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Fabricating Zirconia Parts with Organic Support Material by the Ceramic On-Demand Extrusion Process

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Abstract

Ceramic On-Demand Extrusion (CODE) is an extrusion-based additive manufacturing process recently developed for fabricating dense, functional ceramic components. This paper presents a further development of this process and focuses on fabricating 3 mol% yttria-stabilized zirconia (3YSZ) components that cannot be fabricated without using support structures. The 3YSZ paste is deposited through the main nozzle, and a polycaprolactone (PCL) pellet feedstock is melted and deposited through an auxiliary nozzle to build support structures. After a green part is printed and dried, the support structures are removed by heating the part to ~70 °C to melt the PCL. The part is then sintered at 1550 °C to achieve near theoretical density. The maximum angle of overhanging feature that can be fabricated without support was determined to be 60°. Sample parts were fabricated and evaluated to demonstrate the effectiveness of the PCL support material and CODE's capability to fabricate geometrically complex parts.

Introduction

Several additive manufacturing (AM) processes have been developed for ceramics and glasses, including binder jetting [1,2], material extrusion [3-12], vat photopolymerization [13,14], powder bed fusion [15,16], and directed energy deposition [17-22], among others. Ceramic On-Demand Extrusion (CODE) [8-12] is a recently developed paste extrusion based AM process, which produces ceramic components with near theoretical density (>98%) after sintering. It deposits high solids loading (>50 vol%) aqueous ceramic pastes onto a substrate layer by layer at room temperature. Each deposited layer is partially solidified by uniform infrared radiation drying from above prior to initiation of a subsequent layer. At the same time, undesirable water evaporation from the sides of the part is prohibited by surrounding the part with a liquid [11]. This layered uniform radiation drying approach minimizes the moisture content gradient in the part during the fabrication process and thus enables CODE to produce crack-free ceramic parts (after sintering). The printed parts are then bulk-dried in a controlled environment with appropriate humidity, after which the green bodies are sintered to produce near-theoretical density parts [8-10].

Support structures are needed for the CODE process to produce geometrically complex parts. In a previous study, an inorganic sacrificial support material, consisting of $CaCO_3$ (calcium carbonate), was used as the support material for fabricating Al_2O_3 (aluminum oxide) parts. A two-step sintering process was developed for the support structure removal due to the favorable phase equilibrium between Al_2O_3 and $CaCO_3$ within the sintering temperature range. After the green part was fabricated, the first sintering step was performed at 1100 °C. This step decomposed the support material into CaO (calcium oxide) and partially densified the main material. The part was then placed in water or an acid solution to dissolve the support structures. After the support material was removed, the second sintering step was performed at 1500 °C to obtain the dense ceramic part. Although successful, the multi-step sintering reduces the overall process efficiency. Also, in using an inorganic support material, co-firing is required to remove the support material, which introduces the risk of part cracking due to mismatch in the coefficient of thermal expansion (CTE) between the main material and the support material. Compared to an inorganic support material such as $CaCO_3$, an organic support material can be removed from the part before sintering, and thus the undesirable co-firing process is avoided.

The present paper describes the development of a technique for fabricating 3YSZ parts by the CODE process with the use of an organic sacrificial support material. A CODE system developed for this process was configured for concurrent deposition of two materials, with one auger extruder for depositing 3YSZ paste as the main material and a heating syringe extruder for melting and depositing an organic support material. Polycaprolactone (PCL), which has a melting point of 60 °C, was investigated for use as the support material. Sample parts including an H-shaped part and a spur gear were fabricated for demonstration purposes. The dimensions of these parts after sintering were measured and compared to their CAD models.

CODE Process and Experimental Setup

The CODE process extrudes and deposits aqueous pastes onto a substrate to print layers sequentially. During printing, the level of a liquid medium is controlled to surround the part in order to prevent water evaporation from the sides of the part, thus avoiding moisture gradation from the part's side surfaces to its core. Between the printing of each layer, infrared radiation is applied from the top to uniformly dry and partially solidify the layer. The layered uniform radiation drying prevents part cracking and warping. More details of the CODE process are available from references [8-12].

