Structural Ceramics by Fused Deposition of Ceramics

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Fused Deposition of Ceramics (FDC) is a SFF technique, based on FDM™ technology, for fabrication of advanced structural ceramics from powder/binder filaments. In this study, *in-situ* reinforced (ISR) Si_3N_4 powder and polymer/wax based binder systems were used as filament material for FDC processing using a commercially available FDM™ system, 3D Modeler. Powder/binder feedstocks were mixed using a torque rheometer and filaments were fabricated using a capillary rheometer and twin screw extruder. Green FDC components were built from these filaments and then characterized for inter-road and inter-layer bonding. Binder removal procedures were established for FDC green components to yield brown parts without distortion or shape change. Brown FDC parts were characterized for carbon residue, pore distribution and dimensional changes. Brown FDC parts were then sintered and the sintered density, microstructure, and shrinkage anisotropy were studied.

I. Introduction

The cost of manufacture of a structural component is a direct function of production quantity. Small quantity production, such as prototypes, manufactured by conventional methods lead to long production times and high unit costs. This is especially true for structural ceramic components. The advent of Solid Freeform Fabrication (SFF) technologies in the last decade has created an opportunity to reduce lead times and costs in the development of prototypes and small quantity production runs [1, 2]. Most of the SFF techniques, so far, have been limited to low temperature materials such as polymers and waxes for fabricating prototypes, which are then used for form and fit requirements. However, recently several SFF techniques are being explored for manufacture of functional ceramic and metal components [1, 2].

In this study, a new SFF technique, Fused Deposition of Ceramics (FDC), is being developed for the fabrication of functional ceramic components. FDC is based on existing Fused Deposition Modeling (FDM™) technology, commercialized by Stratasys Inc., Eden Prairie, MN, for processing of polymers and waxes [3-7]. The FDM™ process builds a 3D object layer-by-layer from a CAD design using 70 mils diameter filaments of wax and polymer. The filament is fed into a heated extruder head capable of moving in X-Y directions. The extruder head extrudes fine beads (10 - 50 mils) of material onto a fixtureless platform capable of moving in the Z-direction. The X-Y motion of the head and the Z-position of the platform are controlled by a computer, based on the CAD design of the object. Material is extruded and deposited as roads, layer-by-layer only in areas defined by CAD design, thus building a 3D object.

FDC is being developed to create ceramic components using injection molding type of ceramic-polymer feedstocks. These feedstocks are extruded into filaments, which are then used as feed material for fabrication of three-dimensional green ceramic objects using a commercial FDM™ system, 3D Modeler™ [5,6]. During FDC processing, the polymer/wax acts as a carrier and binder for ceramic particles as the material flows out of the heated extruder head. The green ceramic object thus created is then subjected to conventional binder removal and sintering processes, to produce fully dense structural ceramic components.

II. Experimental Procedure

The entire FDC process involves at least five distinct processing stages which result in a structural ceramic part. In addition to the FDC process itself, there are two pre-FDC and two post-FDC processing stages. First a ceramic formulation with a binder and other additives such as, surfactants, plasticizers, dispersants, etc., must be developed. The next stage involves taking the mixed formulation and fabricating filaments for FDC processing. Once a green ceramic part is created by FDC process, the part is further processed to remove binder and then densified by sintering. In addition to these five processing stages, other pre- and post-FDC stages may also be involved, such as, removal of support structure from FDC part before or after binder removal.

II.a Development of ceramic - binder feedstocks

The ceramic investigated in this study, is an *in-situ* reinforced Si_3N_4, commercially supplied by Allied Signal* and referred to as GS-44. Several thermoplastic wax based binder systems have been investigated for FDC processing of GS-44. Several additives have been explored for tailoring the properties of the mixed feedstock to meet the flexibility, stiffness, viscosity, "tack" or adhesion behavior, etc., required for successful FDC processing. Some of these requirements will become clear as results of FDC processing are discussed. Although several binder systems have been investigated in this study, most of the results discussed here focus on a binder system, RU1.

