Extrusion Freeform Fabrication of Functional Ceramic Prototypes

R. Vaidyanathan, J. L. Lombardi, J. Walish.
Advanced Ceramics Research, Inc., Tucson, AZ 85706

S. Kasichainula, P. Calvert. University of Arizona
Arizona material Laboratories, Tucson AZ, 85712

K. Cooper. NASA Marshall Space Flight Center, Huntsville, AL 35812

Extrusion Freeforming (EFF) and Fused Deposition Modeling (FDM) processes are established freeforming techniques capable of fabricating complex shaped ceramic prototypes by the sequential deposition and solidification of green ceramic feedstock, layer by layer until the final part results. The freeforming of ceramic parts was accomplished using a commercially available Stratasys 3D Modeler retrofitted with a high-pressure extrusion head designed by Advanced Ceramics Research, Inc. (ACR). The manufactured objects had good dimensional tolerances, as well as real engineering compositions and microstructures. Ceramic feedstock based on two different silicon nitride powders were developed and successfully used to make prototype parts. Mechanical properties and microstructural characterization of prototype parts were performed.

I. Introduction

Extrusion Freeform Fabrication (EFF) is an SFF technique based on the Stratasys FDM™ approach[a] for the fabrication of functional ceramic prototypes [1]. More details are given in reference 2. While possessing the benefits of Fused Deposition of Ceramics (FDC™) [1995 Volume from reference 1] and FDM™, EFF has the added advantages that it can handle higher viscosity feed stock materials and higher extrusion temperatures compared to FDC™ and FDM™. Similar to other SFF techniques, EFF also allows the sequential deposition of multiple layers to form a complex ceramic shape. This has been achieved by retrofitting a high-pressure extruder head to a Stratasys FDM™ modeler (figures 1 and 2). The CAD file is processed by the Quickslice™ software and used to control the EFF high-pressure extrusion head [1]. However, the operation parameters that are automatically set by Quickslice, are optimized for polymer filament type of feedstock. These parameters are not necessarily the optimum parameters for the SFF of ceramic parts. To further control process parameters for SFF of ceramic parts, SML Post™, a Visual Basic based post-processing software was developed to modify selected process parameters. SML Post™ could modify the start-delay, preflow, start-flow, start-distance, main-flow, shutoff-distance, roll-back, speed, and acceleration that were originally set by Quickslice™. Presently, the road-width, slice-thickness, and fill-patterns are still set by Quickslice. However, SML Post™ could modify these parameters also, if needed.

The quality of the EFF green ceramic feedstock has a strong influence upon the robustness of the process and its ability to reproducibly fabricate high strength, dimensionally accurate ceramic components. A high degree of homogeneity is desirable in order to minimize density gradients between the binder and ceramic powders. If density gradients are present in the feedstock, it could lead to non-uniform firing shrinkage and formation of defects within the

[a] Stratasys Inc., Eden Prairie, MN

freeformed ceramic bodies[3]. The feedstock should also possess a reproducible rheology so that it can be accurately freeformed into the desired green ceramic component. Further requirements for the rheology of EFF feedstock are a low melt viscosity (extrudable at low pressures) as well as the ability to undergo rapid solidification upon deposition (enabling more rapid part build rates). The binder should be easily removable from the freeformed green bodies under controlled conditions and leave minimal pyrolysis residue. Finally, the resulting bodies should be readily sinterable into dense ceramic components.

