FREEZE-FORM EXTRUSION FABRICATION OF COMPOSITE STRUCTURES

Ming C. Leu[1], Lie Tang[1], Brad Deuser[1], Robert G. Landers[1], Gregory E. Hilmas[2], Shi Zhang[2], and Jeremy Watts[2]

[1]Department of Mechanical and Aerospace Engineering, Missouri University of Science and Technology, Rolla, MO 65409
[2]Department of Materials Science and Engineering, Missouri University of Science and Technology, Rolla, MO 65409

REVIEWED, August 17 2011

Abstract

A Freeze-form Extrusion Fabrication (FEF) process capable of making three-dimensional (3D) parts and structures with graded composite materials is presented in this paper. The process development includes the design and manufacture of a gantry machine with a triple-extruder mechanism and the associated electronics hardware and computer software for fabricating functionally graded parts from multiple aqueous pastes. A rheological behavior study with Al_2O_3 paste is performed to identify an efficient binder for transforming the paste into a pseudoplastic with a high yield stress. A green part is first fabricated using the triple-extruder FEF machine in a layer-by-layer manner with the desired material gradients. The green part is then freeze-dried, its binder removed through a burnout process to obtain a brown part, and the final part obtained by sintering. The final part is analyzed using energy dispersive X-ray spectroscopy (EDS) to determine its material composition. The results demonstrate that the FEF process can be used to fabricate functionally graded composite parts with pre-specified gradients.

1. Introduction

Ceramic components are used increasingly in aerospace, automotive and other industrial applications due to their high heat resistance and material hardness. Traditional ceramic manufacturing processes are time consuming and expensive, especially for components with complex geometries. In recent years, several additive manufacturing processes have been developed to fabricate 3D ceramic components from CAD models in a layer-by-layer manner. They include Fused Deposition of Ceramics [1], Fused Deposition Modeling [2], Extrusion Freeform Fabrication [3], 3D Printing [4], Selective Laser Sintering [5, 6], Shape Deposition Manufacturing [7], and Robocasting [8, 9].

Freeze-form Extrusion Fabrication (FEF) is a novel, environmentally friendly, additive manufacturing process that builds a 3D part layer-by-layer by computer controlled extrusion and deposition of aqueous based colloidal pastes. Unlike most other extrusion freeform fabrication processes, which use organic binders to bond ceramic powders together, the organic binder content is only 2-4 vol% in this process, while the solids loading of the paste is up to 50 vol%. Unlike robocasting, FEF builds a "green" (before post-processing) part in an environment below the freezing point of water so as to solidify the paste after paste deposition on each layer during the fabrication process. This enables relatively large parts to be built compared with robocasting.

Cones and other components from monolithic ceramics, including alumina (Al_2O_3) and zirconium diboride (ZrB_2), have been fabricated using the FEF process; see Figure 1 [10-13]. This process has also been investigated for the fabrication of 13-93 bioactive glass scaffolds with pre-designed porosity and pore architecture [14].
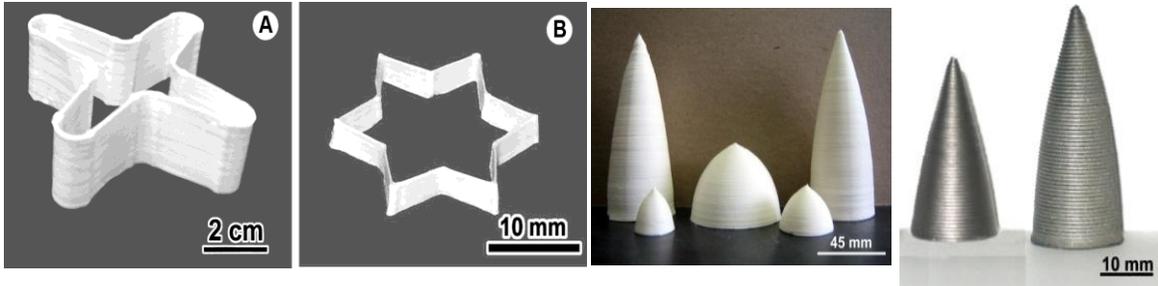

Figure 1: Sintered ceramic samples fabricated using the FEF process.

Some key components in aerospace applications demand extremely high performance, such as the leading edges of hypersonic vehicles, missile nose cones, and nozzle throat inserts for spacecraft propulsion systems. These components must be able to withstand extremely high temperatures (> 2000°C) and integrate into the underlying substructures, which often are made of metals such as aluminum or titanium. To achieve these demanding characteristics, one approach is to build these components with functionally graded materials (FGMs), grading from an ultra high temperature ceramic (UHTC) to a refractory metal. This grading should be done in a gradual fashion so as to minimize the thermal stresses generated due to different thermal expansion coefficients between the different materials, both during the part fabrication process and when the part is in service. Additive manufacturing processes are advantageous for building such components with functionally graded materials.

This paper describes our design and development of a triple-extruder FEF system for fabricating parts with functionally graded materials. The part fabrication process by this system involves computer control of flows of multiple aqueous pastes (each controlled separately), the mixing of these pastes, and the extrusion of the mixed paste to fabricate a 3D part layer-by-layer according to a CAD model and pre-specified material compositions. The system development also includes planning and control algorithms and software for motion control and extrusion control. This paper details the process and system concept, system design and development, and some experimental results with the developed system.

2. Process and system concept

The specific aim of our development of the FEF system is to extrude three different aqueous pastes (made of WC+ZrO_2, W, and ZrC) at controlled rates to build parts having a gradient from ZrC to W, as pre-specified, after binder burnout and reactive sintering of the green part built by the FEF system. Figure 2 shows the concept of fabricating a part with gradient materials using the system. As shown in the figure, a green part is first fabricated by the system in a layer-by-layer manner. The fabricated green part is then freeze-dried, and the binder is removed through a burnout process to produce a "brown" (binder pyrolyzed) part. The brown

part then undergoes reactive sintering to obtain the final part, which has CAD dimensions and FGM compositions that are pre-specified.
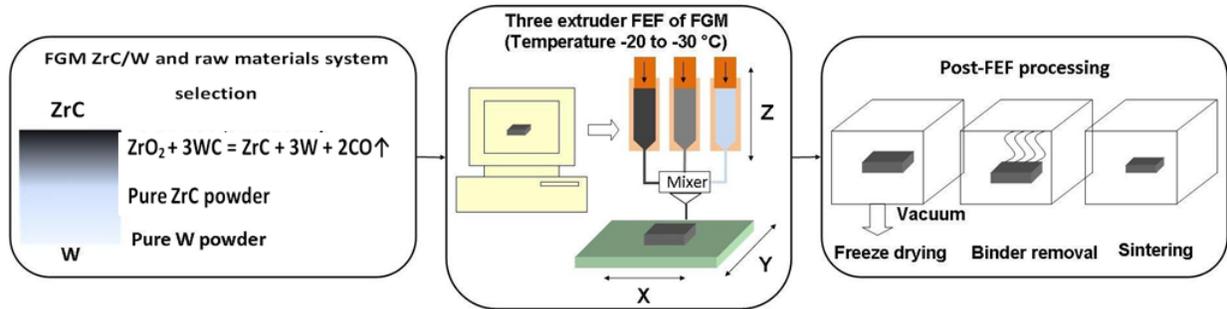

