Computer-derived microstructures by 3D Printing: Bio- and Structural Materials

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Abstract

3D Printing is a rapid prototyping technique to manufacture functional components directly from computer models. The process involves spreading the powder in thin layers and then selective binding of the powder using a technology similar to ink-jet printing. Layers are added sequentially until a part is completed. 3DP has been used to make complex-shaped components from several monolithic materials, including components for use in structural applications. This paper focuses, however, on the ability to control microstructure and local composition by 3DP. We envision cases where computer derived-microstructures can be created by appropriate control of the printing parameters. Thus, one can build components with the desired microstructure independent of the complexity of the desired shape. Examples for both structural materials and biomedical devices are discussed.

Introduction

Three Dimensional Printing (3DP) is a solid free-form fabrication (SFF) method used to create components directly from CAD representations and has been described in several publications[1-3]. Briefly, 3DP creates parts by a layered printing process. The information for each layer is obtained by applying a slicing algorithm to the computer model of the part. An individual two-dimensional layer is created by adding a layer of powder to the top of a piston and cylinder containing a powder bed and the part being fabricated. The new powder layer is selectively joined where the part is to be formed by "ink-jet" printing of a binder material. The piston, powder bed and part are lowered and a new layer of powder is spread out and selectively joined. The layering process is repeated until the part is completely printed. Removal of the unbound powder reveals the fabricated part. The process has been primarily applied to ceramic molds for metal casting. More recently, however, it has been used to make metal parts directly[4], structural ceramic parts[5], and polymer parts[6].

3DP is one of the most flexible SFF technologies. The process can create parts of any geometry, including internal volumes (as long as there is a hole for the loose powder to escape). The support gained from the powder bed means that overhangs, undercuts, and internal volumes can be created. 3D Printing can form any material that can be obtained as a powder. Further, because different materials can be dispensed by different printheads, 3D printing can exercise control over local material composition. Material can be deposited as particulate matter in a liquid vehicle, as dissolved matter in a liquid carrier, or as molten matter. The proper placement of droplets can be used to create surfaces of controlled texture and to control the internal microstructure of the printed part.

The ability to control local composition is a unique feature of 3DP and is the major focus of this article. This type of control permits fabrication of materials with computer derived microstructures or spatially controlled compositions (SCC). These are components in which their microstructure is designed on a computer and built via the 3DP process. 3DP can selectively deposit matter within the structure of a component so that composition can vary from point to point. The macroscopic shape of the component can, however, be specified completely independently. Thus, we envision components where both the macrostructure and microstructure are designed by computer and constructed by 3DP. Potential applications of such a technology are numerous, such as components with anisotropic mechanical properties, microengineered porosity, or constructing composite multilayer modules for electronic packaging. Conventional powder forming technologies cannot provide simultaneous microstructure and macrostructure control. Thus, demonstration of this approach will be a quantum leap beyond current material fabrication and will create a technology that is not unlike the control that photolithography provided the electronics industry.

Structural ceramic components

We have recently modified the 3DP process under ARPA/ONR support to produce alumina components which are greater than 99.3% dense after firing and have average flexural strength of 360 MPa[7]. Sintered silicon nitride parts with average flexural strengths of 570 MPa have also been made by 3DP[8]. The basic elements of the modified process are to spread submicron alumina powder and print latex binder. Green parts are isostatically pressed and sintered to densify the component. The polymeric binder is removed by thermal decomposition prior to sintering.

SCC for structural materials can have many benefits and unusual features. For example, gradual blending of materials with different coefficient of thermal expansion (CTE) is possible with 3DP. Metal parts with surfaces that are ceramic-rich can be made for high temperature applications or for improved wear resistance. Internal residual stresses can be modified with second phases to strengthen or toughen materials. These are just few of the possible applications of 3DP in SCC.

The current 3DP process involves printing of continuous binder jet onto powder bed. Consequently, the ability to prepare a stable dispersion becomes a determining factor for the size and amount of particulate second phase in the final part. Agglomeration in the binder system causes improper nozzle performance and reduces dimensional accuracy and

resolution. Khanuja has established a preparation and filtration scheme for fine alumina dispersion.[9] In his study, electrostatically stabilized submicron alumina dispersions were tested. Alumina slurry with up to 40% in volume has been successfully dispensed through typical nozzle for 3DP. Calculations indicate that the maximum volume fraction of second phase that can have come through nozzle with the current 3DP process is 30 vol% of final parts. However, modifications to the process routes such as the multiple printing cycle per layer and use of porous powder bed may allow the fabrication of parts with larger amounts of second phase.

