

Recent Developments in Freeform Fabrication of Dense Ceramics From Slurry Deposition

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Abstract

A freeform fabrication technique for dense ceramics and composites has been developed. The technique requires less than 2 volume percent of organic additives and relies on the principle of layerwise deposition of highly loaded colloidal slurries. Components can be manufactured into complex geometries with thick solid sections as well as with thin-walled sections with high aspect ratios. Process feasibility and quality is dependent on the processing parameters of solids loading, slurry rheology, deposition rate, and drying rate. These interrelated parameters must be controlled so that sintering defects are prevented and shape tolerance is maintained. A review of this freeform fabrication technique, called robocasting, will be discussed for fabrication of aluminum oxide parts. Recent developments for a finite element analysis technique for modelling the drying process will also be presented.

Introduction

Most of the techniques currently being developed for the freeform fabrication of dense structural ceramics revolve primarily around the sequential layering of ceramic loaded polymers/waxes or modified stereolithography using ceramic loaded ultraviolet curable resins. [1-3] For all of these techniques, pre-sintered parts typically have 45 - 60 vol% ceramic and 40 - 55 vol% polymer. In this regard, these techniques are analogous to powder injection molding of ceramics and require very long and complicated heat treatments to prevent cracking and produce a dense ceramic, free of organics. Consequently, while a part may be rapidly prototyped within a few hours, it may still take several days to densify the part. A typical heating rate is 0.2 °C per minute [4].

A new technique is being developed at Sandia National Laboratories for the freeform fabrication of dense ceramics that utilizes less than 2 volume percent organics. Therefore, a dense ceramic part may be freeformed, dried, and sintered in less than 24 hours. The process is based on the extrusion of highly loaded ceramic slurries that are typically 50 - 65 vol.% ceramic powder, < 1 vol.% organic additives, and 35 - 50 vol.% volatile solvent (usually water). This technique is useful for the near-net-shape fabrication of components with simple or complex shapes. Called robocasting, the technique uses robotics for computer controlled deposition of ceramic slurries through an orifice. The ceramic slurries are extruded in sequential layers. Any conceivable two-dimensional pattern may be "written" layer by layer into a three-dimensional shape (Figure 1). Orifice openings can range from several millimeters to tenths of millimeters. Robocasting is analogous to the ceramic near-net-shape processing techniques, slip casting [5] and gel casting [6]; however, robocasting is moldless and fabrication times are quicker. To maintain structural integrity while building a component, robocasting relies on the rheology of the deposited slurry and on partial drying of the individual layers. In contrast to gel casting and other freeform fabrication techniques, robocasting does not require organic polymerization reactions or solidification of a polymeric melt to maintain the shape of components.

Robocasting is no more conceptually complicated than chalking a bathtub. Except that, during robocasting, the substrate actually moves underneath the point where material is dispensed from a stationary orifice. While conceptually simple, transforming this concept into reality for the manufacture of ceramics requires a synergistic control of the : 1) percent solids in the ceramic powder slurry, 2) viscosity and rheology of the slurry, 3) dispensing rate of the slurry through the orifice, 4) drying kinetics of the dispensed bead of slurry, and 5) computer code for optimal machine instructions.

