FREEZE-FORM EXTRUSION FABRICATION OF FUNCTIONALLY GRADED MATERIALS

ABSTRACT
Presented in this paper is a novel additive manufacturing technology for making three-dimensional parts with functionally graded materials (FGMs), called Freeze-form Extrusion Fabrication (FEF). The system development included extruder modeling and control, composition gradient control for a triple-extruder mechanism, and motion code generation for a 3-axis positioning system. The effectiveness of the developed FEF system was demonstrated first by fabricating alumina parts in complex geometries using a tool path planning software and then by fabricating limestone parts with graded colors. Composition verification was then conducted by building ‘green’ parts with graded compositions between alumina and zirconia. The fabricated part went through post-processing and was analyzed using energy dispersive spectroscopy (EDS) to determine its material compositions.

1. INTRODUCTION
Since the mid 1980s many additive manufacturing processes have been developed, initially for polymers and then metals, for fabricating 3D components from CAD models in a layered manner [1-2]. 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 ceramic components. They include Fused Deposition of Ceramics [3], Fused Deposition Modeling [4], Extrusion Freeform Fabrication [5], 3D Printing [6], Selective Laser Sintering [7-8], Shape Deposition Manufacturing [9], and Robocasting [10-11].

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 [12-13]. Unlike most other extrusion freeform fabrication processes, which use organic binders to bond the ceramic powders, the organic binder content is only 2-4 vol% in this process, while the paste solids loading is 45 to 50 vol% or higher. Also, unlike Robocasting, FEF builds a ‘green’ (before post-processing) part in an environment below the freezing point of water to solidify the paste after the deposition of each layer during the fabrication process. This enables relatively large parts to be built compared with Robocasting. Cones and other monolithic ceramic components, including alumina (Al₂O₃) and zirconium diboride (ZrB₂) parts, have been fabricated using the FEF process; see Figure 1 [14-15]. This process has also been investigated for the fabrication of 13-93 bioactive glass scaffolds with pre-designed porosity and pore architecture [16].

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 to be integrated with underlying substructures, which are typically made of metals such as aluminum or titanium. To achieve these demanding characteristics, one approach is to build these components with grading from a ceramic to a 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 and when the part is in service. Additive manufacturing processes are advantageous for fabricating such components with functionally graded materials (FGMs).

This paper describes the design and development of a triple-extruder FEF system for fabricating parts with FGMs. The part fabrication process involved 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 with pre-specified material compositions. The system development also included 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 evaluation results with the developed system.

2. PROCESS AND SYSTEM CONCEPT
To realize the process of fabricating an FGM part, an FEF machine equipped with three servo controlled extruders and an
inline static mixing unit to combine the pastes through a single orifice has been designed and developed. This mixing technique results in a natural transition between composition changes; however, it introduces a transport delay. This delay must be repeatable and accurately predicted in order for the path planning algorithm to deposit material in the desired location. The system transport delay \( t \) was modeled using linear relationships between the paste volumetric flow rate \( Q \) and the combined internal volume of each segment of the static mixer \( V \):

\[
    t = \frac{V}{\sum_{i=1}^{n} A v_i + A v_2 + A v_3}
\]

where \( n = 3 \) is the number of cylinders being used, \( A_i \) is the cross sectional area of the \( i^{th} \) cylinder, and \( v_i \) is the velocity of the \( i^{th} \) plunger. The combined flow rate from all three extruders, \( Q \), is equal to the sum of the individual flow rates, \( Q_1, Q_2 \) and \( Q_3 \). The ratio of \( Q_1:Q_2:Q_3 \) represents the ratio of the three pastes in the material composition.

The three pastes are extruded simultaneously by a triple-extruder mechanism, as illustrated in Figure 2. Continuous control over the material compositions and their gradients during the part building process can be achieved by planning (with time delay taken into consideration) and controlling the relative flow rates of the different pastes. As an example, assuming that the three cylinders 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 \( v_1:v_2:v_3 = 2:3:5 \), where \( v_1, v_2, \) and \( v_3 \) are the plunger velocities for pastes A, B, and C, respectively.

