Fused Deposition of Ceramics: Progress Towards a Robust and Controlled Process for Commercialization

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The feasibility of using the Fused Deposition of Ceramics (FDC) process to rapidly fabricate functional quality advanced ceramic components has been demonstrated[1-5]. *This direct manufacturing technique, by eliminating the need for costly tooling, dramatically reduces functional prototype development time. This makes it suitable for small quantity production runs and complex parts. The move from "feasibility" to a robust, reliable commercial fabrication tool requires that every aspect of the manufacturing be understood and brought under control. An overview of the five basic process steps in FDC: batch compounding, filament fabrication, fused deposition, binder burnout and sintering will be presented in light of this drive toward a robust process. Tools such as Statistical Process Control and Experimental Design techniques are being used to monitor, improve, and stabilize each step and sub-process. Hardware and software modifications have been made to the FD machine to effect the required changes. This paper will identify the remaining technical barriers to commercialization and our progress in addressing these issues.*

I. Introduction

Direct fabrication of ceramic components using SFF techniques has created an opportunity to reduce lead times and costs in the development of new products. The Fused Deposition of Ceramics process uses a ceramic/polymer filament as feed material to build a part from a CAD file by additive layering. The binder is then removed and the part is sintered to full density. In order to apply this process to existing commercial manufacturing needs, effort has been directed to reduce variability and increase robustness. A reproducible, predictable process creating final parts of specified dimensions and strength within 6σ deviation is crucial for commercialization.

Due to the sequential, "building block" nature of the FDC process, upstream material- or process-variability can result in major part defects such as voids, cracks, and warpage; this is a common issue for conventional ceramic processing. Batch-to-batch variability results in unpredictable filament quality, and operator responses to this deviation often introduce new process variables. It is difficult to isolate the root causes of technical hurdles, such as material contamination, filament buckling, voids and surface irregularities in the FDC parts, and irregular shrinkage, without establishing a baseline process. However, due to time constraints of the program, many of these issues were attacked concurrently. Where the problems could not be eliminated or contained, they were quantified, possible root causes were identified, and experiments were planned.

The first step to process improvement was run-charting, tracking experimental data through time. This evolving database will yield Quality Control measures such as target and limits, introducing Statistical Process Control. Standard Operating Procedures were established to lessen operator-to-operator variability, and environmental controls were digitized. The FDC steps were characterized by measuring viscosity, modulus, and material content in each batch. The application of Design of Experiments (DoE) methodology to FDC sub-processes identified effective parameters and optimized conditions quickly.

II. Batch Compounding and Filament Fabrication[2,3]

The ceramic system employed in this study is an *in situ*-reinforced Si_3N_4, commercially supplied by AlliedSignal (Ceramic Components, Torrance, California) as GS-44. The powder is coated with a surfactant, oleyl alcohol, in a batch ball-milling process. The coated powder is compounded with the proprietary binder system, designated RU9 (Stratasys, Inc., Eden Prairie, Minnesota), in a torque rheometer. The compounded material is granulated and sieved, then fed into a single screw extruder with an attached torque rheometer. Continuous filament of nominal 0.070" +/- 0.001" diameter is extruded through a die and wound on spools for storage and use in the Fused Deposition process.

A homogeneous mix of powder, surfactant, and binder is crucial to ensuring a reproducible FDC process. As such, a number of process characterization techniques monitor the uniformity of the filament fabrication operation. Loss on Ignition (LOI) tests measure the amount of oleyl alcohol (after milling) and binder (after compounding). Torque values are monitored during compounding and extrusion. An Instron capillary rheometer measures viscosity and load by extrusion of the compounded material. The diameter of the filament is monitored by a laser micrometer as it is extruded.

The solvent drying step after ball milling causes a non-uniform distribution of oleyl alcohol, resulting in batch-to-batch variability. Mixing and sieving of six coated batches together increased homogeneity of the feedstock, as seen in **Figure 1**. LOI tests after mixing and subsequent compounding show reduced variability due to the mixing and sieving step. In addition, particle size analysis shows that the mixing and sieving step decreased agglomeration, from 50% (coated powder) to greater than 95% particles finer than 1 μm. This de-agglomeration reduced the torque variation during compounding and pressure variation in the capillary rheometer.