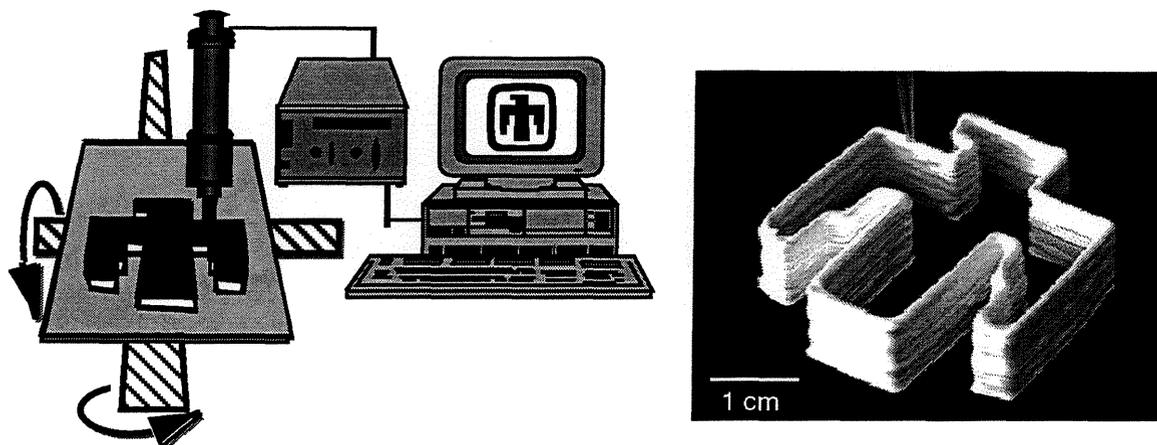


Figure 1. Schematic of the Robocasting process with an inset photo of an aluminum oxide thunderbird made in 20 layers and sintered crack-free to 96% theoretical density.

Experimental

The ceramic powder used was A-15 alumina from Alcoa Industrial Chemicals. The average particle size was $2.2 \mu\text{m}$ with a surface area of $4.3 \text{ m}^2/\text{g}$. Deionized water was used as the solvent and Darvan 821A (R.T. Vanderbilt Corp.) as the dispersant. The aqueous alumina slurries were made according to Cesarano, et al [7] and were 58 to 61 vol% alumina. The slurries were then aged for up to 20 days by gently mixing on a ball mill. The aging process made the slurry rheology suitable for robocasting.

The robotic slides used for the X, Y, Z and dispensing axes were purchased from Velmex, Inc. The slides were controlled with stepper motors and controllers from Arrick Robotics. When fabricating parts, typical table speeds were 0.5 to 1.2 cm/sec and typical slurry dispensing rates were 0.006 to 0.01 ml/sec. The slurry was dispensed onto a copper plate which was temperature controlled and maintained at temperatures ranging between 30 - 50 °C.

Rheological measurements were performed using a Brookfield DV-III programmable rheometer with a concentric cylinder attachment.

Modelling of the change in shape of dispensed beads of slurry with time was performed using GOMA. GOMA is a finite element analysis code for the fluid flow of free surfaces, developed at Sandia National Laboratories [8].

Results and Discussion

The slurry viscosity and the rheological dependence of viscosity with shear rate must be tailored during processing for optimal performance. During dispensing, the slurry will

experience high shear conditions while flowing through the orifice and as the moving substrate interacts with the dispensing slurry. However, immediately following this process, the slurry experiences a shear rate near zero. Therefore, in order to control the shape of dispensed beads, the slurry rheology must be extremely pseudoplastic so that the material can flow smoothly during dispensing but then solidify in place once shear stresses are removed (similar to paint). If the slurry is too fluid, beads will spread uncontrollably. If the slurry is too viscous, beads lay down like rope and maintain rounded tops. When the proper rheology is obtained, beads yield nearly rectangular cross sections with relatively straight walls and flattened tops (Figure 2A). Perfectly, rectangular cross sections would be optimal for filling space when additional layers are sequentially dispensed.