Zirconia toughened alumina (ZTA) system was chosen as the first model composite system and this system requires only 15 to 20% zirconia dispersed in alumina to attain optimum strength[10]. Fine zirconia particle size and narrow size distribution is also required. These requirements match precisely with the capabilities of current 3DP technology. Simple calculations suggest that one only needs to prepare a zirconia slurry of 12.5 vol% solids loading to fabricate parts with 15 vol% zirconia. Khanuja's success with printing 40 vol% alumina slurries suggest a high probability of success with 15 vol% zirconia system. This makes the ZTA system as a perfect candidate for the first SCC system to be explored by 3DP.

ZTA consists of fine, uniformly dispersed zirconia particles in the matrix of alumina. The unusual phase change in zirconia upon cooling

$$ZrO_{2\ \text{tetragonal}} \Leftrightarrow ZrO_{2\ \text{monoclinic}}\ (1170°C)$$

is the basis of the toughening mechanism in this material system. Three to five percent increase in volume and shear accompanies the tetragonal to monoclinic phase transformation. The high strength and toughness of ZTA are results of absorbed energy during the phase transformation of zirconia particles around the crack tip. The fracture energy required to propagate the crack front increases due to the transformation. Volume expansion of the precipitates also causes strengthening[11]. Expanded monoclinic precipitates cause compressive stress build up on the crack tip. Surface grinding of a ZTA part induces the phase transformation near the surface and leads to residual compressive stress[12]. Various techniques developed to fabricate ZTA with thermally inert compressive surfaces include heat treatments in destabilizing atmosphere and surface coating steps[13-18]. Often these processes require prolonged heat treatments and present manufacturability concerns. 3DP technology can be implemented to fabricate ZTA with built in compressive layer by exercising the spatial control of composition.

3DP can be used to deposit zirconia slurry onto a bed of alumina powder to create a green ZTA part with controlled zirconia distribution. Realization of this concept is illustrated in Figure 1. Cross sections of each line printed with 5 vol% zirconia demonstrates 3DP's ability to control the zirconia content in microstructural level. Although Figure 1 shows the first ZTA part with only one zirconia composition, two or more nozzles can be used to deposit zirconia slurries of different stabilizer contents. For example, pure zirconia slurry can be printed in the regions where spontaneous transformation to monoclinic phase is desired. Yttria doped zirconia may be deposited in the rest of the part where the presence of metastable tetragonal phase is preferred. Thus, ZTA parts with user specified residual stress profile can be fabricated by manipulation of

the 3DP process. such as those with surface compression stresses or with a duplex ZTA microsturcture.

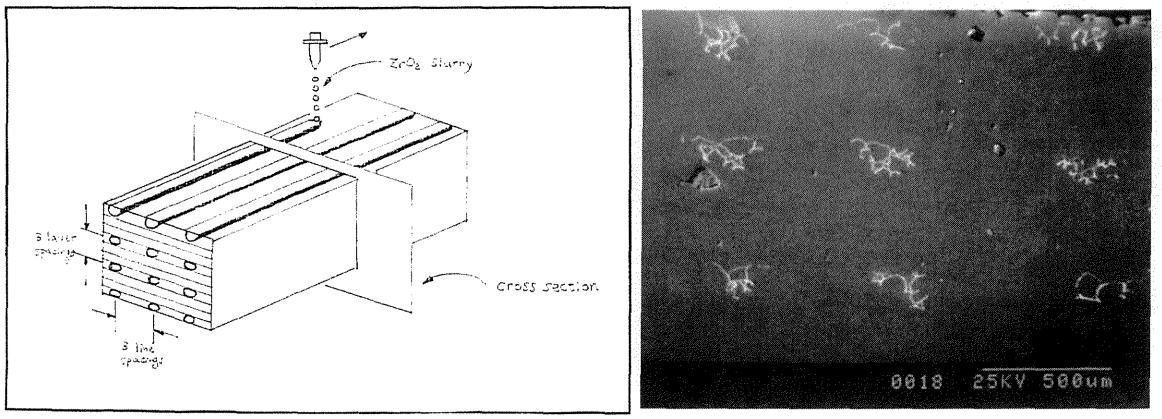

Figure 1: Schematic of the first 3DP-derived ZTA part is shown on left. 5 vol. % ZrO_2 slurry was printed on Al_2O_3 powder. A cross-section of the CIPed and fired sample is also shown. Each bright feature is a cross-section of a printed line.