Figure 2: Procedure for fabricating gradient materials using the FEF process.
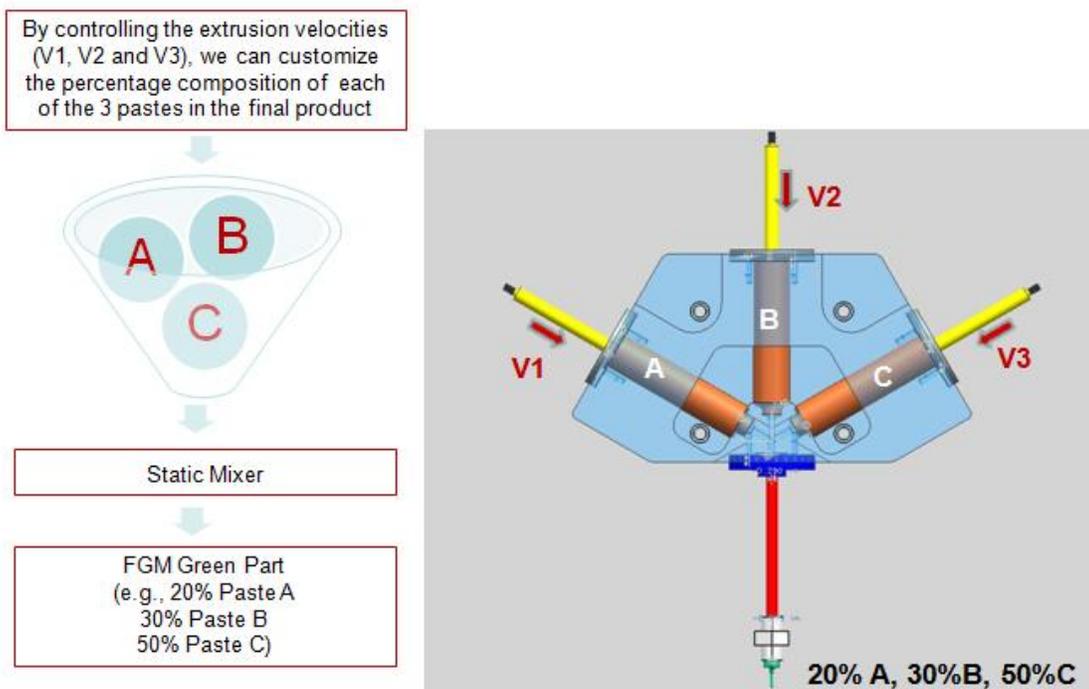

Figure 3: Triple-extruder mechanism design.

To realize the process of fabricating an FGM part, we have designed and developed an FEF machine equipped with three servo controlled extruders and a paste mixer. Fabricating an FGM part that grades between ZrC and W after sintering requires three pastes: ZrO_2+WC, W, and ZrC. The reactive sintering process involves the following chemical reaction:

$$ZrO_2 + 3WC = ZrC + 3W + 2CO\uparrow$$

The three pastes are driven simultaneously by a triple-extruder mechanism, as illustrated in Figure 3. Continuous control over the material compositions and their gradients during the part building process can be achieved by controlling and coordinating the flow rates for the different pastes. As an example, assuming that the three barrels containing the three different pastes have the same cross-sectional area, a desired paste mixture consisting of 20% paste A, 30% paste B, and 50% paste C can be achieved by controlling the three plunger velocities with the ratios of V1:V2:V3 = 2:3:5, where V1, V2, and V3 are the plunger velocities for pastes A, B and C, respectively. Note that the volumetric paste flow rate is equal to the plunger velocity multiplied by the cross-sectional area of the plunger. The different paste flow rates, together with the percentage of solids loading of each paste and also the material density and molar mass data available from the literature, allows for calculation of the material compositions of the final part. For example, assume that paste A is ZrO_2+WC, paste B is W, and paste C is ZrC, and that the percentage solids loading is the same for the three different pastes. From the above ratios of pastes A, B and C, the weight of ZrC from paste B and the weight of W from paste C can be determined. The ratio of ZrO_2 and WC in paste A should be such that both ZrO_2 and WC are fully consumed when they are converted to ZrC and W during the reactive sintering process. This allows for calculation of the weights of both ZrO_2 and WC for a given amount of paste A, and from these weights, the weights of ZrC and W after reactive sintering can be determined. By adding these ZrC and W weights to the weight of ZrC from paste B and the weight of W from paste C, the ratio of ZrC and W in the final part can be obtained. Using the procedure described above, the weight percentage of ZrC vs. W is determined to be 17.3% vs. 82.7% for the given example.

3. Triple-extruder FEF system design and development

The triple-extruder mechanism was designed using three stainless steel barrels, each containing a paste driven by a plunger whose movement is controlled by a DC servo motor (Kollmorgen AKM23D); see Figure 4. The encoder signal from the servo amplifier provides a resolution of 0.62 μm for the plunger's movement. The flow rate of paste in each barrel is controlled by the plunger's velocity, and the force exerted on the plunger is measured by a load cell (Omega LC-305). A key component of the triple-extruder mechanism is a mixer connected to the ends of the three barrels. The FEF system uses a static mixer, which merges the three different pastes and mixes them into a homogeneous stream as the combined pastes pass a series of mixing blades positioned at alternating angles.