Figure 1. Stratasys FDM™ retrofitted With a high pressure head

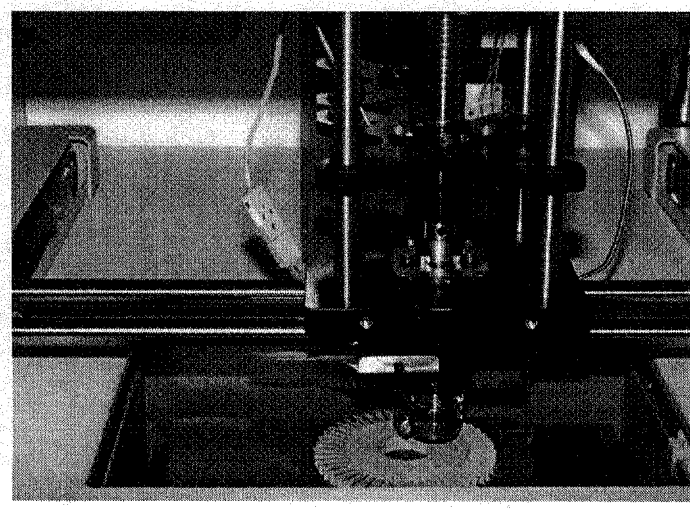


Figure 2. Close up view of the high pressure head creating a ceramic prototype

In contrast to EFF, additional requirements must be met for the filament feedstock used in FDC processing. In particular, FDC compatible filaments should also possess sufficient strength and flexibility such that they can be continuously extruded through a conventional Stratasys Modeler without fracturing. Significant FDC filament breakage could lead to dimensional inaccuracies and flaws within the FDC parts. Consequently, the utilization of filament feedstock possessing reproducible mechanical properties is an important issue in successful FDC part fabrication. Therefore, for successful FDC, the filament feedstock needs to meet two separate and sometimes divergent sets of property requirements. This is extremely difficult to achieve for non-ideal systems such as ceramic-loaded binder systems. The EFF process avoids this problem by the use of a ceramic feed-rod as the feedstock. This provides the EFF process certain advantages over the current FDC process.

II. Experimental Procedure

The entire EFF process involves at least five distinct processing stages that result in a structural ceramic part. In addition to the EFF process itself, there are two pre-EFF and two post EFF processing stages.[4] The first of these stages is the formulation of a binder system which contains plasticizers, surfactants, and dispersants as well as other additives. More details of the present binder system and the rheology of the ceramic-loaded binder system has been discussed in reference 2. After a formulation is decided on, feedrods 0.625"x6" length are made by mixing the binder system with the ceramic powder and sintering aids and then pressing this batch of material into feedrods. The next step is to fabricate a part using the EFF process and burn out the binder. The subsequent sintering stage densifies the part. Other steps could be added if necessary, such as post-finishing, depending on the quality desired.

A. Ceramic/Binder Feedstock Development

The ceramic feedstock for EFF needs many of the qualities commonly desired in raw materials for ceramic injection molding.[5] Consequently, EFF feedstocks were developed with binder formulations similar to those employed by conventional ceramic forming processes. These formulations consisted of ≈ 55 vol% of silicon nitride powder dispersed in an organic binder. The binder is a mixture of polymer, wax, and plasticizer and serves as a vehicle for the freeformed Si_3N_4 ceramic powder. The wax is an important component in the binder since it lowers the melt viscosity of the binder polymer at elevated temperatures (ca. > 100°C) while simultaneously enabling the green body to rapidly solidify and maintaining its dimensional accuracy after freeforming. A liquid plasticizer is believed to be an important binder constituent since it also lowers the binder melt viscosity. Its higher volatility compared to the wax and polymer enables a progressive and more controllable removal of binder components prior to sintering the freeformed ceramic bodies.[6] The suitability of this binder composition in EFF feedstocks was demonstrated after successfully extrusion freeforming and subsequent pressureless sintering >97% dense, crack free silicon nitride parts using this type of formulation. Figure 3 depicts both green and pressureless sintered silicon nitride prototypes that were fabricated using EFF techniques.