Advanced materials for medical devices

Computer-derived microstructures such as for SCC and functionally gradient materials (FGM) have several medical applications such as drug delivery devices and structures for tissue regeneration. Our focus has been to demonstrate use of biomedical polymers with the 3DP process for both of these applications[6,19]. Attempts to control drug release rates of implantable and oral drug delivery devices (DDD) by manipulating the geometric structure of the devices have been reported. Cylindrical rods with internal pie shapes, inwardly-releasing hemispheres, and cylindrical donuts, represent attempts to affect release rates by modifying macroscopic shape[20]. These complex shapes are, however, not easily produced by conventional methods. Conventional manufacturing techniques also tend to produce homogeneous blends of the drug and matrix material[21]. The ability to control local composition, microstructure, and spatial distribution of drugs, makes 3DP a viable processing technique for construction of DDD. Prescriptive dosage regime DDD with controlled gradients in drug composition and matrix microstructure can be created by 3DP. The mechanism of resorption can be controlled by selecting the appropriate binder material.

Tissue regeneration devices are structures used as the matrix for tissue growth during healing. These devices are proposed for use in cases where natural tissues have been damaged by disease or trauma. Generally these materials are resorbable and ultimately become natural tissue, such as skin, cartilage, bone, and organ tissue. Medical procedures based on this approach are being developed for a number of applications. Numerous authors[22-25] have reported that optimal devices require control of their structure over several levels of structural hierarchy, including gross macroscopic shape, oriented pores

and channels, and microporosity. The ability to preferentially promote cell migration and angiogenesis, for example, can be accomplished by directing nutrient delivery in a complex cell seeding structure. Precise structural control beyond random microporosity has not been achieved by conventional processing methods. The potential to also intimately control the orientation and placement of porous channels and the overall macroscopic shape of a device makes 3DP an ideal process for producing tissue regeneration devices. Below we describe several devices that demonstrate reticulated structures.

Polyethylene oxide (PEO) and polycaprolactone (PCL) are selected as matrix materials for trial experiments and methylene blue and alizarin yellow were used as drug models. The dye release kinetics is controlled by either specifying the position of the dye within the device or by controlling the local microstructure with the 3DP process. The dye release rates of the devices are characterized by placing single devices into individual beakers filled with 10 ml water at room temperature (20°C). Sample solutions are collected, and fresh 10 ml of water is replaced at appropriate time intervals. Absorbance for methylene blue (664 nm) and alizarin yellow (353 nm) is measured for all samples on a DU-640 spectrophotometer. Spectrophotometric analysis of dye release yielded reproducible results. Three examples are described below.

The model device used for this study is designed to demonstrate regulation of drug release profiles by controlling position, composition, and microstructure. A diagram of the device is shown in Figure 2a. The top and bottom of the tabular device are composed of relatively nonresorbable PCL while the interior layers are composed of PEO bound by printing binders solutions so as to form perpendicular walls in the interior of the device. Dyes are deposited in selected locations within the device during the build procedure. The top and bottom sheets of dense PCL serve as barriers against dye diffusion since hydrolytic degradation of PCL occurs much slower than that of PEO. Therefore dye diffusion during resorption is confined to the plane of the device since the top and bottom are only slowly resorbable. Figure 2b shows the diagram and release profile of a device with symmetrical spatial distribution of the two dyes and uniform matrix gradients. All walls in this device are identical since they are constructed with the same binder composition, under the same printing conditions. As expected, the blue and yellow dyes are released at identical rates to within the statistical error of the experiment.

One of the printing parameters which can be modified to regulate release rates is the inter-line spacing of the lines which make up the walls. The walls of the device in Figure 3a are chemically identical, but physically different. Six solid walls are built in one direction by printing four lines closely together. Then six walls are constructed in the perpendicular direction by printing only two lines, separated from each other by unprinted powder. All walls are constructed to the same total thickness. The device shown in Figure 3a demonstrates that for walls of equal thickness and composition, modification of internal wall microstructure can affect the release rate. Here, the dyes limited by solid walls (4 connected lines per wall) are released at a slower rate than dyes limited by semi-solid walls (2 lines per wall, spaced apart by unprinted PEO powder). It should be noted that other printing parameters, such as printhead traverse velocity, binder flow rate, and layer thickness, can also be controlled to modify release rates. 3D Printing also feature the ability to control the relative position of the dye to the diffusion barrier. In the device