The triple-extruder mechanism is mounted on a gantry system, which consists of three orthogonal linear drives (Velmex, Bloomfield, NY), each with a 508 mm travel range. The X-axis consists of two parallel slides and is used to support the Y-axis. The use of two parallel slides (vs. a single slide) provides a smoother and more stable motion, thus providing a larger work space for part fabrication. The Z-axis is mounted on the Y-axis, and the extrusion mechanism is mounted on the Z-axis. Each of these axes is mounted with limit switches on both ends. Four DC servo motors (Pacific Scientific PMA22B), each with a resolver for position feedback at a resolution of 1000 counts per revolution, drive the various axes. Each motion axis has a maximum speed of 127 mm/s and a position sensor resolution of 0.00254 mm.
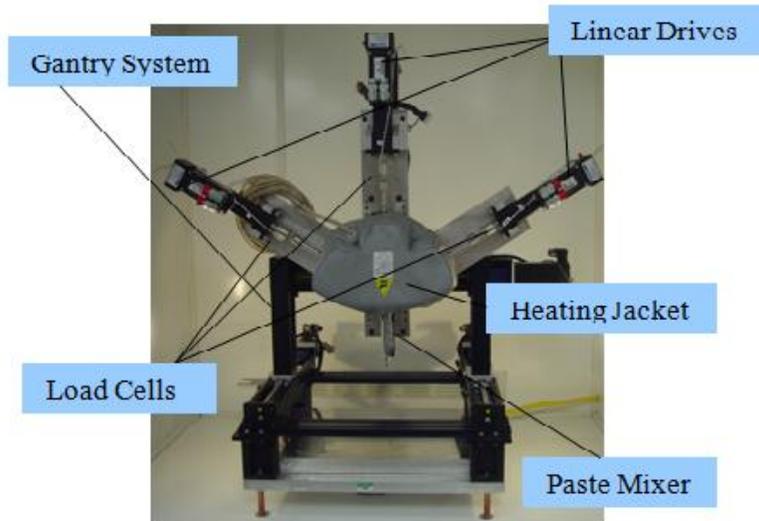
Figure 4: FEF machine with triple-extruder mechanism.

The part fabrication process is carried out in a freezing environment, which can be controlled to as low as -20°C using a liquid nitrogen injection system. This enables the aqueous paste to solidify at temperatures below the freezing point of water after it is extruded. The paste solidification helps avoid part deformation during the fabrication process, thus enabling fabrication of larger parts. To keep the paste from freezing before its exit from the deposition nozzle, a heating jacket is used to keep the paste's temperature above the water freezing point while it is inside the barrels and the mixer. In our present study, the freezer's temperature is kept at -10°C, while the heating jacket's temperature is kept at 10°C.

The FEF control system is developed with a personal computer that has a Turbo PMAC board from Delta Tau Motion System, as shown in Figure 5. The 3-axis movement of the gantry system is controlled by a motion control program with the Delta Tau Turbo PMAC PCI board. The control software is written using the Delta Tau language and downloaded to the Turbo PMAC board via PEWIN32, which is the Delta Tau programming interface. Extrusion of pastes is controlled with three servo motors using a National Instruments PXI chassis and LabVIEW.
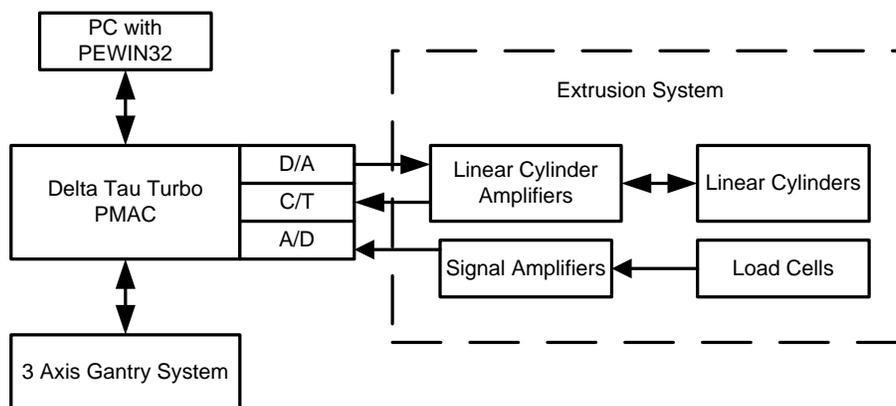

Figure 5: The FEF control system schematic.

4. Paste preparation and testing

The pastes to be extruded each must have an engineered composition and proper rheological behavior for extrusion through a fine orifice to produce a 3D part. The objective of paste preparation is to develop paste recipes that provide high solids loading (>45 vol% to as high as 60 vol% if possible), no phase separation (i.e., liquid phase migration) under pressure, homogeneity of the paste throughout the extrusion process, and pseudoplastic behavior with a defined yield stress. To limit the difference in sintering shrinkage along the cross section of FGM components, $WC+ZrO_2$, W and ZrC were selected as the three pastes. The raw powders (W, ZrO_2, and WC) are characterized using surface areas and particle sizes.

In order to obtain homogeneous aqueous pastes, the raw powders must be well dispersed in water. To this end, a series of settling tests were performed using Darvan C as the surfactant at various pH values in water. The optimal conditions for the ZrO_2, W and WC powders were determined to be 0 mg per gram of ZrO_2 in H_2O at pH=9, 2 mg per gram of W in H_2O at pH=7, and 0 mg per gram of WC in H_2O at pH=8.

To study the rheological behavior of pastes under pressure, a capillary rheometer was designed and fabricated, as shown in Figure 6. The rheological behavior and viscosity of Al_2O_3 slurries containing 40 vol%, 45 vol% and 50 vol% solids loading were determined using the capillary rheometer under various forces based on the following formulae for shear stress, shear rate, and viscosity:

$$ShearStress: \quad \tau = \frac{PR}{2L}$$

$$ShearRate: \quad \dot{\gamma} = \frac{4Q}{\pi R^3}$$

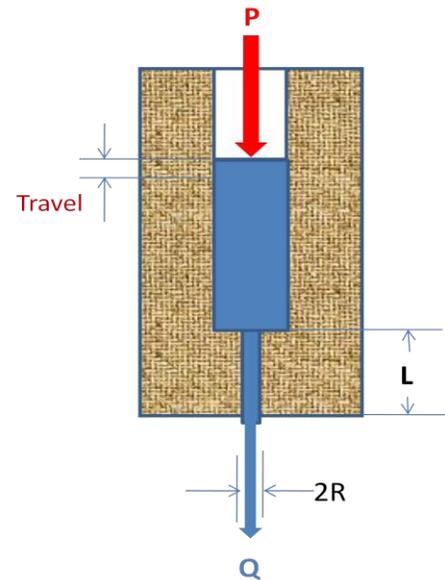$$Viscosity: \quad \mu = \frac{\tau}{\dot{\gamma}} = \frac{\pi PR^4}{8LQ}$$

Figure 6 The capillary rheometer.

where P is pressure, R is nozzle radius, L is nozzle length, and Q is volumetric paste flow rate.