In order to increase the homogeneity of the filaments, a breaker plate and screen were inserted between the extrusion barrel and die in the single screw extruder. The plate and screen reduce agglomeration and inclusions in the mix, and increase the pressure at the die entrance, leading to better mixing efficiency during filament fabrication.

	coated	compounded		
	LOI (% wt.loss) of powders	ave. compounding torque (m-g)	Instron load variation (N)	LOI (% wt.loss) of RU955
coated powders	2.93 ± 1.08	1071 ± 247	61	19.30 ± 0.33
mixed and sieved	2.86 ± 0.18	1033 ± 52	23	19.31 ± 0.12

Figure 1. Increased homogeneity due to mixing and sieving step.

III. Fused Deposition[1,3,4]

In the process of fused deposition, filament is continuously fed between a pair of motorized rollers into a heated liquifier, where the binder melts. The filament acts as both feedstock and piston, pushing the melt through the nozzle and onto the build platform. Software controls the translational motion of the liquifier/nozzle assembly and the height of the platform, thus "writing" the layered part out of extruded "roads". The extruded road hardens as the binder cools. Material is initially deposited as a perimeter, defining the boundary of each layer of the part, then as a fill pattern, either contours or rasters. The enclosed build envelope is maintained at a warm temperature in order to promote bonding between adjacent roads.

One of the most difficult tasks of this program has been the balance of filament properties required by the process: flexible (for spooling), yet stiff (as a piston), low viscosity (reduce shear in the liquifier) but high modulus. A major obstacle to FDC automation has been buckling of the filament under the rollers and above the liquifier. This is caused by low filament modulus, and is exacerbated by high viscosity reducing flow through the liquifier and heat transfer softening the binder. Direct cooling supplied by an air conditioner onto the filament at the rollers has raised the filament modulus in the necessary process location, and increased the robustness of the filament such that uninterrupted builds of 16 hours have been achieved. The cool air is recirculated in tubes, isolating the cooling process from the warm build envelope; this enables the operator to maintain independent warm and cool environments where they are required.

The nozzles supplied by Stratasys have an internal 0.070" channel, which tapers at the bottom to the particular nozzle tip diameter (0.015", 0.025") at a 118° angle. The liquifier flow channel is 0.073" diameter, thus creating two possible dead zones: at the liquifier-nozzle interface and at the nozzle channel-taper interface. The nozzles were redesigned (**Figure 2**) with a constant channel taper from 0.073" at the top to the tip diameter at the bottom, with the flow channel angle optimized (A. Yardimci, the University of Chicago) to maximize the flow rate for the specific tip diameters. Application of the machined nozzles lowered the motor torque driving the filament as well as the torque variability, and helped to eliminate nozzle clogging.

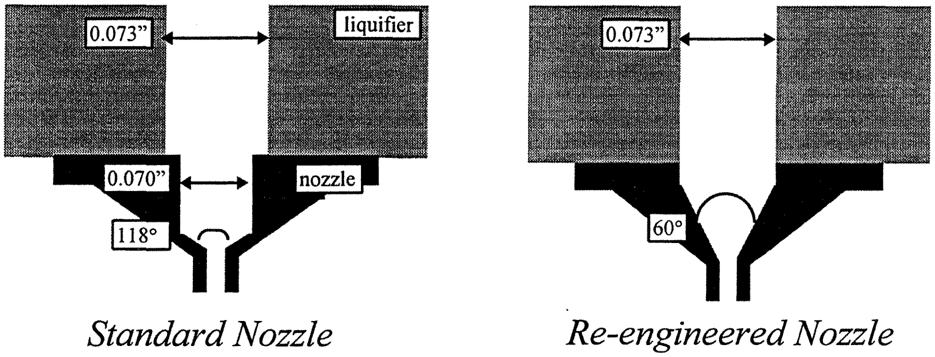


Figure 2. Nozzles re-designed with optimized internal angle and "dead zones" removed.

In order to accurately predict final part dimensions and reduce the necessity for machining, the build roads must be of consistent width and have no apparent seams or bulges at the joints. For contour and raster fills, inconsistent road widths and poor seams can cause internal voids which limit part strength. For perimeter roads, these issues cause sub-perimeter voids and poor surface quality. The parameters which affect flow in the start- and end- zones of the tool path were identified, and the process was optimized for constant width perimeters and controllable seams, as in **Figure 3**.