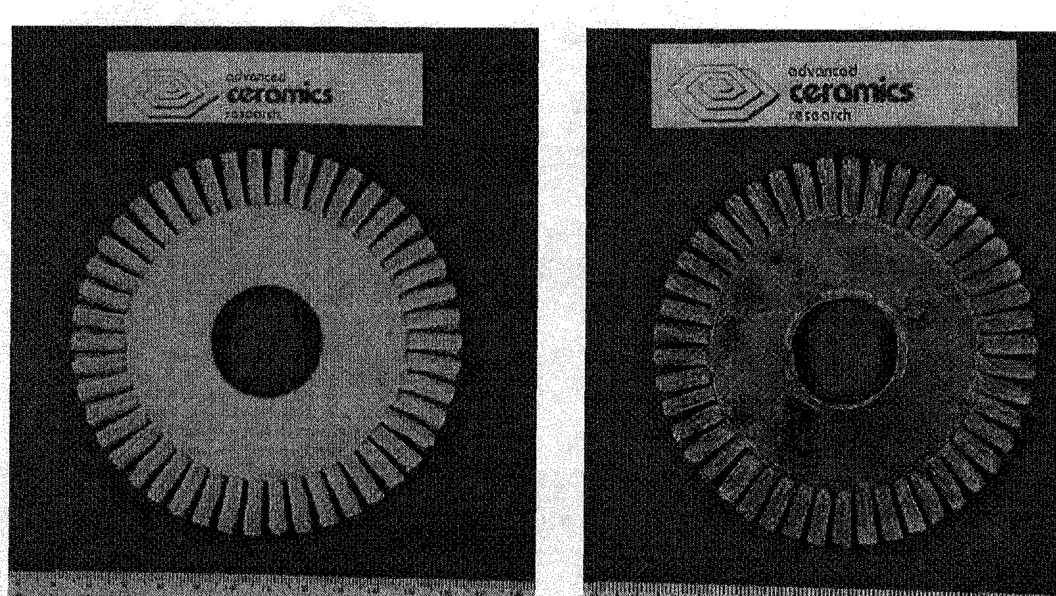


Figure 3. Photograph of green and sintered silicon nitride bladed disk fabricated using EFF techniques.

Green ceramic feedstock having a composition similar to the values in Table I was compounded using an Armoloy Prep Mixer[a]. All raw materials present in the green ceramic feedstock were obtained from commercial sources. The silicon nitride powder was a pressureless

[a] C. W. Brabender, Hackensack, NJ

sinterable composition containing yttrium and aluminum oxide sintering aids in a 9:3 weight ratio. The saturated elastomer in the binder was an amorphous, noncrystallizable copolymer. Gel permeation chromatography of the paraffin wax binder component reported an average molecular weight of 3779 g/mole and a polydispersity index of 2.5. The fatty acid plasticizer was a liquid under ambient conditions.

Component	Concentration (Volume %)
Silicon Nitride	≈ 55
Saturated Elastomer	≈ 25
Fatty Acid Ester Plasticizer	≈ 10
Paraffin Wax	≈ 5
Acryloid Additive	≈ 5

Table I: A typical green ceramic feedstock composition.

For rheology characterization, a plunger type Instron rheometer (Model 3211)[c] was utilized for capillary rheometry at temperatures between 120 and 150°C.

B. Feedrod Processing and the EFF Process

After shear mixing, the green ceramic material was extruded into feedrods measuring 15.9 mm (5/8") in diameter by 152.4 mm (6") in length. These feedrods were then fed into the barrel of the extrusion head and extruded to produce different 3-D shapes with the EFF process. The EFF process itself was optimized by using a Design of Experiment (DOE) procedure[7]. The software-controlled parameters were optimized so that a uniform rate of material deposition was obtained. Figure 4a and 4b show simple parts that were fabricated without optimization of the EFF parameters, while figure 4c shows a simple part that was made after determination of the optimized parameters. The optimization of EFF parameters also improved the on the prototypes. Figure 5 and 6 are prototype parts made with different starting silicon nitride powder, such as Kyocera SN282 and Starck M-11. At present, Alliedsignal AS800 silicon nitride parts are also being made. These results show that the EFF process is capable of handling a variety of starting ceramic powders.

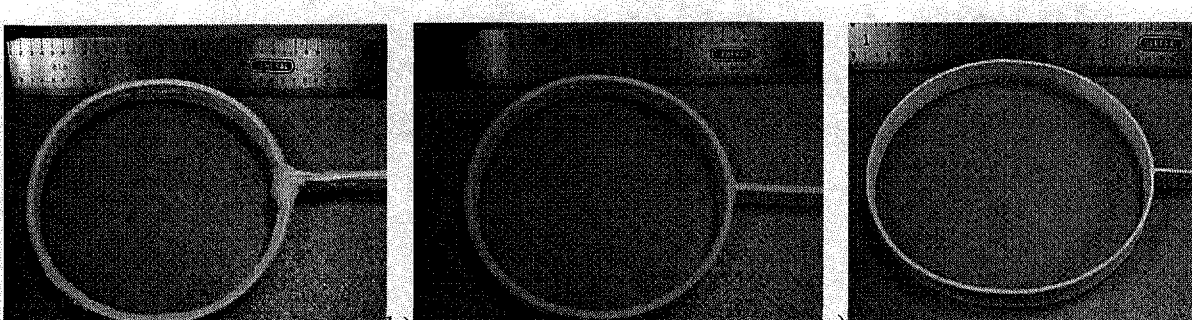
a)  b) c)

Figure 4: Cylinders a and b were fabricated prior to optimization. Cylinder c was constructed with the optimized parameters.