The measured results (Figure 7) show that all of the pastes exhibited pseudoplastic behavior with no visible phase separation. Thus, the Herschel-Buckley model can be used to model and analyze the pastes. The 50 vol% Al_2O_3 paste has the highest yield stress (~60 Pa) among the three tested pastes.
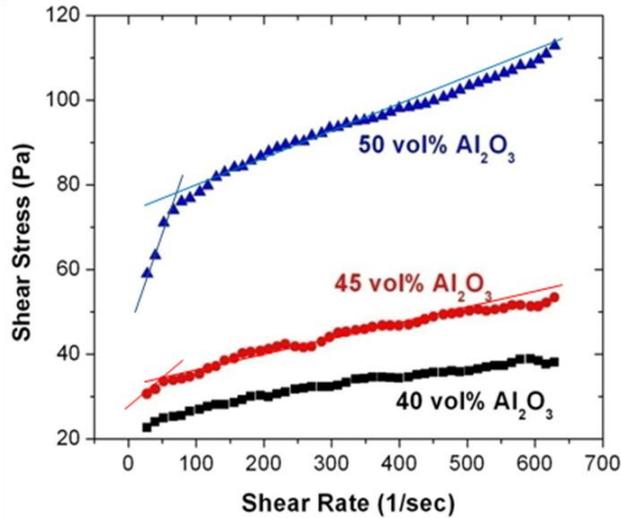
Figure 7: Rheological behavior of Al$_2$O$_3$ paste with different solid loadings.

An appropriate organic binder is required to provide green body strength and to achieve a desirable rheological behavior for extrusion. Three types of water-soluble binders (PVA, Aquazol 200, and Methycell) were examined using Al$_2$O$_3$ as a replacement powder for the ZrO$_2$, W and WC powders in order to minimize experimentation costs. The viscosity and rheological behavior of a series of Al$_2$O$_3$ slurries with various quantities of organic binders were studied. The results indicated that Methycell is the most efficient binder among the three for transforming the rheological behavior of Al$_2$O$_3$ slurries into a pseudoplastic with a high yield stress. As shown in Figure 8, a 0.5 wt% Methylcell addition allows an Al$_2$O$_3$ slurry containing 45 vol% solids to exhibit a yield stress of 220 Pa. In contrast, as shown in Figure 9, an Al$_2$O$_3$ slurry containing 45 vol% solids with a 1.0 wt% Aquazol 200 addition exhibits a yield stress of 130 Pa.
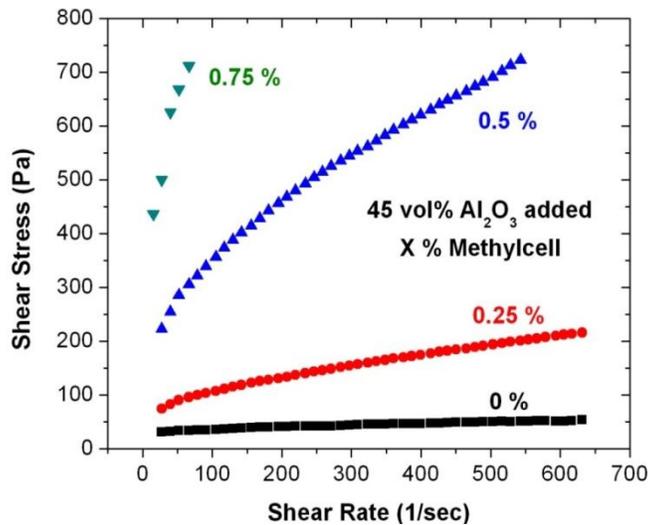

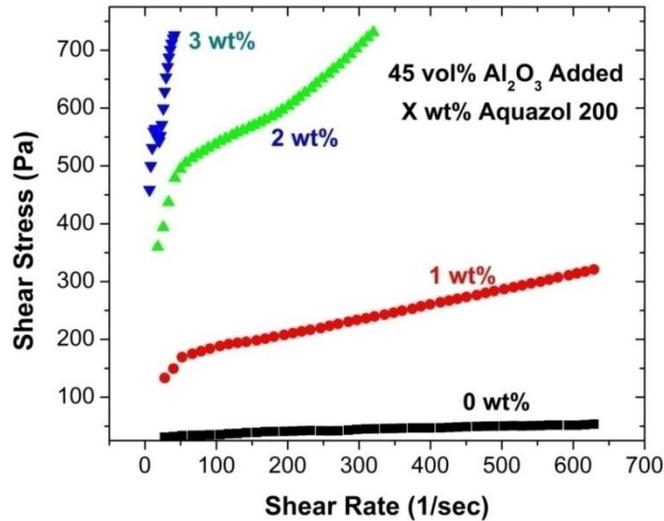Figure 8: Effect of Methylcell on the Al$_2$O$_3$ paste's (45% solid loading) rheological behavior.

Figure 9: Effect of Aquazol 200 on the Al_2O_3 paste's (45% solid loading) rheological behavior.

5. Results of system evaluation

To test the capabilities of the FEF system for building parts with gradient materials, a cylindrical part with a 50 mm diameter was fabricated with two extruders filled with limestone ($CaCO_3$) pastes, one in green color and the other in pink color. The fabrication result is shown in Figure 10. The color of the fabricated cylinder part starts in pink (A) and shifts to brown (B), then green (C), then brown (D), then pink (E), and finally green (F). The color distribution of the part is consistent with the velocity profiles of the two extruders shown in Figure 11. In section A, only extruder 1 was moving, which resulted in the pink color. When both extruders are controlled to move at the same velocity, the extrudate becomes light brown, as shown in section B. Figure 11 also shows that the extrusion force for both extruders remains in the range of 300 to 400 N. Figures 10 and 11 demonstrate that a part can be built with material gradients by varying extrusion velocities for different pastes. Note that the planning and control algorithms must take into consideration a delay between the time the extrusion material is switched to the time the switched material exits the nozzle.