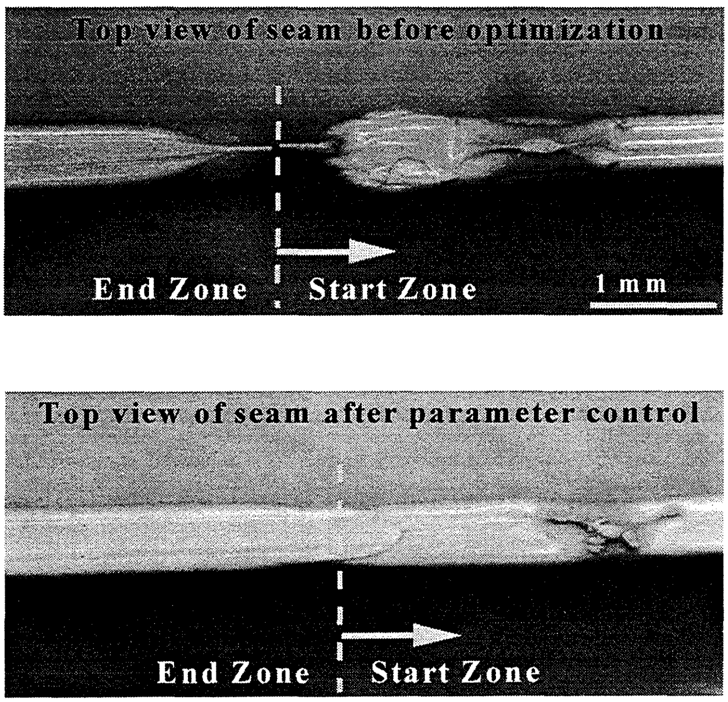


Figure 3. DoE identified critical parameters and optimized perimeter consistency.

Two locations of internal part voids[1,4] are inter-lamellar (between adjacent roads) and sub-perimeter (caused by deviation from the set toolpath, due to control limitations), **Figure 4**. Inter-lamellar voids have been addressed by offsetting the road location such that roads overlap by ~20% of their width. Sub-perimeter voids are also addressed by over-filling, either by raster offset (impinging the raster into a contour or perimeter by ~10% of the latter width) or toolpath alteration to fill the gaps at the corners of the raster turn ("dog-earing"). Figure 4 illustrates the results of experiments to optimize the internal fill of parts, ensuring full green density and consistent strengths.

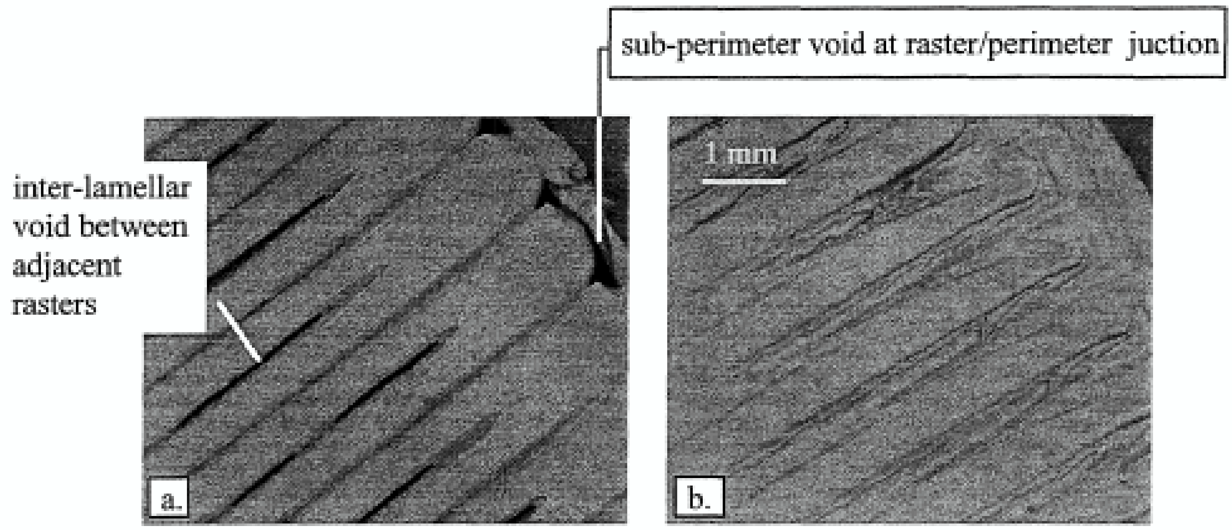


Figure 4. Internal voids reduced by flow control, off-setting, and toolpath alteration; (a.) standard build, (b.) build with inter-lamellar correction and dog-earing.