![Fig. 2. Triple extruder mechanism design.](image)

In order to build complex three-dimensional parts, the machine must be able to start and stop extrusion on demand. This can be achieved with a controller that uses load cell feedback to regulate the force applied to each plunger. A hybrid force-velocity control scheme is used to have good control over the steady state extrusion flow rate (velocity controller) and the extrusion on demand (force controller).

### 3. SYSTEM DESIGN AND DEVELOPMENT

#### 3.1. Equipment Setup

The triple-extruder mechanism was designed using three stainless steel cylinders, each containing a paste driven by an individual plunger whose movement is controlled by a DC servo motor (Kollmorgen AKM23D); see Figure 3. The encoder signal from the servo amplifier provided a resolution of 0.62 μm for the plunger’s movement. The paste flow rate in each cylinder was controlled by the plunger’s velocity, and the force exerted on the plunger was measured by a load cell (Omega LC-305). The FEF system used a static mixer to blend the three different pastes and mixed them into a homogeneous stream as they passed a series of mixing blades positioned at alternating angles.

The triple-extruder mechanism was mounted on a gantry system, which consisted of three orthogonal linear drives (Velmax BiSlide), each with a 508 mm travel range. The X-axis consisted of two parallel slides and was used to support the Y-axis. The Z-axis was mounted on the Y-axis, and the extrusion mechanism was mounted on the Z-axis. Four DC servo motors (Pacific Scientific PMA22B), each with a resolver for position feedback at a resolution of 1000 counts per revolution, drove the various axes. Each motion axis had a maximum speed of 127 mm/s and a position sensor resolution of 2.54 μm.

![Fig. 3. Triple FEF system in a temperature-controlled enclosure. Three servo motors control linear cylinders for extrusion and a three-axis gantry system controls motion.](image)

The part fabrication process was conducted in a freezing environment, which could be controlled to as low as -20°C using a liquid nitrogen injection system. This enabled the aqueous paste to solidify at temperatures below the freezing point of water after it was extruded to solidify the paste, thus avoiding part deformation during the fabrication process and enabling fabrication of larger parts. A heating jacket was used to keep the paste temperature above the freezing point of water until it was deposited. In the present study, the freezer’s temperature was kept at -10°C, while the heating jacket’s temperature was kept at 10°C.

The 3-axis gantry system movement was controlled by a motion control program with the Delta Tau Turbo PMAC PCI board. Paste extrusion was controlled with three servo motors using a National Instruments PXI chassis and LabVIEW Real Time 8.6.

#### 3.2. General Tracking Velocity Controller Design

A general tracking controller, as shown in Figure 4, was designed to track the reference velocity \( v_r \) of each linear cylinder. The sampling period for digitization, \( T_s \), is 10 ms.
The transfer function of the servo motor for the plunger velocity is
\[
\frac{V(z)}{U(z)} = \frac{K(1-e^{-\tau_1/z})}{z - e^{-\tau_1/z}} \frac{b(z)}{a(z)}
\]
where \(r\) is the time constant of the servo motor and \(K\) is the voltage gain. The term \(d(z) = zI\) is the disturbance-generating polynomial in Figure 4. By including this polynomial, the Internal Model Principle was utilized to robustly reject constant disturbances such as Coulomb friction. The characteristic polynomial \(a(z)g(z)\) was designed to have two poles located at \(-e^{-\tau_1/z}\) and \(-e^{-\tau_2/z}\), where \(\tau_1\) and \(\tau_2\) are the desired closed-loop time constants. Thus the controller polynomial \(g(z)\) is
\[
g(z) = g_1(z) + g_2 = \left(e^{-\tau_1/z} + e^{-\tau_2/z} - 1 - e^{-\tau_1/z}\right)z
+ \left(e^{-\tau_2/z} - e^{-\tau_1/z}\right)
\]
where \(v_i\) is the reference velocity and the velocity error is
\[
e_i(k) = v_i(k) - v(k)
\]
\[
u(k) = u(k-1) + \frac{v_i(k+1) - \left(1 + e^{-\tau_1/r}\right)v_i(k)}{K\left(1 - e^{-\tau_1/r}\right)}
+ \frac{e^{-\tau_2/r}v_i(k-1) - g_1e_i(k) - g_2e_i(k-1)}{K\left(1 - e^{-\tau_2/r}\right)}
\]
where \(e_i(k)\) is the velocity error.