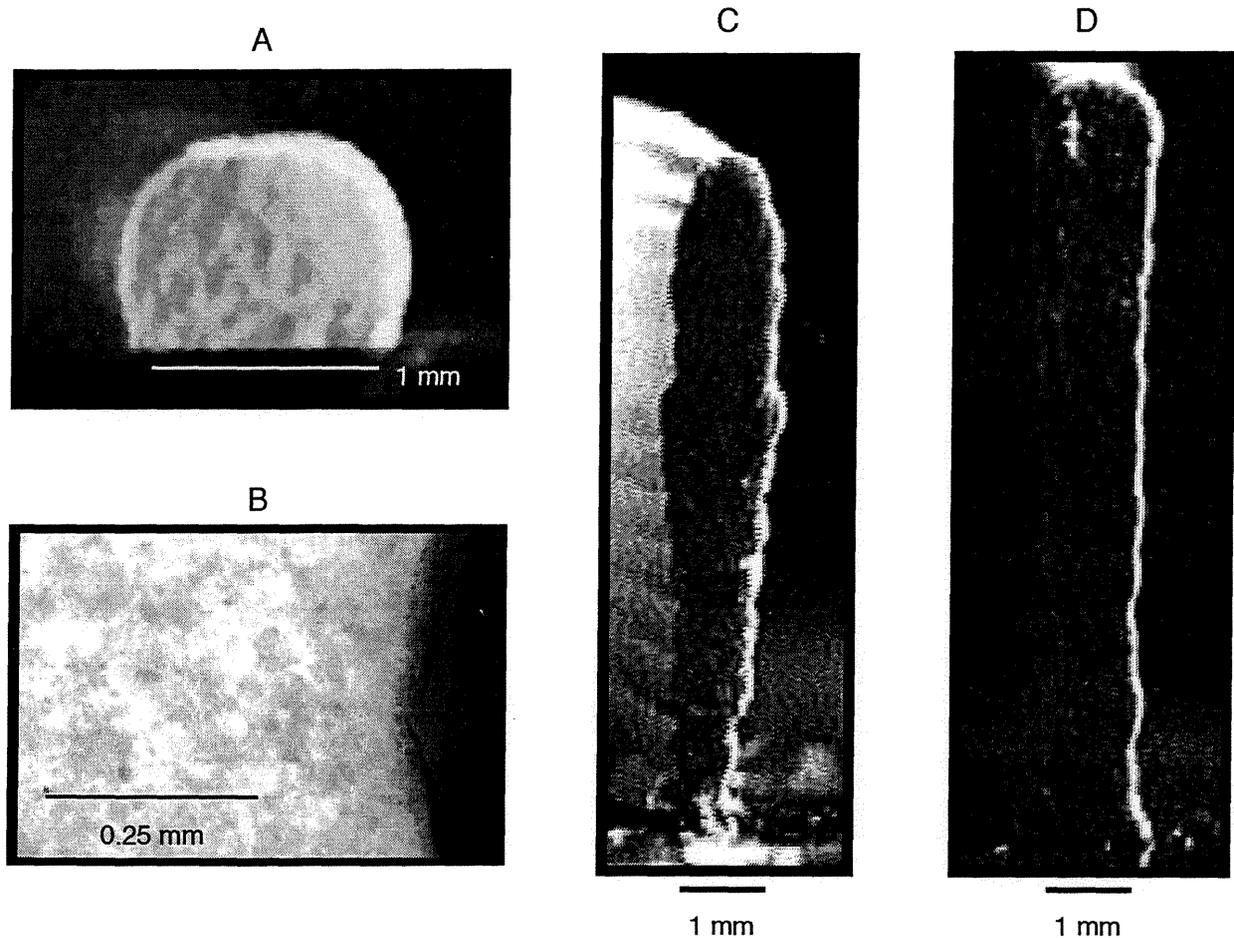


Figure 2. Cross sections of beads of aluminum oxide: (A) beads which flow into a shape with relatively straight walls and flat tops improve space filling; (B) properly dried layers mesh together without any defect detection using 10X optical microscopy; (C) Low viscosity and slow drying results in slumping of layers, forming nonuniform walls; (D) Proper rheology and drying yields beads which stack relatively straight and uniform.

Figure 3A shows the rheology for a slurry that yielded good behavior during robocasting. After 16 days of gentle mixing, a 61 vol% slurry exhibited the necessary yield stress and pseudoplastic rheology to make beads similar to those shown in Fig. 2A. Note that the 16 day old curve is practically level and that after the slurry begins to yield, only a very small increase in shear stress is required to induce substantial flow and large increases in shear rate. In practical terms, this slurry shows an appreciable resistance to flow but once flow has been initiated, the

viscosity decreases dramatically and there is very little resistance to flow. In fact, the viscosity of the 16 day old slurry decreases from nearly 1 million cP (at 0.07 s^{-1}) to 40,000 cP (at 1.7 s^{-1}). This is a very large decrease in viscosity over a small increase in shear rate. A typical shear rate through a robocasting orifice is 20 s^{-1} .