---

[b] Instron, Canton, MA

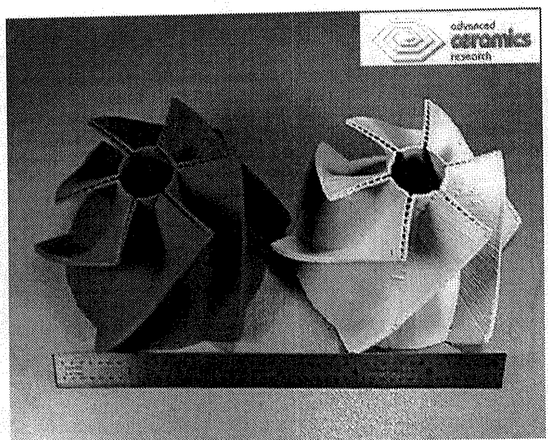


Figure 5: Impellers made with Kyocera (left) H.C. Starck (right) silicon nitride powders.

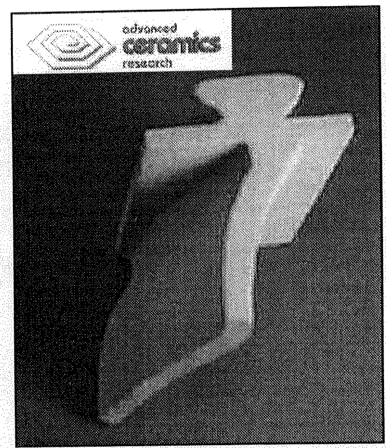


Figure 6: A turbine blade made with the Starck M-11 powder.

C. Binder Burnout and Sintering

Once the green prototype has been fabricated using EFF, the organic binder must be removed. The optimum situation is one in which all of the binder has been removed, yet there are no defects created by the removal of the binder system. Thermogravimetric Analysis (TGA) was used to study the compositional loss and degradation of a binder relative to temperature. After TGA is performed, a binder burnout cycle is then devised. Binder burnout cycles are currently being studied so that prototypes with thick cross-sections can be successfully burned out and sintered without fear of producing defects. The current binder burnout and sintering processes can produce parts with greater than 97% theoretical density.

III. Results and Discussion

A. Ceramic/Binder Feedstock Development and EFF optimization

Formulation modifications were performed in order to obtain lower viscosity and a less shear-rate dependent Si_3N_4 formulation compared to the standard binder formulation. Capillary rheology of EFF feedstock with an acryloid addition for improving the dispersion of the Si_3N_4 powders in the binder system was performed. A comparison of the shear rate-viscosity behavior on standard binder formulations with and without the acryloid addition is shown in Figure 7. The capillary rheology data shows little difference in viscosity at all shear rates. However, at the shear rate ranges operative in the EFF process, there was no difference in the viscosity between the EEA binder formulations with and without the acryloid additions. However, the significant finding here was that the extrusion forces during EFF were an order of magnitude lower for the modified formulation compared to the standard formulation. For example, the extrusion pressures for the modified formulation were of the order of 150-200 pounds, while the extrusion pressures with the standard formulation were of the order of 1500 pounds. High extrusion pressures beyond the capacity of the load cell tend to create a situation where the extrusion stops shortly and starts again, creating missed layers and defects in the part. The modified formulations resulted in improved average strength and eliminated missed layers in the part.