3.3. General Tracking Force Controller Design

A force controller was developed using an analytical dynamic force response model for the paste extrusion process [1]. This model is a nonlinear relationship between the extrusion force and extrusion velocity as
\[
\frac{df}{dt} = \left(f_f(t) - f_{friction} + A_p \rho L / \rho_0\right)^2 \frac{u_p(t) - u_{sp}(t)}{A_p / \rho L}
\]
where \(u_p\) (mm/s) is the plunger velocity, \(f_f\) (N) is the load force, \(f_{friction}\) (N) is the friction force (N), \(A_p\) (m²) is the plunger cross sectional area, \(\rho_0\) (atm) is the initial pressure in the syringe and \(L_0\) (m) is an effective air layer thickness. This “air layer” represents an effective entrapped volume of air within the paste that causes the paste to behave as a compressible fluid. The \(u_{sp}\) (m/s) term describes the steady state velocity achieved at a given force, which is a function of paste rheology and can be explicitly determined from experimentation as a power law function
\[
u_{sp} = 10^{-4} \left(\frac{f_f + \alpha}{\beta}\right)^{\gamma}
\]
The model was linearized for controller design
\[
\tau_L \frac{\dot{f}}{f} + \frac{\dot{f}}{f} = \tau_L \frac{\dot{u}_p}{u_p} - K_L \dot{u}_p
\]
This controller tracks a reference force by regulating the plunger velocity, using the internal velocity controller developed in section 3.2.

Controller response can be seen in Fig. 5 for a step input of 60 to 500 N (i.e., for start commands), and then from 500 to 60 N (i.e., for stop commands). For positive changes in reference force, the time constant is approximately 400 ms, comparable to the desired time constants of the system (set as 200 and 600 ms). Negative changes in reference force result in a time constant of 100 ms. Start commands are issued by dwelling at the desired start point for 400 ms before continuing in the direction of travel. After the force stabilizes, the controller switches to velocity control to regulate the steady state extrusion speed. A trajectory-based method is used in order to stop extrusion – from experimentation it had been found that stopping 20 to 60 ms early (before the end of a track) would cause extrusion to stop accurately at the desired stopping point.
Test parts were fabricated using the automated path planning software to evaluate its feasibility (Fig. 7). The velocity and extrusion on demand force controller operated well in conjunction with the tool path planning software for Al₂O₃ ceramic paste and the FEF fabricated parts were successfully freeze-dried and sintered.

4.2. Control of Grading Between Two Pastes

To test the capabilities of the FEF system for building continuous geometry parts (i.e., no extrusion on demand) with gradient materials, a cylindrical part with a 50 mm diameter was fabricated using two extruders filled with limestone (CaCO₃) pastes, one with a green color and the other with a pink color. The fabrication result is shown in Fig. 8. The color of the fabricated part starts 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 plungers shown in Figure 9. In section A, only plunger 1 was moving, resulting in the pink color. When both plungers were moving at the same velocity, the extrudate became light brown, as shown in section B. Figure 9 also shows that the extrusion force for both plungers remained in the range of 300 to 400 N. Figures 8 and 9 demonstrate that a part can be built with material gradients by varying plunger velocities for extrusion of different pastes.