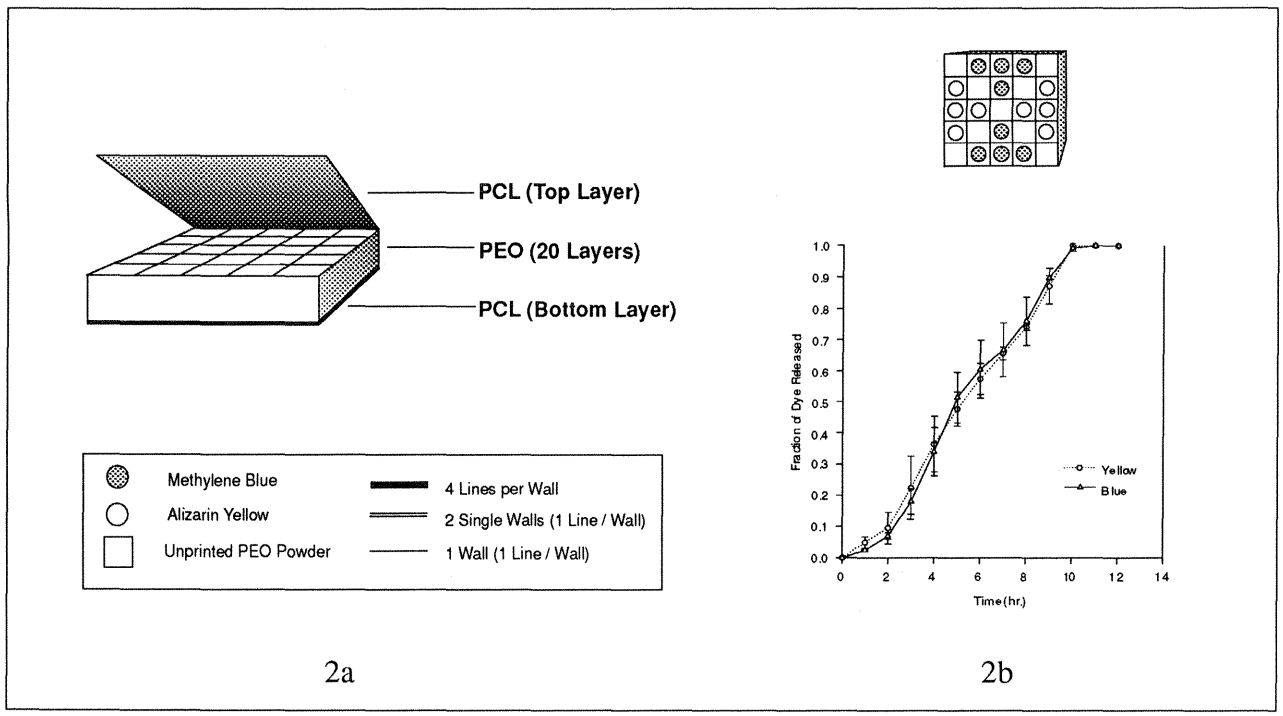

Figure 2a: Diagram of the model drug delivery device.
Figure 2b: Release profile of device with equal spatial distribution of dyes, and identical wall structures.