After the visual validation, an investigation of the capability of the FEF system to build an FGM part by varying the ratios of two pastes consisting of different materials, one pure alumina (Al_2O_3) and the other 50Vol% Al_2O_3 + 50Vol% ZrO_2, was performed. For examining the material compositions of the built part, pre-mixed compositions of 50% Al_2O_3 + 50% ZrO_2, 75% Al_2O_3 + 25% ZrO_2, and 100% Al_2O_3 were lab-prepared into pellets, freeze-dried, and sintered as a control set. They then were coated with gold palladium in preparation for energy dispersive X-ray spectroscopy (EDS). The EDS results are shown in Figure 12 for 50% Al_2O_3 + 50% ZrO_2 and in Figure 13 for 75% Al_2O_3 + 25% ZrO_2. Figure 14 shows the calculated ratio of the peak height of zirconium (Zr) vs. the peak height of aluminum (Al) for the pellets made of the three different pastes. These ratios were then used as the basis to examine the material compositions of parts fabricated by the FEF system.
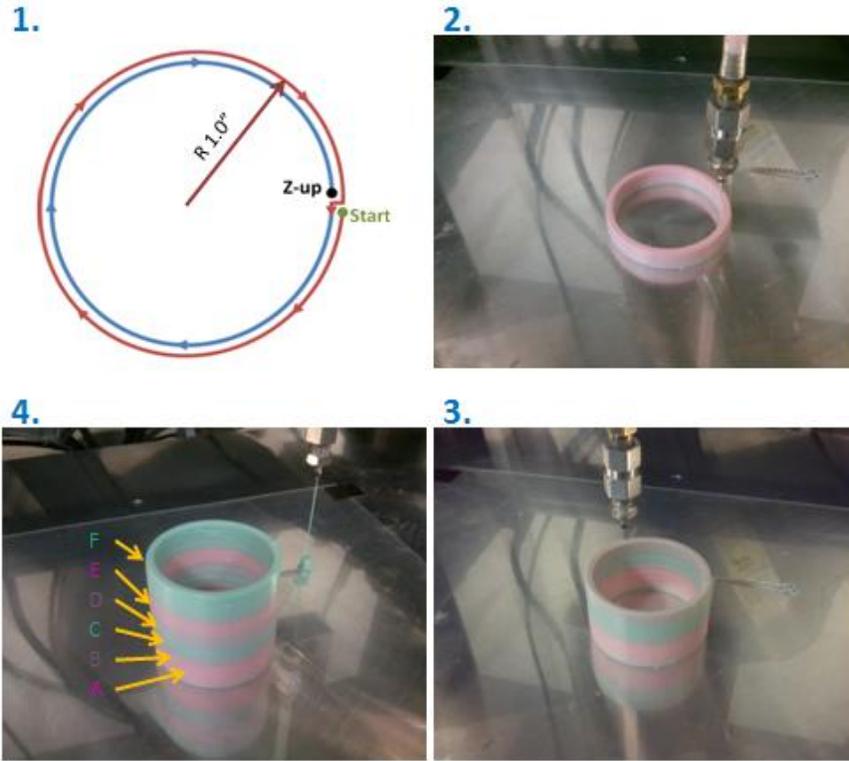
Figure 10: Fabrication of cylindrical part with discrete material gradients.
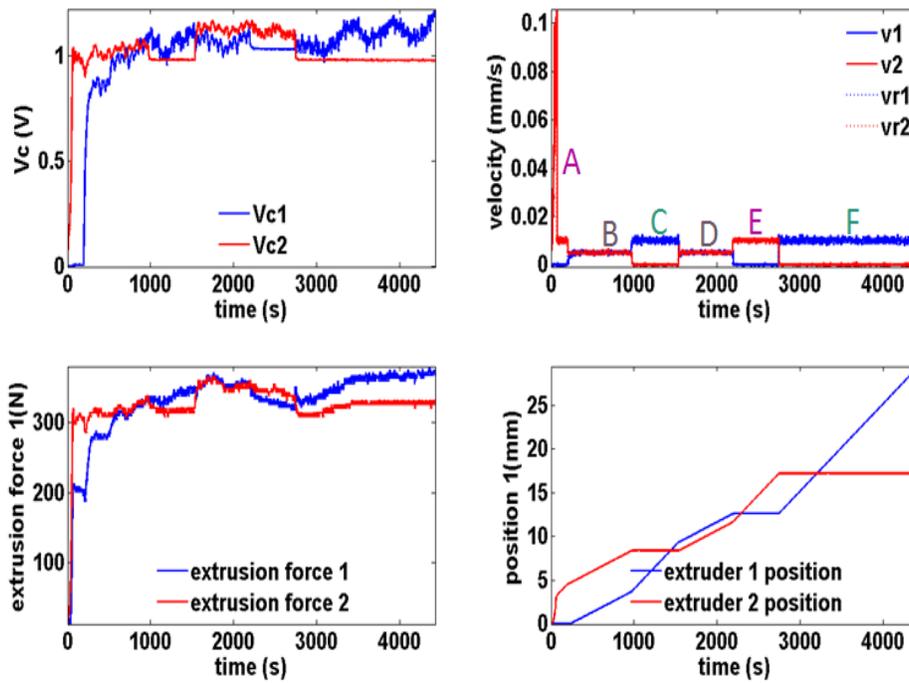

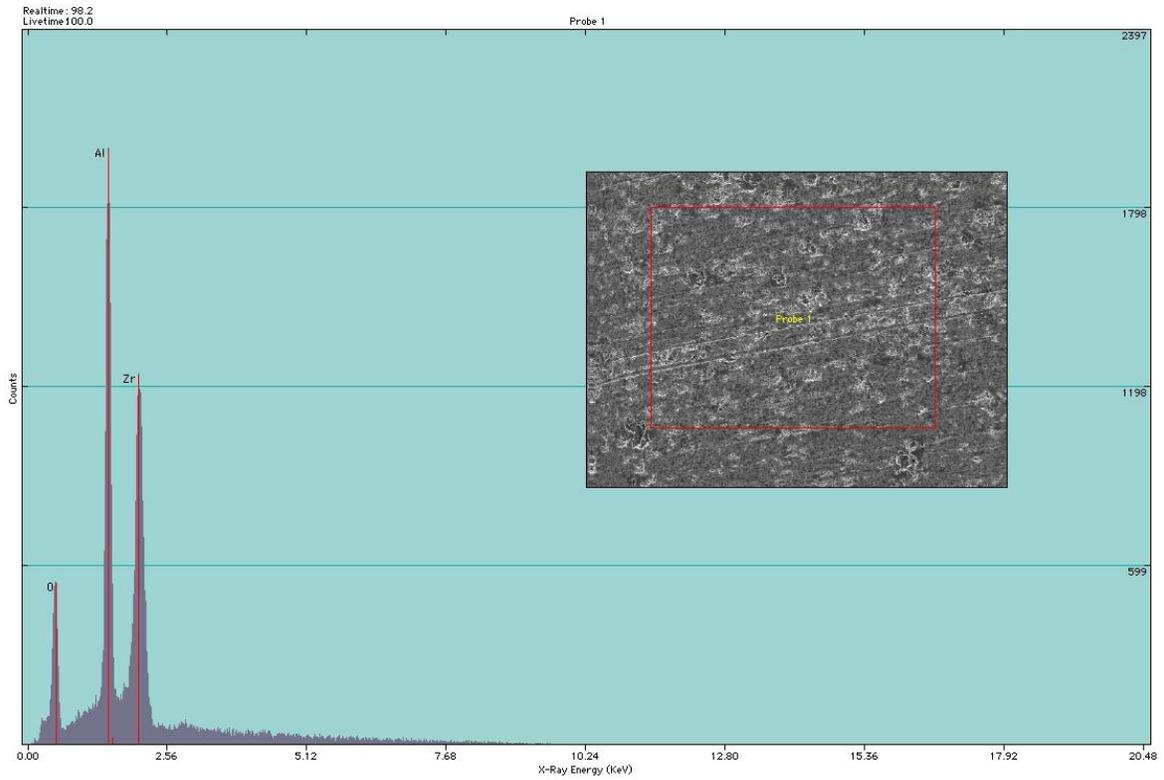Figure 11: Control signal and measured extrusion force and velocity profile.