The compounding procedure for incorporating GS-44 into a binder system involves the use of a Haake System 40 Rheocord torque rheometer# and adding GS-44 in measured increments to the molten polymer. Additives, such as surfactants, dispersants, plasticizers, etc., are incorporated into the system in one of two ways; either the GS-44 powder is pre-treated with the additive before addition to the molten polymer or it is added to the molten polymer before any addition of GS-44. Calcined GS-44 was added in incremental amounts of 20 to 40 grams, depending on the viscosity of the binder system. After each addition the torque of the system increases instantaneously and then slowly decreases and stabilizes over a few minutes. The next incremental amount is added after the steady state torque is reached. The rotor speed is kept constant at 100 rpm throughout the process. The process is continued until a desirable ceramic loading is achieved or until a certain steady state torque value is reached, whichever is first. The compounded GS-44/binder system is granulated and sieved for viscosity measurement and filament fabrication. Capillary rheometry is used for viscosity measurements due to its similarity to the heated extruder head on a FDM™ system. Capillary viscosity measurements are made at two-three different temperatures over a shear rate range of 10^0-10^3 sec^{-1}.

II.b Fabrication of filaments for FDC processing

Compounded and granulated GS-44/binder systems are used for fabrication of filaments of 70 mils nominal diameter using a capillary rheometer as a piston extruder with a 70 mils capillary die. Depending on the viscosity of a given GS-44/binder system, the filament fabrication temperatures varied from 70°C to 200°C. However, the rate of extrusion was kept constant at 30 mm/minute. The filaments were extruded vertically under gravity with lengths varying from 8" to 12". Recent efforts have focussed on fabricating continuous lengths of filaments using a Haake System 40 Rheocord torque rheometer drive unit# with a twin screw extruder and a horizontal conveyor type take-up device. Efforts are currently underway to establish extrusion parameters such as, temperature profile along the extrusion barrel, extrusion rates, conveyor take-up speeds, etc., to fabricate continuous lengths of flexible filaments with uniform diameter.

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II.c FDC Processing

FDC feasibility of any developmental GS-44/binder system is performed in three stages. A 8"-12" piece of filament is first used to fill an empty extruder head. Material is then extruded out of the extruder head, without any nozzles attached to it. Once the extrusion is successful, a nozzle is attached to the liquefier and the process of extrusion is repeated. If the extrusion through one or more of the nozzles is successful at a certain temperature and flow rate, the test of building a simple object, such as right angle cylinder, is done to demonstrate deposition and adhesion of adjacent roads and layers. A road is a single strand of material extruded and deposited onto the substrate or a previous layer [6,7]. Once FDC feasibility is established, three dimensional objects of varying complexities are made by varying slice thickness, road width, fill pattern, speed, and other FDM™ system parameters. Due to brittleness and lack of flexibility in the filaments used in the study so far, 8"-12" long pieces of filaments are manually fed into the liquefier one piece at a time, instead of continuous feeding of the filaments.

II.d Binder removal and Sintering

After fabrication of a green FDC part, it is further processed to remove the 40 to 45 volume % organic binder. The key requirements at this stage are to be able to remove all the organic components without any residue and yet leave the part without any structural damage. In this study, thermal degradation is used for binder removal. Thermogravimetric analysis (TGA) is used to study the thermal degradation of binders and to devise a binder burn out (BBO) cycle. BBO is done in two stages at 1°C/minute in nitrogen with the part embedded in a powder bed of charcoal or alumina. The first stage involves soaking the part at an intermediate temperature (250°C to 450°C) for several hours. The final stage of the cycle is done at a high temperature (>600°C).

Brown GS-44 FDC parts are sintered by a standard sintering cycle developed by AlliedSignal for the material. The process involves liquid phase sintering in two stages using gas pressure sintering in a high purity nitrogen atmosphere. Characterization of the sintered parts are carried out by using optical and scanning electron microscopes and X-ray diffraction (XRD).