The rheology demonstrated in Fig. 3A is actually quite ideal for robocasting. The slurry will readily flow upon shear and then return to a state exhibiting a yield stress once shear has been removed. However, there are other factors that must be considered for multilayering and actual part fabrication. During multilayering, slumping may occur as a freshly dispensed bead is smeared over a previously dispensed bead. The smearing may induce a shear stress on the previously dispensed bead that exceeds the yield stress. Also, added weight due to multilayering may accumulate enough stress to induce flow in previously dispensed beads. Therefore, it is necessary to be able to permanently lock in the structure of a dispensed bead before smearing or weight build up can cause slumping. This may be accomplished by transforming the pseudoplastic slurry that behaves like a liquid into a dilatant mass that behaves like a solid. Typically, a ceramic slurry will start to behave like a dilatant solid once the solids loading is increased above approximately 64 vol%. Even though there is approximately 36 vol% water present, all of the water is entrapped in voids between the particles and particle mobility is restricted. If fact, as more stress is applied, particle mobility becomes even more unlikely and the structure of the solid/liquid mass is locked (i.e., dilatant). For robocasting this phenomenon is taken advantage of for "solidifying" beads of slurry before appreciable slumping can occur. For alumina slurries only minimal drying is required in order to increase the solids loading from 61 vol% solids to 64 vol% solids and transform the slurry rheology from pseudoplastic to dilatant. At this time, the shrinkage is virtually complete and shape changes are minimal as the remaining water is dried from the pores between the particles. The final dried density is typically 65 vol% alumina. The change in rheology due to the pseudoplastic to dilatant transition is shown schematically in Fig. 3B.

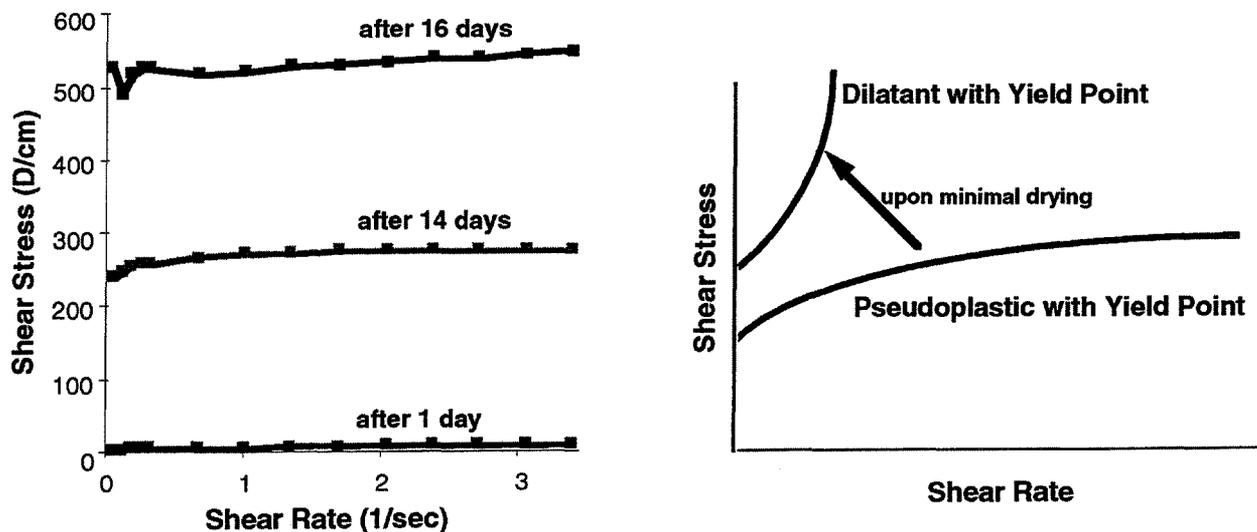


Figure 3. Shear stress vs. shear rate curves for pseudoplastic alumina slurries: A) 61 vol% alumina aged for 1, 14, and 16 days; B) schematic showing the transition of a pseudoplastic slurry into a dilatant slurry by drying.

