶, as shown in Figure 10.

Figure 9: Optical microscope cross section image of the S-3DP™ ribs

Figure 10: The minimum line width produced by vector DOD printing

Edge smoothness has also been improved with the DoD printing. The cross section of the printed RF filter is shown in Figure 11⁷. The edges in Figure 11 are smooth and show high accuracy of definition. The mm-wave package in Figure 12⁷ also shows sharp and accurate edge definitions.

Figure 11: SEM cross section image of the S-3DP™ RF filter

Figure 12: Green S-3DP™ mm wave package

Structures, such as EBG (electromagnetic band gap) devices and RF filters, with through and blind holes have been produced by the DoD printing. Figures 13(a) and 13(b) show the front and rear views of the S-3DP™ RF filter while Figures 14(a) and 14(b) show those of the S-3DP™ EBG device⁷.
Complex structures with higher accuracy for various applications can now be produced using S-3DP, as shown in Figures 15, 16, 17, 18, 19, and 20. The green packing density of the parts is higher than 58% and therefore the final density with more than 99.9% of the theoretical density after sintering is easily obtained.

**Conclusion**

Slurry based Three Dimensional Printing has been shown to fabricate high-density ceramic components of complex geometry. S-3DP™ component production has been achieved with alumina, titania, silica, silicon nitride, MR2, and Tungsten Carbide-Cobalt with no foreseeable material limitations. The results presented for the process capabilities can still be optimized for further accuracy or resolution and systems for mass production are under development.

**References**

2. Polito, Ben., unpublished work.
5. Li, Yawen, personal communication.

Figure 15: Green and dense BaTiO$_3$-based RF filters

Figure 16: Green and dense BaTiO$_3$-based EBG devices

Figure 17: Dense Al$_2$O$_3$ stator

Figure 18: Dense Al$_2$O$_3$ toroid

Figure 19: Dense Al$_2$O$_3$ rotor

Figure 20: Dense Al$_2$O$_3$ sample geometry