III. Results and Discussion

As mentioned earlier, although several binder systems have been explored for FDC processing of GS-44, most promising results have been obtained with the binder system RU1 loaded with 60 volume % GS-44, hereinafter referred to as RU1 60GS-44. However, before proceeding with these results, it is important to understand the basic mechanism by which the FDM™ technology deposits material and some of the key process parameters affecting the process.

III.a Materials deposition mechanism in FDM™ systems

The commercial FDM™ system, 3D Modeler™, uses a continuously wound spool of filament of diameter 70± 1 mils as feed material. The filament is made available to the liquefier from the spool continuously via a winding path. The filament is guided into the heated extruder head (or liquefier) by means of a pair of counter rotating rollers, Figure 1. The feed material melts or softens as it enters the heated extruder head, which also has a nominal internal diameter of 0.07". The molten material is then extruded out of a fine nozzle (10 to 50 mils) attached at the bottom of the extruder head. The pressure required to extrude the molten material is provided by the solid filament which is being pushed into the liquefier by the counter rotating rollers [6,7]. In essence, the extruder head in the FDM™ system is similar to a conventional piston extruder, where the filament not only acts as a continuous feed material for the extruder but it also acts as the piston in the system. The process variables that affect FDM™ or FDC process can be classified into four distinct categories and are outlined in Table 1. Effects of some these variables will become apparent as results of FDC of GS-44/binder systems are discussed.

III.b FDC of GS-44 loaded RU1 binder system

RU1 binder is a multicomponent thermoplastic wax based binder. The torque rheometer compounding at 100°C of this binder system with GS-44 results in a stabilized torque of ~1400 mg at solids loading of 60 volume %. Capillary viscosity vs. shear rate, Figure 2, indicates a shear thinning behavior for the system over a temperature range used for filament fabrication and FDC processing of the system. The shear thinning behavior of the RU1 60GS-44 is consistent with the viscosity behavior of commercial FDM™ wax materials, such as investment casting wax, ICW04.

Filaments fabricated by capillary extrusion, shown in Figure 3 along with some green FDC parts, were typically 8"-12" in lengths and the diameter of the filaments varied from 65 to 70 mils, when using a 70 mils capillary die. The filaments extruded from RU1 60GS-44 were brittle and not flexible enough to be wound around a spool for continuous feeding. Recent filament fabrication efforts using a twin screw extruder have resulted in continuous lengths of filaments with diameter varying from 63 -70 mils. However, these filaments are still too rigid and brittle to allow continuous winding and feeding. Due to its brittleness and rigidity, the filament tends to break while passing through the feed path in the 3D Modeler™. Therefore, in an effort to allow trouble-free, continuous, automated supply of filaments to the liquefier from a spool, current effort is ongoing to improve flexibility of the RU1 60GS-44 system by varying the composition of its components and also by adding suitable plasticizer(s) into the system.

FDC processing of RU1 60GS-44 system was successful at temperatures well above 100°C. As shown in Figure 2, capillary viscosity of the RU1 60GS-44 system at these temperatures is one order of magnitude higher than that of a commercial FDM™ material, ICW04, at its FDM™ processing temperature [7]. Despite its high viscosity, FDC processing of RU1 60GS-44 was possible due to high stiffness or "column strength" of the system relative to that of commercial FDM™ materials, such as ICW04. A high column strength to viscosity ratio is needed for successful FDM™ or FDC processing. If this ratio is low then the filament fails to act as an efficient piston for the extrusion of the viscous material through fine nozzles attached to the liquefier. This requirement becomes more critical as the nozzles become finer in size due to higher back pressures required for finer extrusion [6,7]. With the RU1 60GS-44 system, FDC was feasible for the entire range of nozzles (10 to 50 mils) available in the 3D Modeler™ system. Extrusion through fine nozzles is critical in obtaining fine road widths which determine the resolution and surface finish of a part being built. As shown in Figure 3., green parts with simple and complex geometries with fine features and moderate overhangs were successfully built from this formulation using road widths as fine as 10 mils. The parts with overhangs were easily built without any support structure.