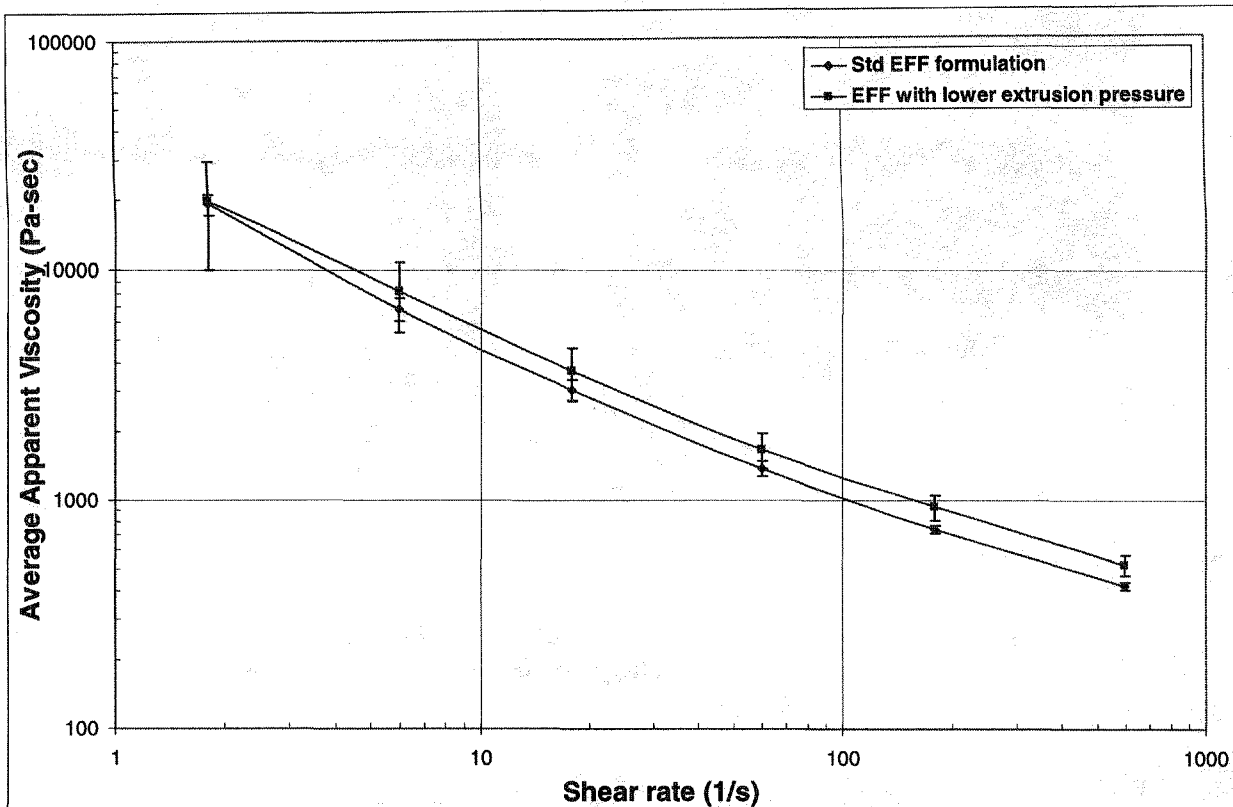


Figure 7. Comparison of shear rate-viscosity behavior of EEA binder formulations with 55 vol% Si_3N_4 with and without an acryloid addition, at 150°C.

The above result suggests that rheology measurements by themselves are not sufficient to evaluate the effectiveness of a binder formulation for EFF. The high-pressure extruder head is capable of overcoming the rheology limitations of the EFF formulations and therefore, other simple indicators of extrudability need to be developed for the EFF process. This could include extrusion force, mechanical properties of flexural bars, as well as SEM analysis of fracture surfaces. Room temperature four-point bend tests were performed on flexural bars prepared from EFF formulations with the acryloid addition. An average strength of 641 ± 107 MPa was obtained, compared to an average strength of 525 ± 110 MPa for flexural bars from the standard formulation. Figure 8 shows the fracture surface of a test bar. The fracture surface did not show any delaminations or missed layers during the freeforming process. Figure 9 shows a higher magnification image of the fracture surface from figure 8.

Room temperature flexural tests were performed on bars produced with the optimized parameters. These results are shown in table II. The strength of these bars were comparable with that of previously made bars (polished – 613 ± 12, unpolished – 594 ± 80). These results suggest that optimization of the EFF parameters provided a good surface finish to the samples.