The time that it takes to transform a dispensed bead of slurry into a stable dilatant mass is dependent on the size of the bead and the rate of drying. If the drying rate is too slow and the yield stress of the slurry too low then transformation to dilatancy may not occur until several layers have already been deposited. In this case, the added weight of slurry may induce

slumping. An example of this behavior is shown in Fig. 2C. Figure 2C shows a cross section of a wall built by multilayering 12 beads of slurry on a heated substrate. Above the fifth layer, appreciable slumping was observed. Heat transfer from the heated copper plate up through the beads of slurry was not great enough to sustain adequate drying kinetics on the freshly dispensed beads. Therefore, the slower drying beads in layers 5 through 11 did not have sufficient time to make the transformation from pseudoplasticity to dilatancy. As a result, the yield stress of these beads was exceeded and slumping occurred. Conversely, Fig. 2D shows that relatively uniform walls may be built with high aspect ratios when the drying kinetics can induce dilatancy before any external forces induce yielding and slumping of previously dispensed beads. However, if drying is forced to be too fast with respect to the rate of slurry deposition, warping, cracking, and delamination may occur.

When a functional balance between the bead dimensions, time between layers, and drying rate is achieved; not only can complicated shapes be fabricated but boundaries between layers disappear. Defect free boundaries are created under optimal drying conditions because fluid from freshly dispensed beads permeate into the partially dried bead that was previously deposited. The fluid transport naturally drags some powder particles with it and creates a finite interpenetrated region between the two beads that is free of defects or delaminations (Figure 2B).

Finite Element Analysis Of Drying

The drying process for dispensed beads of slurry is anisotropic and obviously very complicated with changes in solid content, dimensions, shape, and rheology all occurring simultaneously. The final structure is far from an equilibrium condition. However, in an effort to further understand the drying of slurries, we have started a study that utilizes a finite element analysis program, GOMA, developed at Sandia National Laboratories. [8] The GOMA program is being used to analyze the interplay between the mass transfer of water and fluid mechanics (viscosity) of the slurry to predict the size and shape of beads as a function of time. The time effects are not necessarily intuitive because the drying is anisotropic and the drying rate is dependent on the volume fraction of solids. Therefore, factors that need to be included in the finite element interaction calculations are changes in diffusivity and viscosity as the volume fraction of solids increases. The changes in viscosity with increasing solid volume fraction is represented by

$$\mu = \mu_r (1 - \emptyset / \emptyset_m)^n \quad (1)$$

where μ is the viscosity of the slurry, μ_r is the viscosity of the solvent, \emptyset is the solid volume fraction, \emptyset_m is the maximum solid volume fraction, and n is an empirical exponent. [9] The diffusivity of the solvent through the slurry during drying is represented by an equation attributed to Batchelor [10]

$$D_s = \left[\kappa T / 6\pi\mu_r A \right] (1 + 1.45\emptyset) \quad (2)$$

where κ is Boltzmann constant and A is the average particle diameter. The drying rate of water from the free surface is controlled by the mass transfer coefficient of water (k) and the vapor pressure.

The GOMA model was used to simulate shape and dimensional changes of beads of ceramic slurry that contained 58 vol% solids at the beginning of drying. The diagrams in Fig. 4 represent the predicted shape of beads that have been drying for 5 minutes at three different

drying rates. Since the beads should be symmetric, each diagram is drawn as one-half of the cross section of the bead. Fig. 4A has a drying rate that is fast enough to cause the entire bead to exhibit the maximum viscosity within five minutes. The maximum viscosity is defined as the viscosity at the solid content ϕ_m (typically 64 vol%). In the case of Fig. 4A, the fast drying rate induces the formation of a very high viscosity shell that "freezes in" a rounded shape. The rounded shape is maintained until drying is complete. Conversely, Fig. 4C shows that for very slow drying rates, appreciable slumping can occur and the bead still doesn't form a shape preserving shell after 5 minutes. Under intermediate drying (Fig. 4B), high viscosity regions may form on the edges and cause the formation and maintenance of relatively straight walls. However, the formation of a high viscosity shell on the top of the bead is delayed so that appreciable flattening of the bead may occur during drying. This shape is similar to the shape observed experimentally in Fig. 2A and approaches the optimal rectangular shape that is best for space filling. With further study, this code may become a very useful tool for understanding the mechanisms in successful robocasting and for optimizing slurries and operational parameters to form optimally shaped beads.