The capabilities of the FEF system were further tested by fabricating a cylindrical part with a 50 mm diameter with 10% composition step change from 100% blue paste to 100% pink paste, by changing the velocity of each plunger to achieve this composition change every 4 mm height. The fabricated part from the CaCO₃ pastes of two different colors is shown in Figure 10.

4.3. Composition Verification

An investigation of mixing behavior was conducted to verify the actual deposited composition for a gradient from pure alumina paste (Al₂O₃) to a paste composed of 50Vol% Al₂O₃ + 50Vol% ZrO₂. Pellets were prepared from pre-mixed compositions of 50% Al₂O₃ + 50% ZrO₂, 75% Al₂O₃ + 25% ZrO₂, and 100% Al₂O₃, then freeze-dried and sintered as a control set. The sintered specimens were then coated with gold palladium in preparation for energy dispersive spectroscopy (EDS) analysis. The EDS intensity charts for the 50% Al₂O₃ + 50% ZrO₂ pellet and for the 75% Al₂O₃ + 25% ZrO₂, and 100% Al₂O₃ pellets are shown in Figure 11. Note that the ratio of Al:Zr in these charts does not indicate actual composition, but can be used for comparison to FEF prepared specimens.

Test parts fabricated using the FEF system began with 100% Al₂O₃ paste, transitioned to one half of 100% Al₂O₃ paste and one half of 50% Al₂O₃+50% ZrO₂ paste (thus, 75% Al₂O₃+25% ZrO₂ in overall composition) and ended with 50% Al₂O₃+50% ZrO₂ paste. Once fabricated, the Al₂O₃-ZrO₂ parts were freeze-dried and sintered to a final height of 32 mm. The freeze-drying was conducted at a temperature of -25 °C and a pressure of 3000 Pa. 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 for EDS measurements. The average EDS intensity measurements were taken over 9 sections with an area 3 mm wide by 4 mm high per section. Figure 12 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 as 62% for the composition of 50% Al$_2$O$_3$+50% ZrO$_2$, as compared to the FEF fabricated part having a ratio of 55% for the same composition. This slight discrepancy could be due to the width of the scan area edging into the transition region of the next composition in the FEF built part. Because the intensity measurement was taken as an average over the area, and the edge of the area could contain a portion of the 75% Al$_2$O$_3$+25% ZrO$_2$ mixture, the respective measurement of Zr:Al intensity ratio would decrease slightly. In another comparison, the 75% Al$_2$O$_3$+25% ZrO$_2$ test pellets were measured and calculated to have a ratio of 20% Zr:Al. This value was found to be the same (20%) for the FEF fabricated part. For this region of the FEF part the scan area was contained fully within the desired region, resulting in greater measurement accuracy.

5. CONCLUSIONS

A Freeze-form Extrusion Fabrication (FEF) process aimed at fabricating 3D parts with functionally graded materials 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 the water’s freezing temperature. Based on this concept, a triple-extruder FEF system including the mechanical machine, electronics, and computer software has been developed. The capability of the developed FEF system for fabricating 3D parts was tested using tool path planning software for several geometry parts. The feasibility of the FEF system for fabricating FGM parts with desired material gradients was validated by observing the transitions between pink and green colored CaCO$_3$ pastes and relating them to the measured velocities of the corresponding plungers. The validation was further done by fabricating specimens that consist of a ceramic composite graded from 100% Al$_2$O$_3$ to a 50:50 Al$_2$O$_3$:ZrO$_2$ mixture. Energy dispersive spectroscopy (EDS) measurements were used to verify the compositional changes across the graded specimen in comparison with a control set of specimens having known Al$_2$O$_3$:ZrO$_2$ compositions.

6. ACKNOWLEDGEMENTS

This project is funded by NSF grant #CMML-0856419 with matching support from the Boeing company through the Center for Aerospace Manufacturing Technologies and the Intelligent Systems Center at the Missouri University of Science and Technology, and by the Air Force Research Laboratory contract #10-S568-0094-01-C1 through the Universal Technology Corporation.

7. REFERENCES