As shown in Figure 4, the green FDC parts do not exhibit any delamination or any debonding between adjacent roads. However, several defects were observed in these parts and their origins have been identified, as discussed elsewhere in these proceedings [8]. None of the defects currently present in the FDC parts are unique to FDC processing. These defects can be classified into three distinct categories. The first type of defects are those arising due to limitations in current FDC methodology of manually feeding small pieces of filaments with non uniform diameters. This results in defects during transition from one piece of filament to another and also due to non uniform flow rate arising from variations in filament diameter as well as due to filament slippage between the counter rotating rollers. A decrease in filament diameter by 1 mils can result in as much as 5% of underflow causing incomplete fills. The above mentioned defects can be overcome as more progress is made in fabricating continuous lengths of flexible, uniform filaments. The next origin of defects are limitations in the current state of FDM™ system, 3D Modeler™, hardware and software. Defects arising due to these limitations have been observed in commercial FDM™ materials also, such as P301 and ICW04 [8]. Origins of these defects have been identified and strategies are being developed and implemented for defect-free FDC processing

[8]. The third type of defects, such as surface finish, stair-step form, etc., are due to limitations in current state of SFF technologies [1].

III.c Binder removal

Different binder systems that are under investigation for FDC are multi component having different thermal degradation temperature ranges. For these binder systems, binder removal is done in two stages. In the first stage (250°C to 450°C) known as wicking, the major component of the binder is in a liquid state with low viscosity. This liquid binder is removed from the FDC parts via capillary action. A porous particle bed or setter bed of alumina or charcoal is provided to soak the liquid binder from the part. At this stage, other low temperature melting component of the binder may also get eliminated by the same capillary action. Binder component(s) with low thermal degradation temperature may also be lost at this stage by evaporation. Such an action creates internal pore channels for better wicking of the liquid components. This is followed by the second stage of binder removal where the remaining binders are removed via evaporation. The time parts are subjected to these stages depends on the cross-section of the part. Part cross-section also determines the heating rate during the BBO cycle. Heating rates less than 1°C/minute are currently being explored for thick cross-section parts.

Since there is a great deal of mass and heat transfer during the BBO process, a poor BBO cycle can cause internal or surface cracking, bloating or blistering types of defects during the process. Figure 5 shows the cross-section of a RU1 60GS-44 FDC part after BBO with no significant defects such as inter-road or inter-layer defects arising due to BBO. Most of the defects observed after BBO are those which were present in the FDC part prior to BBO process [8].

III.d Sintering

The GS-44 raw material powder contains $\alpha-Si_3N_4$ and a small volume (<10%) of oxide sintering aids, Y_2O_3 and $MgAl_2O_4$. During sintering, these oxides melt and provide a liquid phase for desnification of the porous compact. As densification proceeds, the $\alpha-Si_3N_4$ transforms to β-Si_3N_4 through a solution-reprecipitation process. When densification is complete, the sintering aids remain in the grain boundaries as amorphous phases which can be crystallized by further heating at high temperatures. Sintered GS-44 prepared by iso-pressing or slip casting typically has a crystalline phase composition of 100% β-Si_3N_4. Phase analysis of sintered FDC parts by XRD indicates incomplete transformation of $\alpha-Si_3N_4$ to β-Si_3N_4, with up to 26% residual $\alpha-Si_3N_4$. In addition, the grain boundary phase had crystallized into a phase which is slightly different than that typically observed in iso-pressed or slip cast GS-44 parts subjected to high temperature heating after sintering. Incomplete $\alpha-Si_3N_4$ to β-Si_3N_4 transformation and formation of crystalline grain boundary phases in sintered FDC parts is being investigated further.

The "skeletal" density of sintered FDC parts, measured by He pycnometry, is above 95% of theoretical density, clearly showing that FDC parts are sinterable. The low bulk densities, around 75% to 90%, observed in the FDC parts are largely due to build defects present from the FD process, which are not eliminated during the sintering process. It should be noted that these same defects seen in FDC parts are also seen in FDM™ polymer parts, and are not due to the presence of the ceramic particles [8]. One of the major areas of concern in SFF processing of metals and ceramics has been significant distortion or warpage after post-processing, such as sintering. Figure 6 shows a sintered FDC part without significant distortion or warpage and Figure 7 shows the polished cross section of a sintered FDC part without any delamination or inter-road defects after sintering. Linear shrinkages during sintering are in the range of 15%-20%.