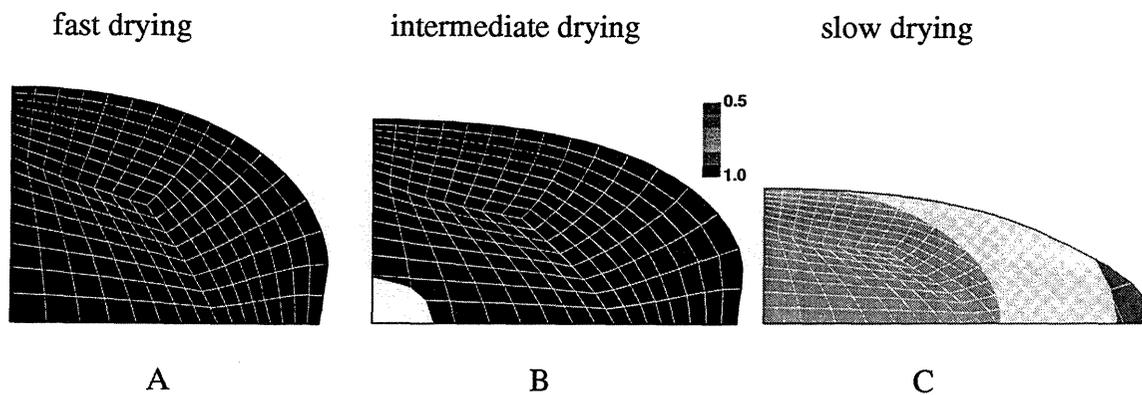


Figure 4 Finite element models of 58 vol% slurries that have been dried for five minutes at: A) fast drying rate, $k = 0.001$ cm/s, B) intermediate drying rate, $k = 0.0001$ cm/s, and C) slow drying rate, 0.00001 cm/s. The color scale represents the slurry viscosity throughout the grid. A viscosity of 1.0 indicates that the slurry has become dilatant.

Example Parts

In actual practice, when the materials issues discussed above are properly controlled, the processing window is quite large and forgiving and several different shapes have been robocasted from alumina slurries and sintered into relatively strong dense parts. Upon drying, the consolidated densities of aluminum oxide bodies are routinely approximately 65%. Upon sintering, crack-free alumina components have sintered densities greater than 95%. The entire process from fabrication through sintering may be completed in less than 24 hours. Components may be fabricated into bulk solids with large thicknesses unobtainable using slip casting; or, thin walled pieces made with aspect ratios greater than 20 and wall thicknesses less than 1 mm. Some examples of robocast alumina parts are shown in Fig. 5. Parts with overhangs up to 30 degrees have been built (Fig. 5A). The part with tailored porosity in Figure 5B is particularly interesting. It demonstrates the precision capability of robocasting and the possibilities for fabricating structures, with undercuts and closed porosity, that are not currently possible by traditional manufacturing methods. The part shown in Fig. 5B is actually an example of a substrate that is infiltrated with metal and used for fabricating graded ceramic/metal interlocking joints.