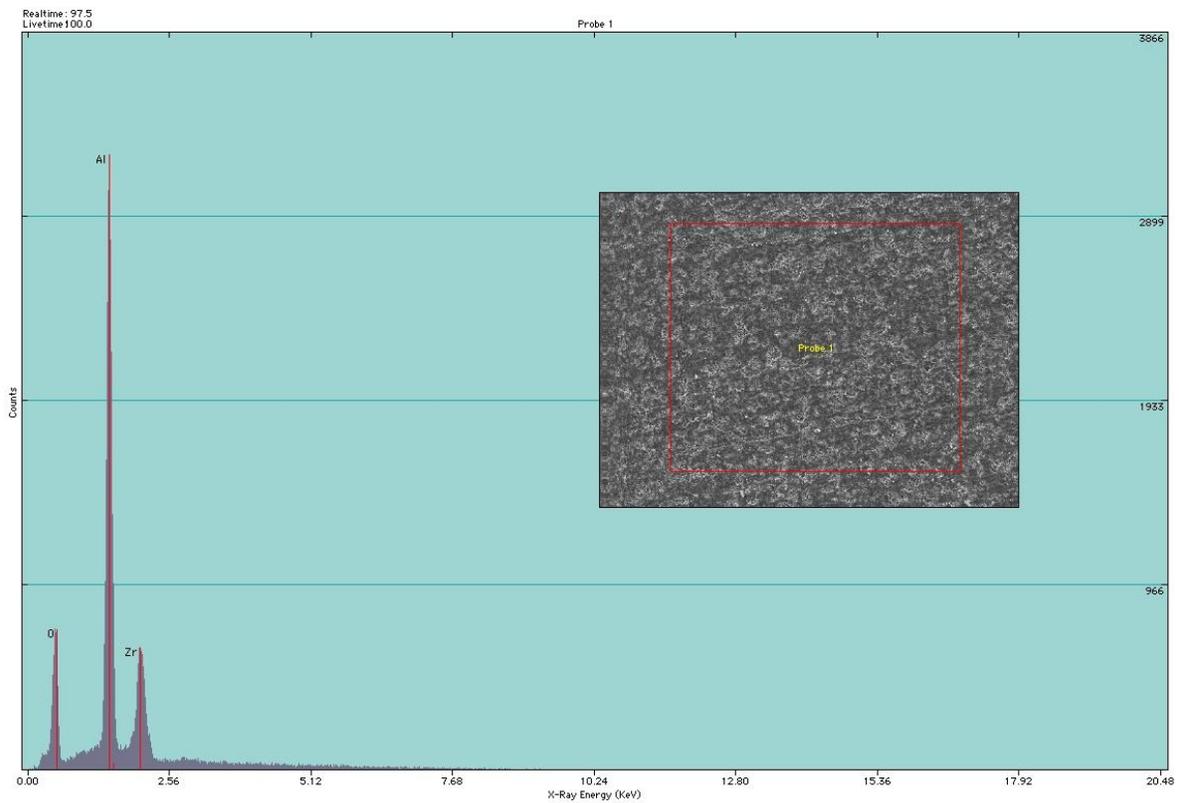Figure 12: EDS intensity distribution of lab-prepared specimens with 50% Al_2O_3 + 50% ZrO_2.

Figure 13: EDS intensity distribution of lab-prepared specimens with 75% Al_2O_3 + 25% ZrO_2.

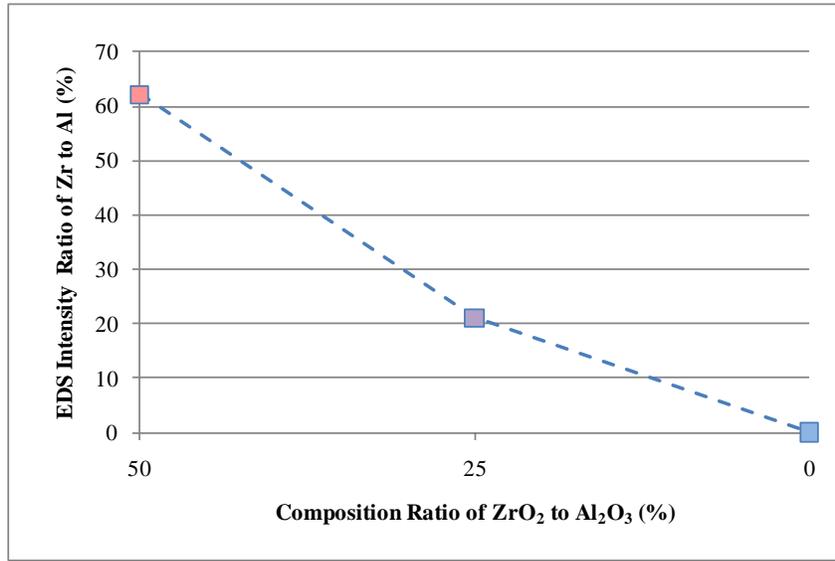Figure 14: Ratio of Zr peak height vs. Al peak height from EDS results for three test pellets.