B. Binder Burnout and Sintering

Binder burnout and sintering currently produce parts that are greater than 97% dense with x-y shrinkages of 18 ± 3% and z shrinkage of 20 ± 5%. These numbers are similar to numbers obtained from other ceramic freeforming processes[8].

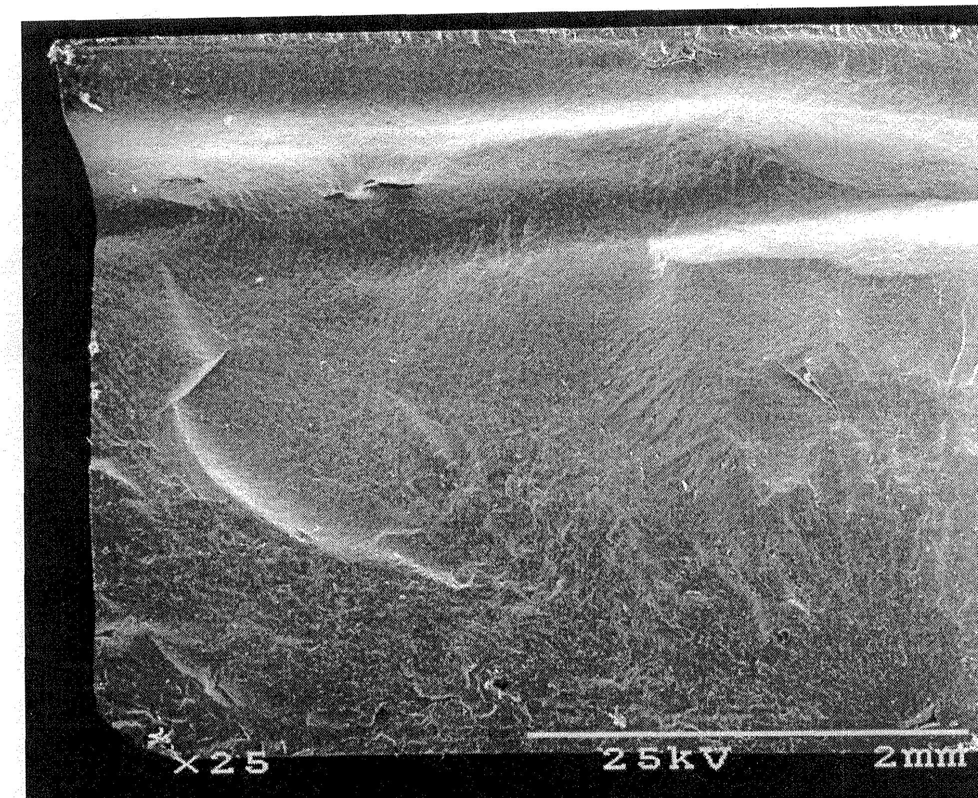


Figure 8. Low magnification image of the fracture surface of freeformed flexural test bars.