IV. Binder Burn-Out

The binder matrix must be removed from the green FDC parts before the ceramic particles can be sintered to full density. Thermal degradation occurs during Binder Burn-Out (BBO), a two stage process in which most of the binder is removed slowly at moderate temperatures in a N_2 atmosphere, followed by rapid degradation of residual carbon at higher temperature in air. The parts may crack if binder is removed too quickly, and reproducible shrinkage is critical for meeting final part dimensional specifications.

In order to characterize the critical temperatures in the binder removal process, draw trials were used to measure weight loss and shrinkage of samples soaked at incremental temperatures. The results in **Figure 5** show maximum shrinkage at low temperatures with minimal binder weight loss. This may be due to microstructural rearrangement toward ceramic particle-particle contact and void removal. At higher temperatures, less shrinkage occurs as more binder volatilizes, creating residual pores. Draw trial results were incorporated into the BBO schedule (170° C dwell to maximize shrinkage) and a DoE (critical intermediate temperatures as binder degrades) which considered the effects of ramp rates, environment, and sample size on shrinkage and cracking. Results indicate that extended dwell times increase shrinkage and lower ramp rates eliminate cracks. The BBO schedule was optimized to ensure reproducible, predictable shrinkage with no part cracking.

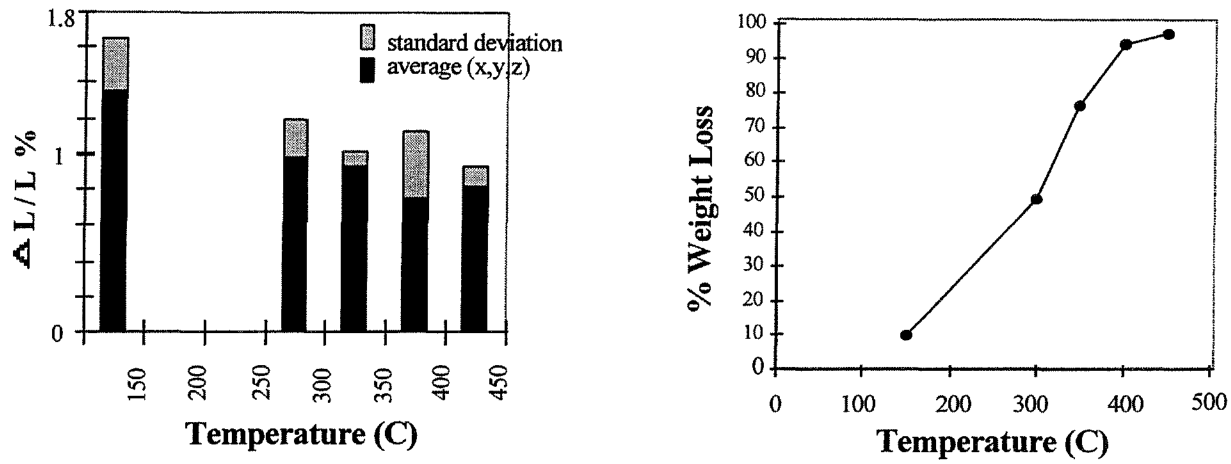


Figure 5. Draw trials of Binder Burn-Out process show critical temperatures.

The application of process improvement tools such as quality control and DoEs, from feedstock and filament fabrication through fused deposition and binder removal, have reduced shrinkage variability to ± 0.5%. This controlled, reproducible shrinkage from FDC to final sintered component (**Figure 6**) allows a more accurate CAD file estimation and reduces the need for machining of the part, which increases cost and can introduce damage.

V. Mechanical Properties of FDC Samples

In order to manufacture functional ceramic parts, strengths comparable to conventional ceramic processing are required. Also, the strengths must be reliable and predictable, with low variability. To evaluate the evolving FDC process, both 4-pt. bend strengths and toughness values are measured on fabricated bars. As the FDC process variability has been reduced, strengths have been consistently high (~900 MPa) with large standard deviation (~135 MPa). Fractography was used to identify large (~100 μm) pores as the root cause of low strengths. A Weibull distribution of the strengths, with samples segregated by failure mechanism, illustrates