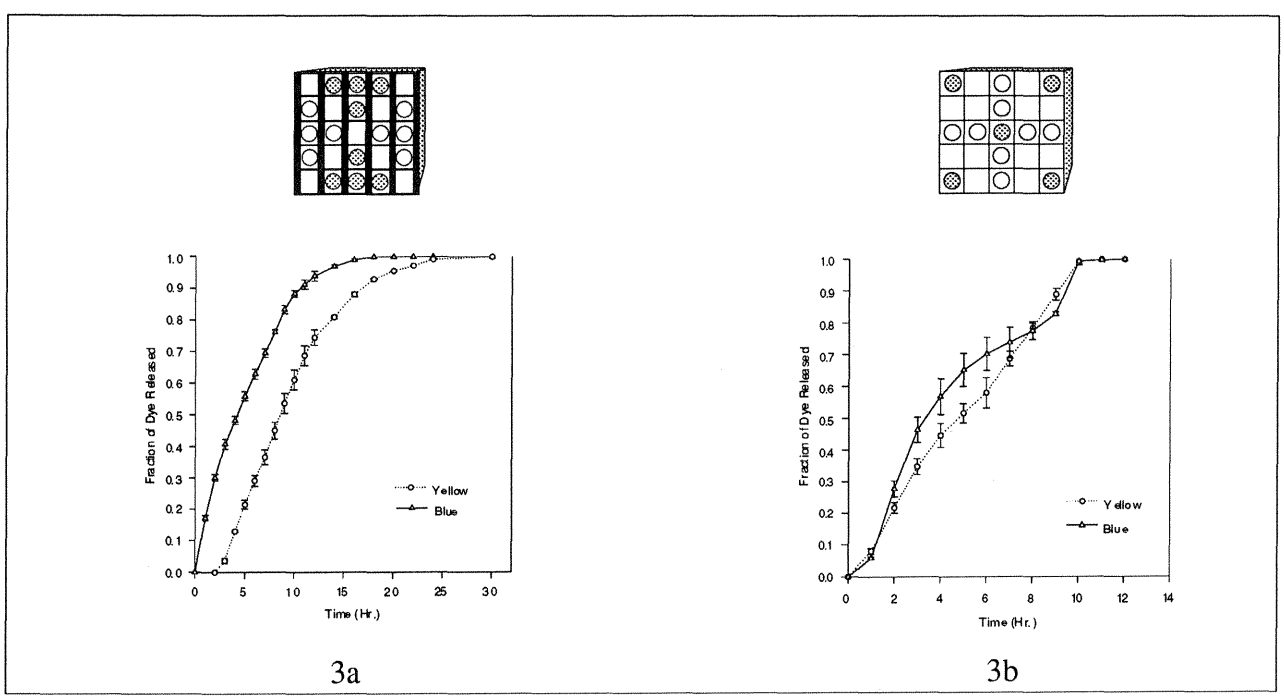

Figure 3a: Release profile is affected by controlling microstructure.
Figure 3b: Release profile is affected by controlling spatial distribution of dyes.

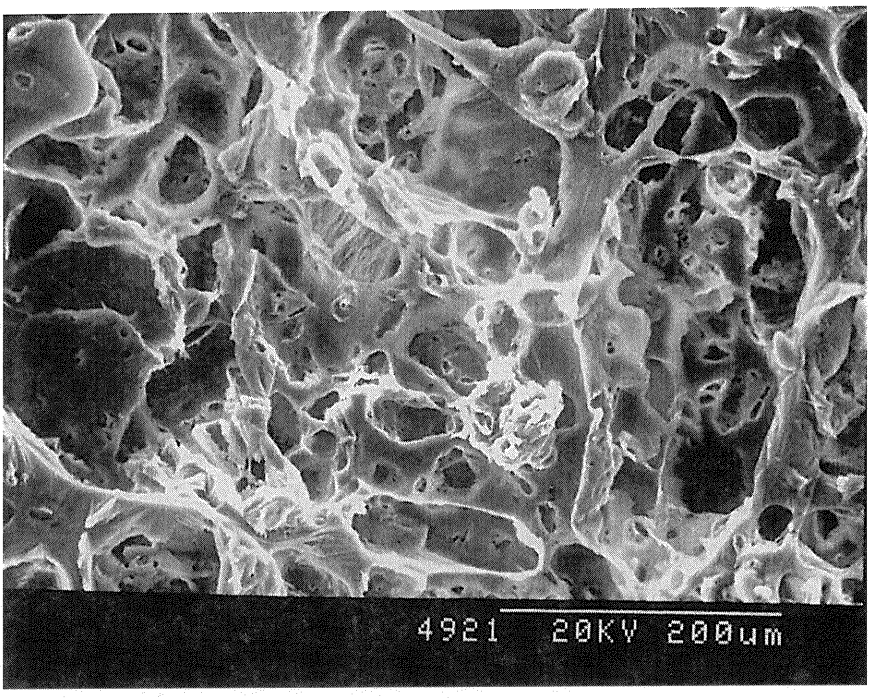

Figure 4: Binder: 30 wt% acid modified PCL in chloroform; Binder per Line Length: 2.85 x 10^{-4} cm^3/cm; Powder: NaCl 75-150 um; Layer thickness: 150 um; These devices were leached in water for 24 hours after printing and drying to produce the microporosity visible.