The CODE fabrication system [11] consists of a motion subsystem (gantry), an extrusion device mounted on the gantry and capable of extruding viscous ceramic pastes at controlled flowrates, an oil feeding device to regulate the oil level in the tank, and an infrared radiation heating device capable of moving the infrared source and providing on/off control. In the present work, the CODE system was configured for deposition of two materials. As shown in Figure 1, extruder A is an auger extruder for ceramic paste deposition [23], and extruder B is a heating syringe extruder for depositing a molten organic material by pneumatic force.

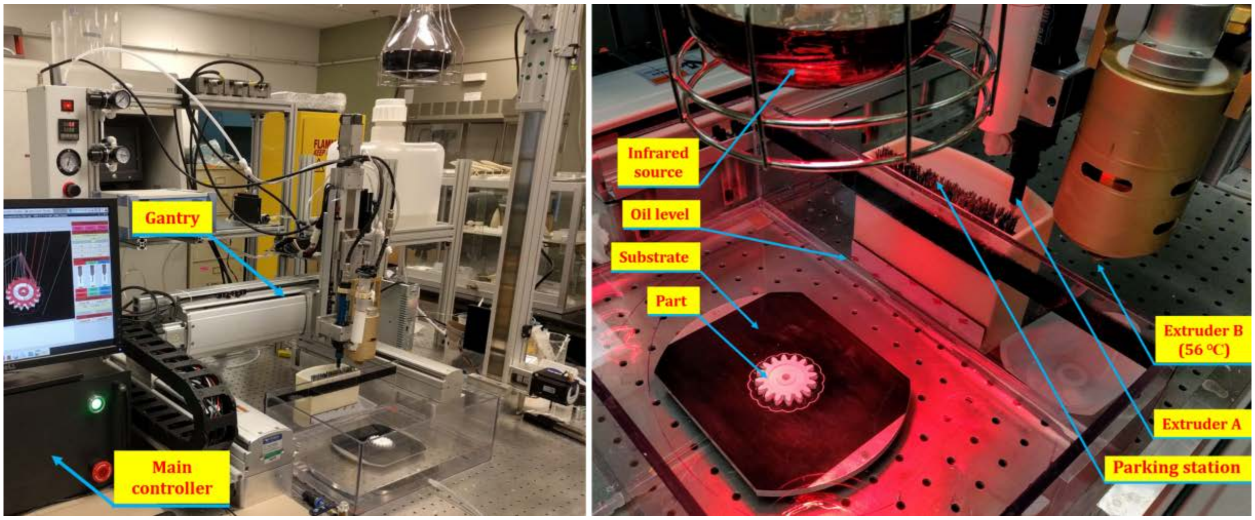

Figure 1. An overall view (left) and a close-up view (right) of the CODE fabrication system configured for dual-extruder printing.

Experimental Procedure

A commercially available zirconium oxide powder (TZ-3Y-E, Tosoh USA, Inc., Grove City, OH, USA) was selected as the raw material. Batches of ceramic paste were produced in 100 ml quantities and consisted of 52 vol% ceramic particles dispersed in distilled water, 30% ammonia ammonium hydroxide solution (NH_4OH, Sigma Aldrich, St. Louis, MO, USA), R-C(O)OH (Dolapix CE 64, Zschimmer & Schwarz, Inc., Lahnstein, Rhineland-Palatinate, Germany) dispersant, polyethylene glycol (PEG 400, Sigma-Aldrich, St. Louis, MO, USA) and hydroxypropyl methyl cellulose (METHOCEL J 75 MS-N, DOW Chemical Company, Midland, MI, USA). The suspensions were mixed within 24 hours prior to part fabrication. The solvent pH was adjusted drop-wise using ammonium hydroxide solution until an alkaline pH ≈ 9-10 was achieved, as measured by a pH meter (HI 2210, Hannah Instruments, Woonsocket, RI, USA). A zirconia slurry was prepared by combining the solids, ammoniated water, dispersant, and spherical 3 mm zirconia milling media (YSZ grinding media, Inframat Advanced Materials LLC, Manchester, CT, USA) in a HDPE jar, and was milled for 18-20 hours. PEG 400 and METHOCEL were then added and the contents were milled for an additional 3 hours to achieve homogeneity. The final two added components increased the viscosity such that the slurry became a paste, which was then agitated on a vibratory table to remove entrapped air prior to transfer to a pneumatic syringe for deposition.