IV. Conclusions

This study has demonstrated the feasability of using commercial FDM™ systems for rapid fabrication of ceramic loaded green FDC parts. Green FDC parts can be created with attributes similar to those present in FDM™ processed wax and polymer parts. It is further demonstrated that such FDC green parts can then be fired to obtain nearly fully dense components with no defects induced during post-FDC processing steps such as binder removal and sintering. Current limitation of inflexible filaments and limitations in FDM™ system hardware and software are being addressed to fabricate FDC parts of high quality needed for structural ceramic applications.

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Table 1

FDM™ and FDC Process Variables

Operation Parameters	Machine Specific	Materials Specific	Geometry Specific
• Slice thickness • Road width • Head speed • Extrusion temperature • Envelope temperature • Fill pattern	• Nozzle diameter • Filament feed rate • Roller speed • Flow rate • Filament diameter	• Viscosity • Stiffness (Column strength) • Flexibility • Thermal conductivity • Powder characteristics • Binder characteristics	• Fill vector length • Support structure

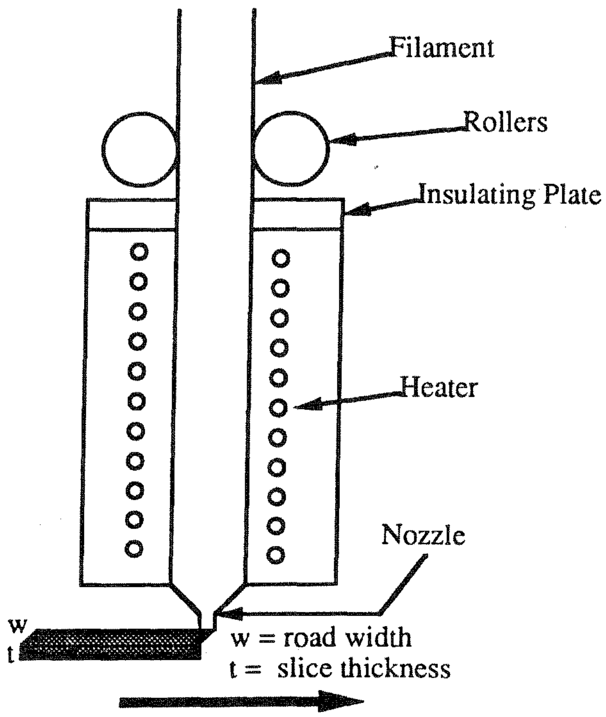

Figure 1 : Conceptual schematic of material feeding and deposition in the commercial FDM™ System, 3D Modeler™.

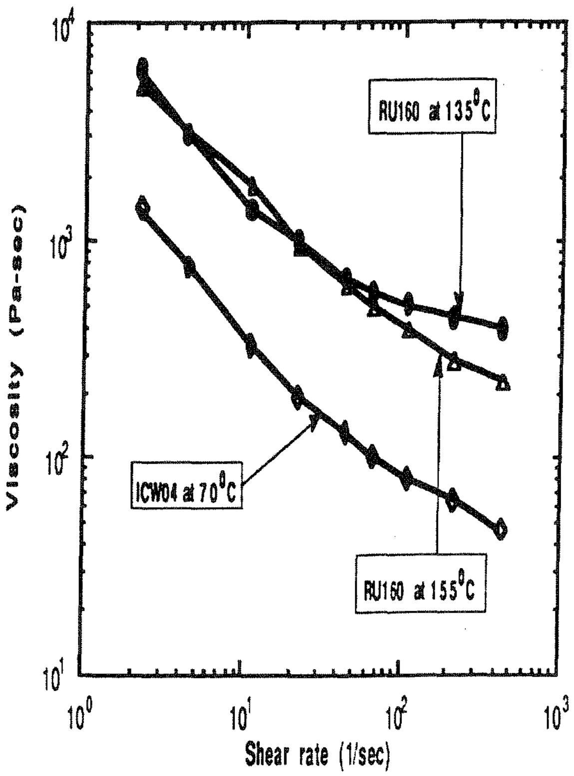

Figure 2: Capillary viscosity vs. shear rate of RU1 60GS-44 system and commercial FDM™ material ICW04.