Parts fabricated using the FEF system began with 100% Al_2O_3 paste, transitioned to one half of 100% Al_2O_3 paste and one half of 50% Al_2O_3+50% ZrO_2 paste (thus, 75% Al_2O_3+25% ZrO_2 in overall composition) and ended with 50% Al_2O_3+50% ZrO_2 paste in building a test bar. Once fabricated, the Al_2O_3-ZrO_2 parts were freeze-dried and sintered to a final height of 32 mm. The freeze-drying was carried out at a temperature of -25 °C and a pressure of about 3000 Pa. The sample was held at this temperature and pressure for 24 hours. The sample was then allowed to warm to room temperature (25 °C) while maintaining the same vacuum pressure and held for an additional 24 hours. Binder burnout was accomplished by heating the samples at 1 °C/min up to 600 °C and holding for 1 hour. From there, the samples were heated at 10 °C/min up to 1550 °C and held for 90 minutes. Following the 90-minute hold, the samples were cooled back to room temperature at 25 °C/min.

The sintered part was then cut, polished, and coated with gold palladium in preparation for EDS measurements. The results are shown in Figure 15 for average EDS intensity measurements over 8 sections with an area 4 mm wide by 3 mm high per section. Figure 16 plots the ratio of Zr peak height vs. Al peak height calculated for each of these sections. For the control test pellets, the ratio of Zr peak height vs. Al peak height was calculated to be 62% (Figure 14) for the composition of 50% Al_2O_3+50% ZrO_2, compared to the FEF fabricated part, which achieved a ratio of 55% for the same composition (Figure 16). This slight discrepancy could be due to the width of the scan area edging into the transition region to the next composition in the FEF built part. Because the intensity measurement is taken as an average over the area, and the edge of the area could contain part of the 75% Al_2O_3 + 25% ZrO_2 mixture, the respective measurement of Zr/Al intensity ratio would decrease slightly. As another comparison, the 75% Al_2O_3 + 25% ZrO_2 test pellets measured a ratio of 20% Zr/Al, and the FEF fabricated part was calculated to be 20% as well. This compares very well because the scan area was contained fully within the desired region.
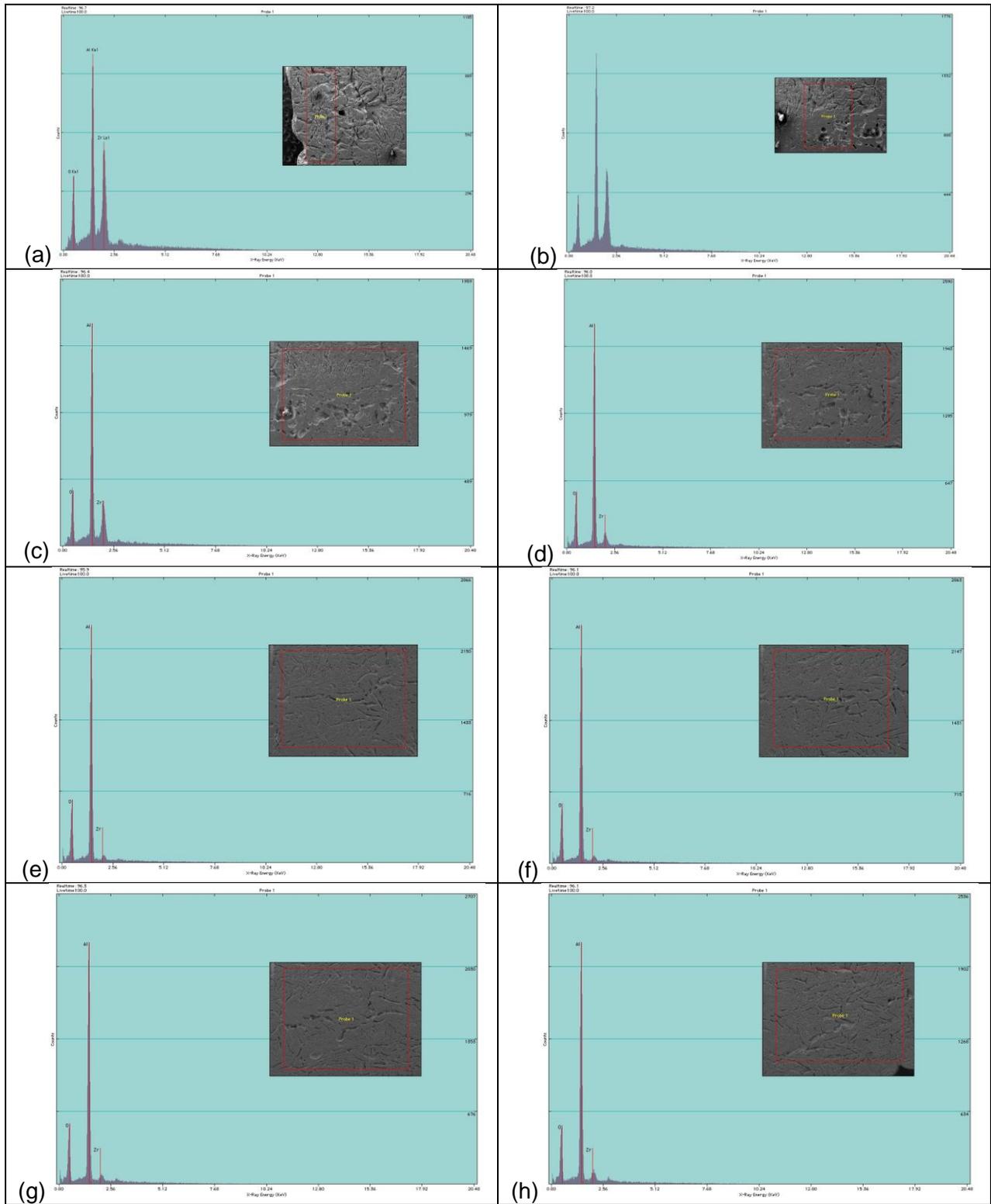
Figure 15: EDS intensity distribution measured for different sections of an FEF fabricated part with varying ratios of Al_2O_3 and ZrO_2 along the measurement direction.
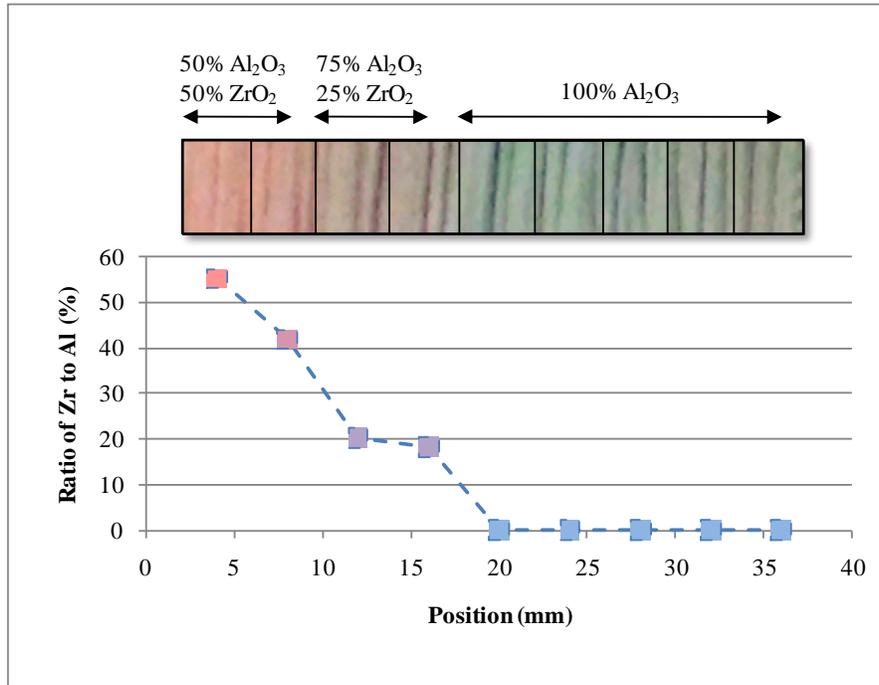
Figure 16: EDS intensity measurements for FEF fabricated test bar**.**