Several organic materials were considered for potential use as the support material. Methyl cellulose solution was first examined. It was previously shown to work as a support material in the fabrication of Al_2O_3 parts by the Freeze-Form Extrusion Fabrication process at -10 ℃ environment temperature [6]. However, this material turned out to be not printable in the CODE process since it could not solidify at room temperature until being dehydrated for hours. Candle wax and microcrystalline wax were then examined, but they are soluble in oil and became soft during the printing process. Support materials for the Fused Deposition Modeling (FDM) process including PLA, ABS and PVA were not examined here since they would require about 200 ℃ printing temperature, which is not safe with the mineral oil used in the CODE process. Finally, PCL (polycaprolactone, Sigma Aldrich, St. Louis, MO, USA) was tested and turned out to be workable at about 60 °C. PCL pellets were loaded into the syringe of the heating extruder in the CODE system, and the heating temperature was regulated at 56 °C, which is the lowest temperature to melt PCL pellets. An air pressure of 85 psi was applied to extrude the molten PCL.

Results and Discussion

Determination of maximum overhang angle

The maximum angle of overhanging features that can be printed without using support structures in the CODE process was determined for the 3YSZ paste. Several wedge-shaped parts with different overhang angles were examined. The process parameters in this experiment are listed in Table 1. As shown in Figure 2, the overhanging feature started to deform when the test part with 65° overhang was attempted, and the part with 70° collapsed. Hence the maximum overhang angle for the 52 vol% solids loading 3YSZ paste in the CODE process was identified to be 60°. Note that the upper limit of the overhang angle may vary for different part material, part geometry and process parameters.

Table 1. Process parameters for printing wedge-shaped test parts

Parameter	**Value**
Nozzle diameter	610 µm
Layer thickness	300 µm
Line spacing	600 µm
Printing speed	20 mm/s
Paste drying time	25 s per layer

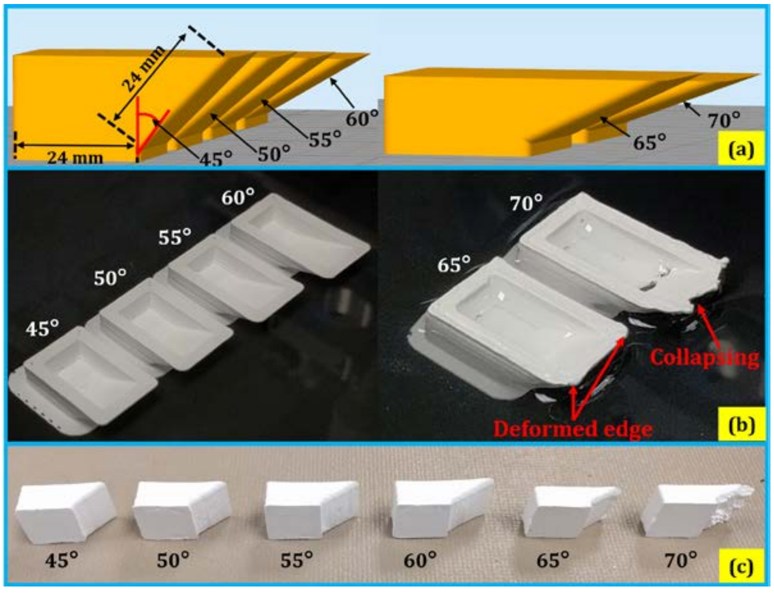

Figure 2. Wedge-shaped test parts attempted: (a) CAD models, (b) As-printed parts surrounded by oil in a tank, (c) Dried parts.

Part fabrication

Several sample parts which required support structures during the CODE process were fabricated to validate the feasibility of using PCL as a support material and to evaluate the shrinkage of the fabricated parts due to sintering. An H-shaped part was chosen as the first sample geometry for evaluating the fabricated 3YSZ parts. Figure 3 shows the printing of an H-shaped part. Three H-shaped parts were fabricated using the process parameters in Table 1. The temperature of the heating extruder was 56 °C and the air pressure used for extruding PCL was 85 psi. The infill density for both the main material and the support material was 100%, i.e., solid infill. In addition to the H-shaped part, a spur gear with grooves was fabricated using the CODE process, as shown in Figure 4. Note that in Figure 4(b) red light was emitted from the infrared heater for drying each newly-deposited paste layer. The values of process parameters used for printing the spur gear were the same as those used for printing the H-shaped part.