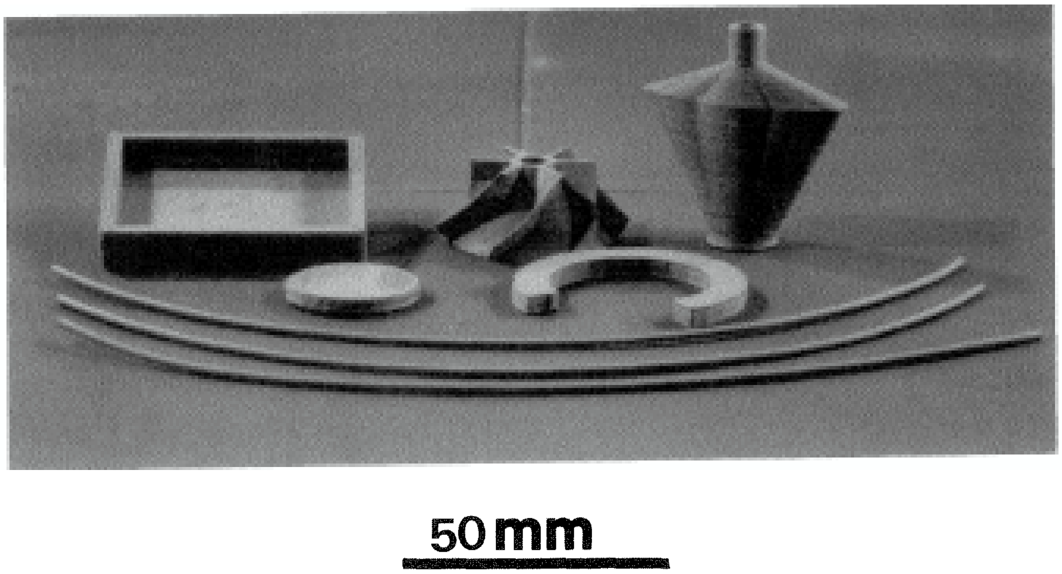

Figure 3: RU1 60GS-44 filaments fabricated by capillary extrusion, simple and complex FDC parts fabricated from RU1 60GS-44 using commercial FDM™ system, 3D Modeler™.

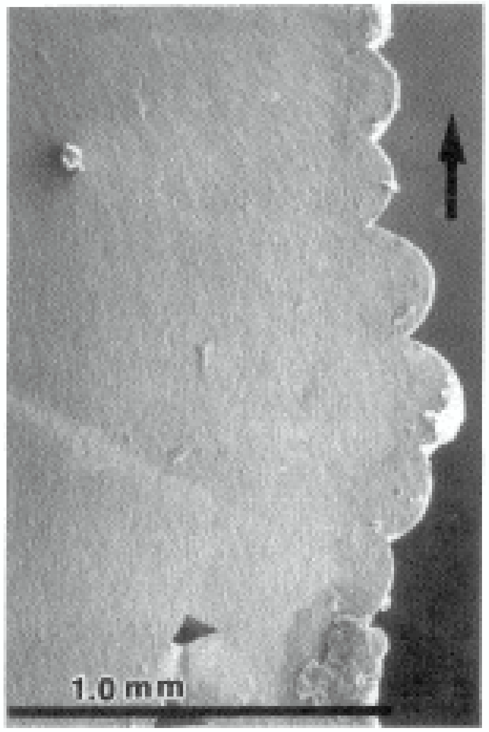

Figure 4: SEM micrographs of cross section of a green FDC part showing no delamination or debonding between adjacent roads and layers.