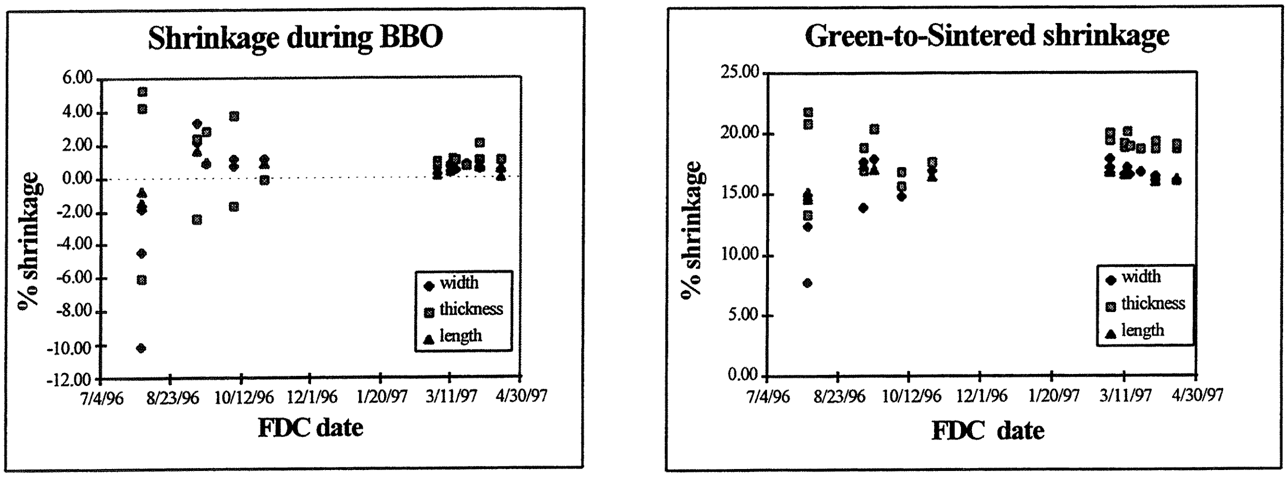


Figure 6. Application of process improvements decreased linear shrinkage variation to ± 0.5%.

the effect of the process improvements (**Figure** 7). "Vintage 1" samples were made before the topics in this paper were addressed, and "Vintage 2" samples were made as the results of quality control and DoEs were incorporated. "Vintage 2" samples which failed due to large pores have a Weibull modulus (slope of curve) of 4.2, comparable to the 5.6 modulus of "Vintage 1" samples. The distribution of "Vintage 2" samples which broke with no discernible root cause has a Weibull modulus of 15.1, which estimates the process potential if large pores could be eliminated (full sintered density).

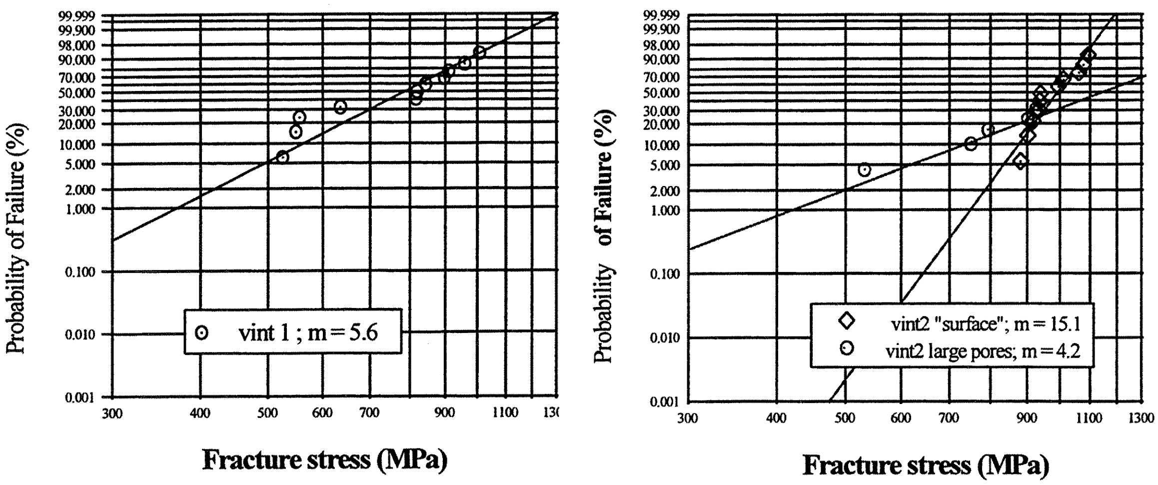
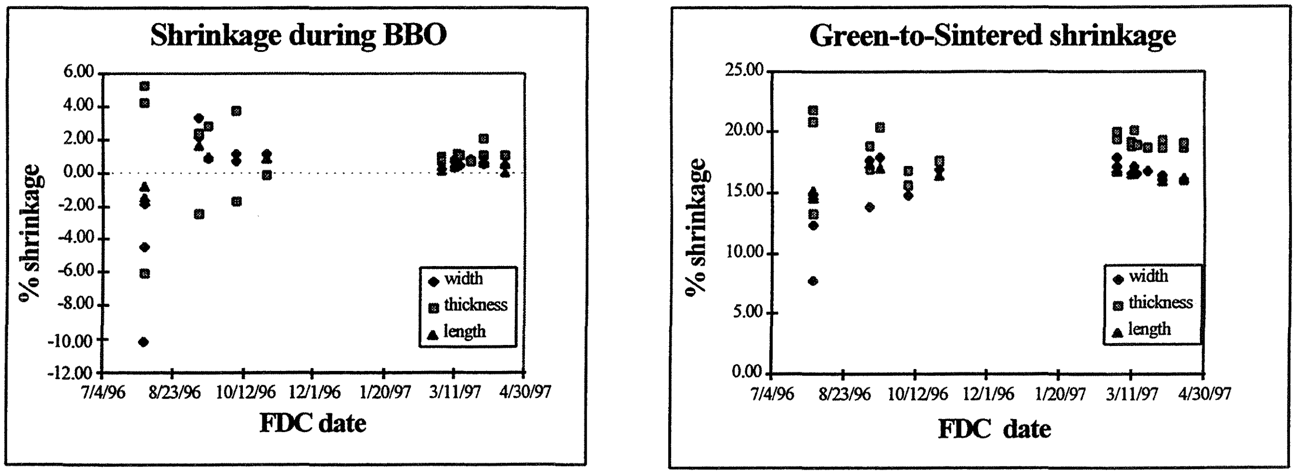