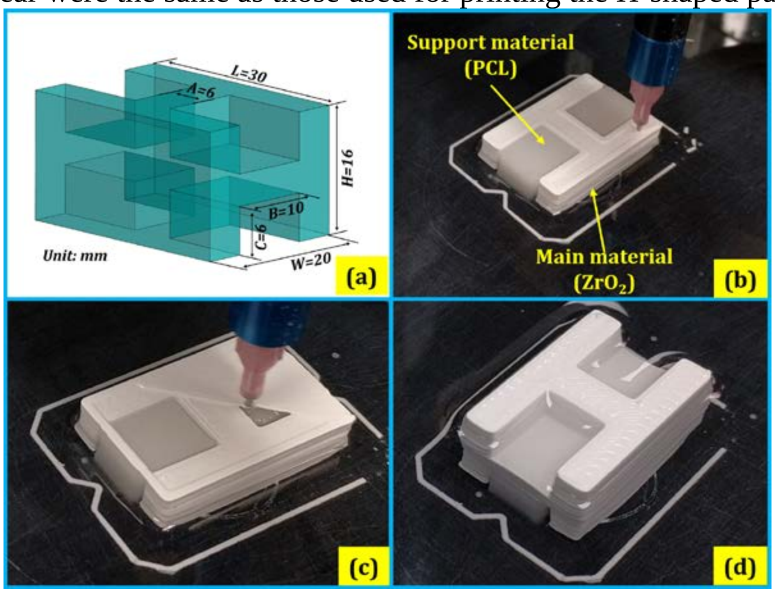

Figure 3. H-shaped part fabricated with using PCL as the support material: (a) CAD model, (b) & (c) Part being printed, (d) Part printed completely.

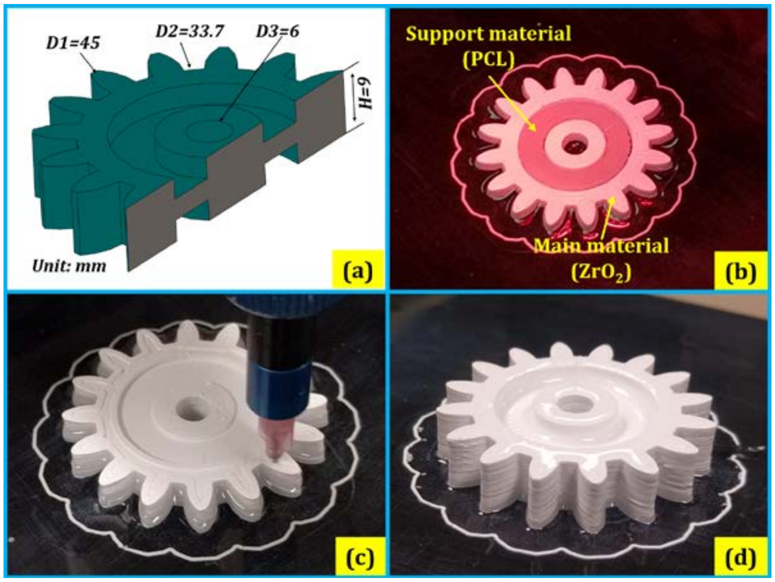

Figure 4. Printing of a spur gear sample part: (a) CAD model, (b) & (c) Part being printed, (d) Part printed completely.

After each part was printed, the oil in the tank was drained and the part was removed, along with the substrate, from the tank for post processing. Post processing included bulk drying for removing the remaining water content inside the part and also the oil on the part's surface, followed by support material removal and part sintering.