6. Conclusions

A Freeze-form Extrusion Fabrication (FEF) process aimed at fabricating 3D parts that grade between ultra high temperature ceramics and refractory metals after reactive sintering is presented in this paper. The main process concept is to mix multiple aqueous pastes according to part material composition requirements and to extrude the mixed paste to fabricate a 3D part layer-by-layer in an environment below water's freezing temperature. Based on this concept, a triple-extruder FEF system including the mechanical machine, electronics hardware, and computer software has been developed. For paste preparation, a rheological behavior study using Al_2O_3 paste indicates that Methycell is an efficient binder for transforming the paste's rheological behavior into a pseudoplastic with a high yield stress. The capability of the developed FEF system for fabricating 3D parts with desired material gradients is validated first by observing the color transitions and the corresponding extrusion velocity profiles in a fabricated limestone part and then by measuring energy dispersive spectroscopy (EDS) peak intensities in a fabricated test bar with varying Al_2O_3/ZrO_2 ratios along the measurement direction. In the future, investigations using the developed FEF system to fabricate parts with the three pastes: ZrO_2+WC, W, and ZrC, followed by post-processing to produce parts that grade between ZrC and W after reactive sintering, will be performed. The sintered specimens will be evaluated by measuring density, material compositions, and mechanical properties and by characterizing microstructures.

7. Acknowledgements

8. References

[1] A. Bandyopadhyay, P. Panda, M. Agarwala, S. Danforth, and A. Safari, "Processing of Piezocomposites by Fused Deposition Technique," Journal of the American Ceramic Society, Vol. 80, No.6, pp. 1366-1372, 2000.

[2] S. Crump, "Apparatus and Method for Ceramic Three-Dimensional Objects," U.S. Patent No. 5121329, 1992.

[3] G. Hilmas, J. Lombardi, and R. Hoffman, "Advances in the Fabrication of Functional Graded Materials Using Extrusion Freeform Fabrication," Proceedings of Solid Freeform Fabrication Symposium, Austin, TX, pp. 319-324, 1996.

[4] M. Cima, M. Oliveira, H. Wang, E. Sachs, and R. Holman, "Slurry-Based 3DP and Fine Ceramic Components," Proceedings of Solid Freeform Fabrication Symposium, Austin, TX, 2001.

[5] J. Kruth, P. Mercelis, L. Froyen, and M. Rombouts, "Binding Mechanisms in Selective Laser Sintering and Selective Laser Melting," Proceedings of Solid Freeform Fabrication Symposium, Austin, TX, 2004.

[6] M. C. Leu, E. Adamek, T. Huang, G. E. Hilmas, and F. Dogan, "Freeform Fabrication of Zirconium Diboride Parts Using Selective Laser Sintering," Proceedings of Solid Freeform Fabrication Symposium, Austin, TX, 2008.

[7] J. Stampfl, A. Cooper, R. Leitgeb, Y. Cheng, and F. Prinz, "Shape Deposition Manufacturing of Microscopic Ceramic and Metallic Parts Using Silicon Molds," U.S. Patent, No. 6242163, 2001.

[8] J. Cesarano III, R. Segalmen, and P. Calvert, "Robocasting Provides Moldless Fabrication from Slurry Deposition," Ceramics Industry, Vol. 148, pp. 94-102, 1998.

[9] G. He, D. Hirschfeld, J. Cesarano III, and J. Stuecker, "Processing of Silicon Nitride-Tungsten Prototypes," Ceramic Transactions, Vol. 114, pp. 325-332, 2000.

[10] T. Huang, M. S. Mason, G. E. Hilmas, and M. C. Leu, "Freeze-form Extrusion Fabrication of Ceramic Parts," International Journal of Virtual and Physical Prototyping, Vol. 1, No. 2, pp. 93-100, 2006.

[11] M. S. Mason, T. Huang, R. G. Landers, M. C. Leu, and G. E. Hilmas, "Aqueous-Based Extrusion of High Solids Loading Ceramic Pastes: Process Modeling and Control," Journal of Materials Processing Technology, Vol. 209, No. 6, pp. 2946-2957, 2009.

[12] T. Huang, M. S. Mason, G. E. Hilmas, and M. C. Leu, "Aqueous Based Freeze-form Extrusion Fabrication of Alumina Components," Rapid Prototyping Journal, Vol. 15, No. 2, pp. 88-95, 2009.

[13] X. Zhao, R. G. Landers, and M. C. Leu, "Adaptive Extrusion Force Control of Freeze-Form Extrusion Fabrication Processes," ASME Journal of Manufacturing Science and Engineering, Vol. 132, No. 6, 2010.

[14] N. D. Doiphode, T. Huang, M. C. Leu, M. N. Rahaman, and D. E. Day, "Freeze Extrusion Fabrication of 13-93 Bioactive Glass Scaffolds for Bone Repair," Journal of Material Science: Materials in Medicine, Vol. 22, No. 3, March 2011.