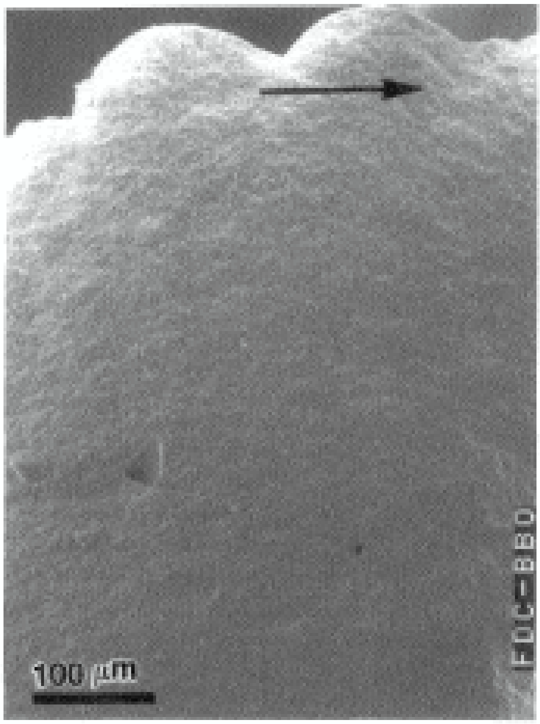

Figure 5: SEM micrograph of a cross section of a RU1 60GS-44 FDC part after binder removal showing no inter-road or inter-layer defects introduced by binder removal.

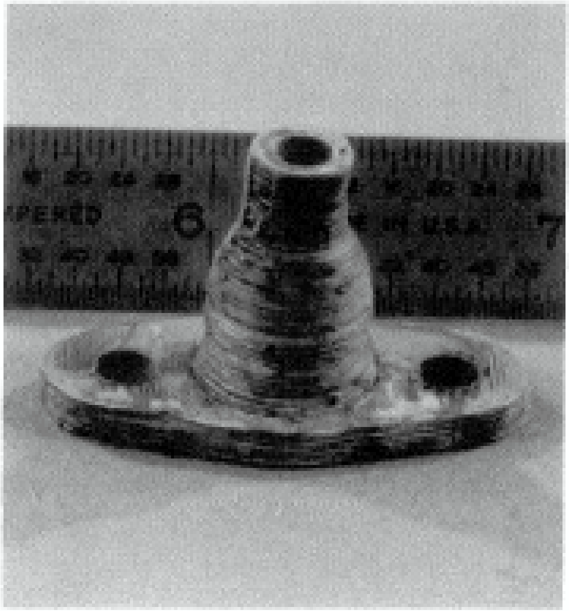

Figure 6: A sintered FDC GS-44 part without significant distortion or warpage.

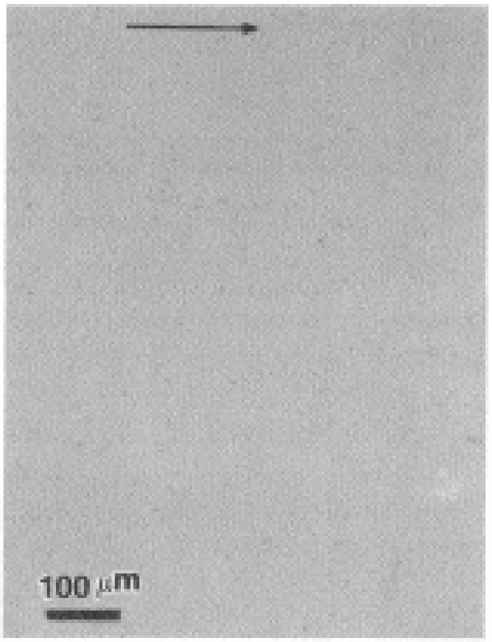

Figure 7: Optical micrograph of cross-section of a sintered FDC GS-44 sample showing no delamination or inter-road defects.

(Arrows in Figures 4, 5, and 7 indicate the FDC build direction)