Bulk drying was accomplished by placing the CODE fabricated parts in an environmental chamber (LH-1.5, Associated Environmental Systems, Ayer, MA, USA), where the relative humidity and temperature were kept at 75% and 22 °C, for 12 h. The high humidity in the chamber provided a low drying rate, so that warpage and crack formation could be avoided. The substrate with the dried part was placed on a hot plate and heated to 70 °C to melt the PCL support structure. The ceramic green part was then removed from the substrate and sintered in a furnace (Deltech Inc., Denver, CO, USA), as shown in Figure 5. The furnace first heated the part to 500 °C and was held for 1 h to remove the binder content and residual PCL support material, and next ramped to 1550 °C and held for 1 h to sinter the 3YSZ part. Figure 6 shows the sintered spur gear.

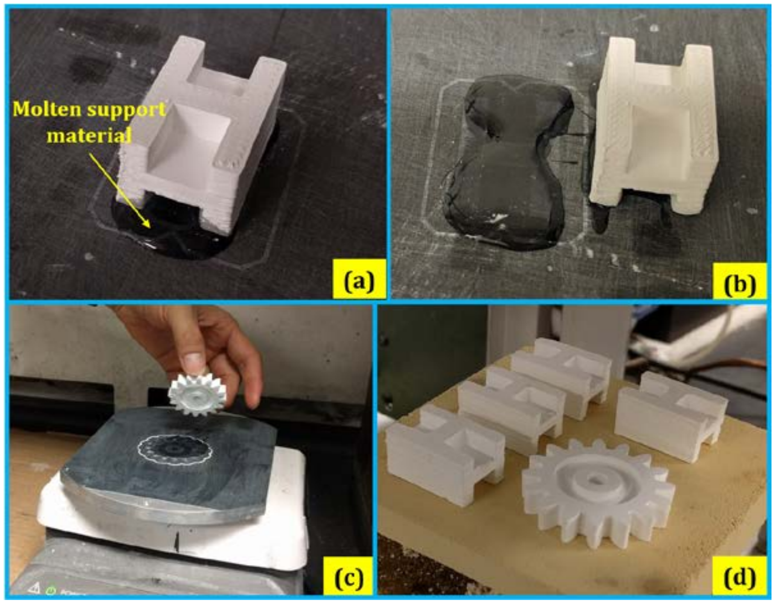

Figure 5. Support material removal and sintering: (a) Substrate heated to melt PLC, (b) & (c) Part separated from substrate, (d) Parts placed inside a furnace for sintering.

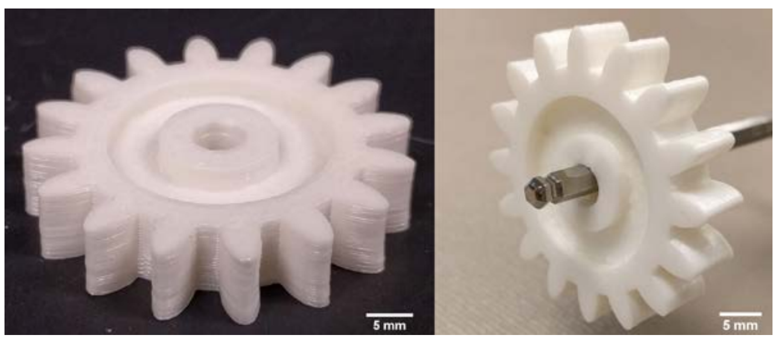

Figure 6. Final spur gear part after sintering.

Part Characterization

The key dimensions of the sample parts (H-shaped part and spur gear) are given on the CAD models in Figures 3(a) and 4(a). These dimensions were measured on the sintered parts and compared to the values in the CAD models to evaluate part shrinkage.

Measurements were taken from three H-shaped parts, with each dimension measured six times at random locations. The mean values and standard deviations of the six measurements are provided in Table 2 for each key dimension for each of the three samples. The overall mean values and average shrinkages (over the three samples) for the key dimensions compared to the CAD model dimensions are also given in Table 2. The key dimensions measured from the sintered spur gear and their means and standard deviations compared to the CAD model dimensions are given in Table 3. For the spur gear ten measurements were taken at random locations for each dimension.

Table 2. Dimensional measurements for the sintered H-shaped parts.