Figure 7. Weibull distributions of FDC bar strengths before current process improvement efforts ("Vintage 1") and during process control evolution ("Vintage 2").



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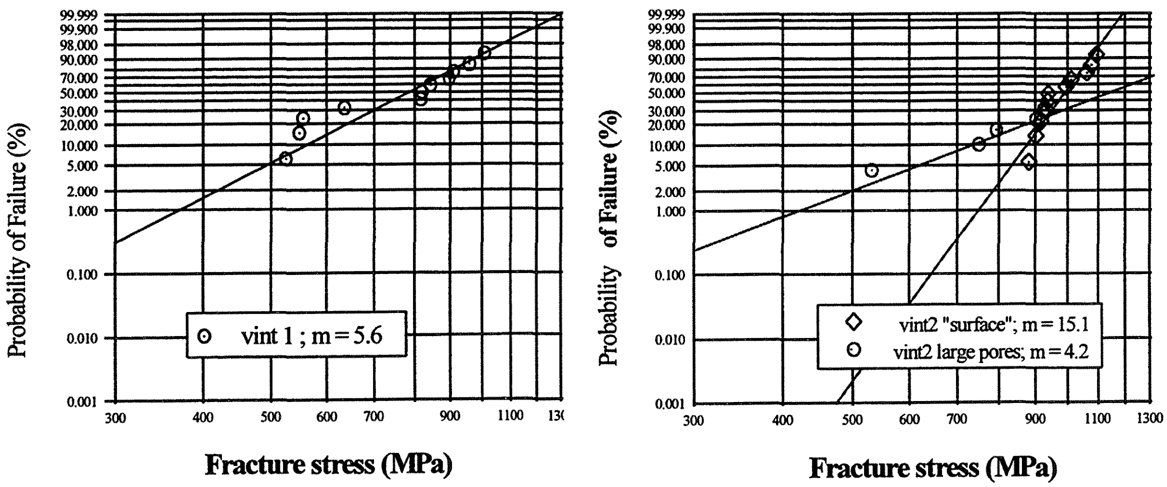

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VI. Remaining Technical Barriers to Commercialization

Efforts in the near future will focus on eliminating remaining obstacles to commercialization. Large pores must be eliminated from FDC parts to ensure high Weibull modulus and predictable strengths. Internal voids which occur due to insufficient bonding between adjacent roads will be addressed via dynamic, "on the fly" flow control, rather than by less precise off-setting. Sub-perimeter voids remain a problem at the high-incidence angle intersection of rasters and perimeter, as well as at start-stop zones of the raster fills, and flow control will be investigated in conjunction with off-setting. Statistical Process Control will be instituted to monitor deviation from process targets, and quality control feedback will track each feedstock batch through processing to final sintered part dimensions and strength and isolate aberrant samples.

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