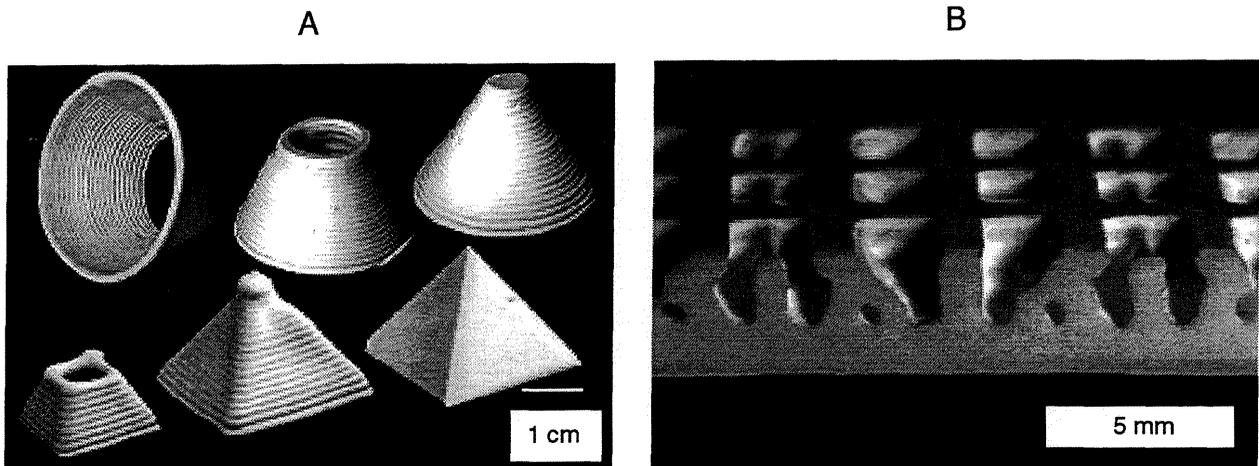


Figure 5 Examples of sintered aluminum oxide parts made by Robocasting: (A) Shows thin walled and solid parts. Notice that with minimal machining surfaces can be made smooth; (B) This cross section shows the symmetry and control that can be obtained in an intricate structure with tailored porosity. Due to regions with closed porosity and undercuts, this part could probably not be made by traditional molding or machining techniques.

Summary

It has been demonstrated that robocasting may be useful for the solid freeform fabrication of dense ceramic parts that may not be fabricated using traditional means. And, this near-net-shape technique is essentially binderless, utilizing less than 2 vol% organic processing aids. Successful robocasting requires controlled interactions among the solids loading of the slurry, the slurry rheology, the extrusion rate, the bead dimensions, and the drying rate. Finite element modelling of bead drying is yielding information for the understanding and optimization of extruded bead shape.

Sandia is now exploring the possibilities for multimaterial deposition for the moldless manufacture of intricately shaped composites and hybrid electronic packages. This task requires a significant effort in the development of computer software that can analyze a CAD file for a component and convert the file into a set of machine instructions that optimize processing parameters to produce high quality robocast components with precise control of feature resolution. Additionally, there is an effort to incorporate smart processing capabilities into robocasting with the aid of sensors and computer modeling. Sensors that monitor build conditions in real time are being incorporated into the system to provide closed loop sensor-based feedback for adjustment of build parameters during component fabrication.

Acknowledgment

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References

- 1) Agarwala, et al, American Ceramic Society Bulletin (1996), **75**, 11, 60-65.
- 2) Griffin, Mumm, and Marshall, American Ceramic Society Bulletin, (1996), **75**, 7, 65-68.
- 3) Griffith and Halloran, J. Am. Ceram. Soc., (1996), **79**, 10, 2601-08.
- 4) Heuer, Kernan, Baldwin, Ko, Liu, and Cawley, "Properties of Engineering Materials Made by CAM-LEM Technology, presented at the Solid Freeform Fabrication Symposium, University of Texas at Austin, August 11-13, 1997.
- 5) Reed, Introduction to the Principles of Ceramic Processing, John Wiley & Sons, (1988), chapter 22.
- 6) Omatete, Janney, and Strehlow, American Ceramic Society Bulletin (1991), **70**, 10, 1641-49.
- 7) Cesarano and Aksay, J. Amer. Ceram. Soc., (1988), **71**, 12, 1062-67.
- 8) Schunk, Sackinger, Rao, Chen, Cairncross, Baer, and Labreche, "GOMA - A Full-Newton Finite Element Program for Free Surface and Moving Boundary Problems with Coupled Fluid/Solid Momentum, Energy, Mass, and Chemical Species Transport: User's Guide," SAND95-2937, Sandia National Laboratories, Albuquerque, NM, January 1996.
- 9) Krieger, Adv. Colloid. Interface Sci., Vol. 3, 111-36, (1972).
- 10) Batchelor, J. Fluid Mech., Vol. 74, No. 1, (1976).