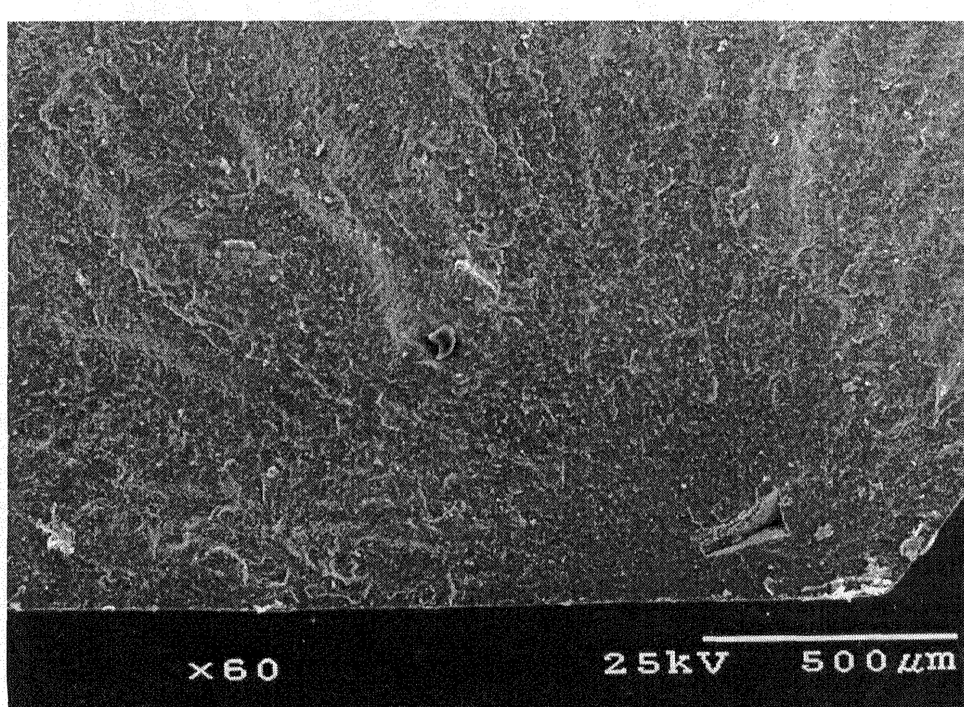


Figure 9. Higher magnification of fracture initiation point from figure 8.

IV. Conclusions

Through the improvement of feedstock and process parameters, the EFF process has demonstrated the capability to fabricate complicated ceramic prototypes using a commercially available Stratasys 3D modeler. Prototypes with excellent surface finish and few defects can be made. Binder burnout schedules are currently being modified to assure that parts with thick cross-sections can be burned out without warping or defects.

Table II. Flexural strength data for EFF test bars as a function of raster-build direction

Raster-build direction	Surface condition	Flexural strength (MPa)
0°	Unpolished	594 ± 80
0°	Polished	613 ± 12
0°/90° alternating	Unpolished	227 ± 39
0°/90° alternating	Polished	312 ± 71

Acknowledgments

This work has been performed under NASA STTR program contract number NAS8-98025.

REFERENCES

1. Proceedings of the Solid Freeform Fabrication Symposium, Vol. 1990-1998, Edited by H.L. Marcus, et al., the University of Texas at Austin, Austin , TX.
2. R. Vaidyanathan, J. L. Lombardi, B. Tennison, S. Kasichainula and P. Calvert, "Rheological properties of ceramic formulations for Extrusion Freeform Fabrication," presented at the 23rd Annual Cocoa Beach Ceramic Society meeting on Ceramics and Composites, Cocoa Beach, FL, Jan. 1999 (in press).
3. R.M German and A. Bose: *Injection Molding of Metals and Ceramics,* Metal Powder Industries Federation, Princeton, New Jersey, pp. 23, (1997).
4. J. L. Lombardi, R. A. Hoffman, J. A. Waters, D. Popovich, C. Sovignier, and S. Boggavarapu, "Issues associated with EFF and FDM ceramic filled feedstock formulation," *Proceedings of the Eighth Solid Freeform Fabrication Symposium*, Vol. 1997, Edited by D. L. Bourell, J. J. Beaman, J. W. Barlow, H. L. Marcus and R. H. Crawford, The University of Texas Press, Austin, TX., pp. 457-464, (1997).
5. M.J. Edirisinghe and J.R.G. Evans: *Materials and Design,* vol. 8, pp. 284-8, (1987).
6. M.J. Edirisinghe and J.R.G. Evans: *Journal of Materials Science,* vol. 22, pp. 269-277, (1987).
7. J. Walish, et al., "Application of Design of Experiments to Extrusion Freeform Fabrication (EFF) of Functional Ceramic Prototypes," *Proceedings of the Eighth Solid Freeform Fabrication Symposium*, Vol. 1999, Edited by D. L. Bourell, J. J. Beaman, J. W. Barlow, H. L. Marcus and R. H. Crawford, The University of Texas Press, Austin, TX.
8. M.K Agarwala, R. van Weeren, R. Vaidyanathan, A. Bandyopadhyay, G. Carrasquillo, V. Jamalabad, N. Langrana, A. Safari, S.H. Garofalini, S.C. Danforth, J. Burlew, R. Donaldson, P. Whalen, and C. Ballard, "Fused Deposition of Ceramics," *Proceedings of the Sixth Solid Freeform Fabrication Symposium*, Vol. 1995, Edited by D. L. Bourell, J. J. Beaman, J. W. Barlow, H. L. Marcus and R. H. Crawford, The University of Texas Press, Austin, TX., pp. 1-8, (1995).