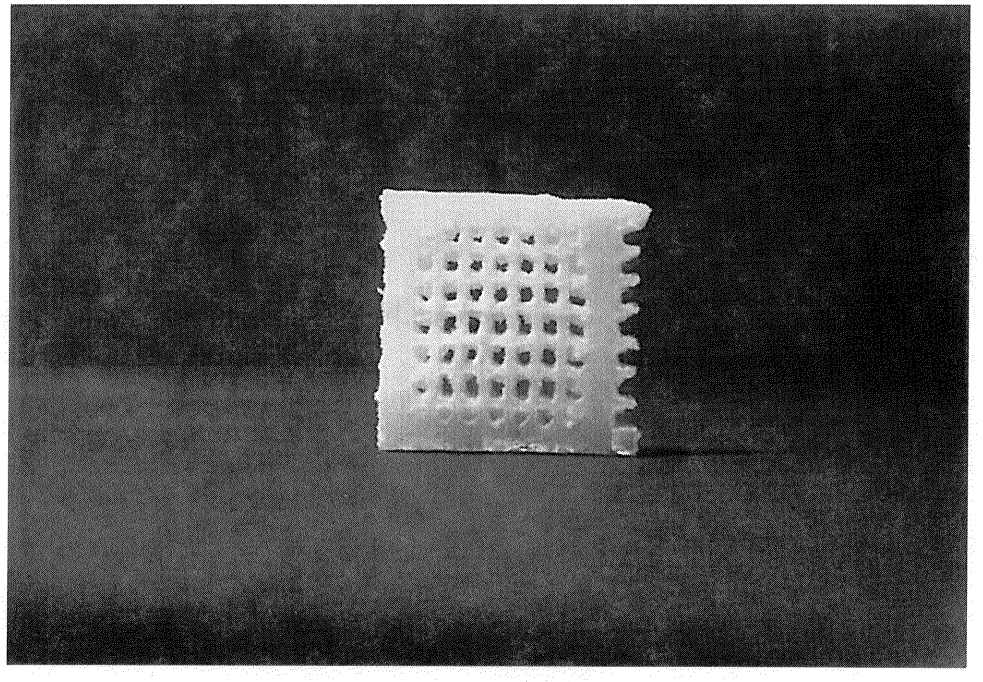

Figure 5: Binder: 26.5 wt% acid modified PCL in chloroform; Binder per Line Length: 3.33 x 10^{-4} cm^3/cm; Powder: PCL 75-150 um; Layer thickness: 250 um; This device was printed horizontally (vertical direction in figure) to produce regions with different density. The figure shows a cross section of this device. Note the outer channels that are not completely open due to bleeding of the binder into those regions.

shown in Figure 3b, the walls are identical in both directions. The difference in release patterns for the two dyes can only be attributed to the difference in spatial distribution of the dyes within the device. This release profile exhibits two maxima in the methylene blue release rate and a relatively constant release rate of alizarin yellow.

Interconnected pores on the order of 50-250 μm within a device provide a structure for cell proliferation, migration, excretion of matrix materials, and blood vessle formation. Pores with width greater than approximately 100 μm can be built directly with the 3DP process. Building a device with smaller pores requires the inclusion of a leachable component. This leachable component can then be removed after printing. An example of the microporosity created by this process is shown in Figure 4. These pores are of the correct size for viable cell function and angiogenisis. The powder bed material, in this case NaCl, has been completely leached out of the final device. Thus, the device is the first 3DP device of any kind to consist only of material delivered through the printhead. Other 3DP devices incorporating natural materials, such as bovine bone, have been constructed. In this case, bone powder was mixed with PCL powder. A solvent polymer solution was used as the binder.

A cross section of a macroscopic device constructed with PCL and polymer solution is shown in Figure 5. All of the interior channels are open, but some of the channels near the dense, high binder delivery regions are obstructed. This is likely due to the bleeding of some of the binder into the void regions.

Final perspective

This brief report represents some of the first experiments to exploit the unusual capabilities of solid-free form fabrication methods. We have already demonstrated unprecedented control of microstructure and local composition using the 3DP method, but other SFF technologies will undoubtedly be used along similar lines. Never before have materials and product designers had the ability to specify structure on the macro *and* micro level. The number of possible applications seems innumerable. Indeed, our most difficult task may be to select applications to develop first. An important consideration for selection of the appropriate process will, however, be the production rate. Components with unique microstructures will only be useful if thousands of parts can be made. 3DP may be uniquely qualified to address this manufacturing issue. Multijet printing is now possible on 3DP machines as has been demonstrated at Soligen[26] and at MIT. This has dramatically increased the production rate of the 3DP process. Commercial ink-jet print heads are available with thousands of individually controlled jets. Thus, future 3DP machines may be closer to production tools rather than tools for prototyping.

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