Measurements		L (mm)	W (mm)	H (mm)	A (mm)	B (mm)	C (mm)
Sample 1	Mean	23.4	15.4	12.4	4.7	7.7	4.7
	Std. Dev.	0.09	0.05	0.05	0.05	0.07	0.05
	Shrinkage	22.1%	22.8%	22.3%	22.5%	22.7%	22.5%
Sample 2	Mean	23.4	15.5	12.3	4.7	7.7	4.6
	Std. Dev.	0.05	0.08	0.05	0.07	0.07	0.07
	Shrinkage	22.1%	22.5%	22.4%	22.2%	22.7%	22.8%
Sample 3	Mean	23.3	15.4	12.4	4.6	7.7	4.7
	Std. Dev.	0.07	0.05	0.10	0.05	0.04	0.06
	Shrinkage	22.4%	22.8%	22.3%	22.8%	22.8%	22.2%
All	Mean	23.3	15.5	12.3	4.7	7.7	4.7
	Shrinkage	22.2%	22.7%	22.4%	22.5%	22.7%	22.5%

Table 3. Dimensional measurements for the sintered spur gear part.

Measurements	H1 (mm)	D1 (mm)	D2 (mm)	D3 (mm)
1	7.0	34.8	26.2	4.7
2	7.0	34.8	26.3	4.6
3	7.0	34.9	26.3	4.7
4	7.0	34.9	26.2	4.7
5	7.0	34.9	26.2	4.7
6	6.9	35.0	26.2	4.7
7	6.9	34.8	26.3	4.7
8	7.0	35.0	26.2	4.7
9	7.0	34.9	26.2	4.7
10	7.0	34.9	26.2	4.7
Mean	7.0	34.9	26.2	4.7
Std. Dev.	0.04	0.07	0.05	0.03
Shrinkage	22.5%	22.5%	22.2%	21.9%
Max.	7.0	35.0	26.3	4.7
Min.	6.9	34.8	26.2	4.6

Discussion

For the H-shaped part, the standard deviations of the measurements in Table 2 varied from 0.04 mm to 0.1 mm, and the shrinkages were in the range of 22.1% to 22.8%. The amounts of shrinkage of the spur gear after sintering given in Table 3 were in the range of 21.9% to 22.5%. For both parts, no significant anisotropic shrinkage was observed in both horizontal and vertical directions. The diameters of the circular features of the spur gear, i.e., D1, D2 and D3 in Table 3, had standard deviations between 0.03 mm and 0.07 mm, corresponding to a range of 0.2% to 0.6%. This indicates good circularity in the fabricated spur gear.

The above experiments and results validated PCL as a feasible support material for the CODE process. With the PCL support material, the green part can be separated from the substrate after being heated above 60 °C, and the remaining PCL support material in the green part can be burned out in the furnace during the sintering process. However, there were issues observed when the molten PCL was deposited on top of a ceramic paste layer instead of the substrate. When PCL material was deposited onto a ceramic paste layer, it would warp and eventually detach from that paste layer after printing PCL for several layers. The warped and detached support structure affected the dimensional accuracy of the printed part and imposed a high risk of damaging the part.

This is because when the deposited molten PCL on a ceramic paste layer started to deform due to thermal stresses while cooling down [24,25], the surface bonding provided by the ceramic paste was not strong enough to avert warping and detachment. A potential solution is using an organic material as the support material in the form of a paste, which is extruded and deposited without melting and hence avoid the warping and detachment. This idea will be investigated in a future study.

Conclusions

A method of fabricating ceramic parts by the Ceramic On-Demand Extrusion (CODE) process with an organic sacrificial support material has been developed. PCL (polycaprolactone) was identified as a feasible sacrificial material, which is melted and extruded to build support structures during the CODE process. The support structure can be removed from the part by heating the part above 60 ℃ to melt PCL and separate the green body from the support structure. The remaining PCL in the green body is then burned out during the part sintering process. Sample zirconia (3YSZ) parts including an H-shaped part and a spur gear were successfully fabricated by the CODE process using PCL as the support material. The dimensional shrinkages for the sintered parts compared to their CAD models ranged between 21.9% and 22.8%, and no significant anisotropic shrinkage in the horizontal and vertical directions were observed. The diameters of the circular features of the sintered spur gear had standard deviations ranging between 0.2% and 0.6%, indicating good circularity.

Acknowledgements

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