Effect of parameters on 3D printing of alumina ceramics and evaluation of properties of sintered parts

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ABSTRACT
Paste rheology and printing parameters contribute to a great extent to engineer the properties of ceramic parts produced through 3D printing process. Alumina paste, which showed shear thinning behavior, was prepared using optimum concentration of additives. Paste was 3D printed and effect of printing parameters such as printing speed, length to diameter (L/D) ratio of nozzle, self-standing distance of extrudate, filling pattern and filling angle have been studied. Additionally, effect of the substrate material on which the extrudate is printed was also elucidated. A printing speed of 5–6 mm/s, an L/D ratio of 25 mm and self-standing distance of 1.25 ± 0.25 mm are found to be optimum. Further, a filling pattern of rectilinear geometry along with filling angle of 90° is found to be desirable. Out of the substrates evaluated, polished metal surface is found to be relatively better to achieve close tolerances. The alumina samples printed under optimized conditions are found to possess integrity with respect to the structure and close to pre-designed dimensions. Sintered samples were found to be free of crack and exhibited a density of 3.88 g/cc (97.5% of theoretical density). Density and hardness (16.5 GPa) of printed part correlates well with the microstructure consisting of grains of average size of 9.68 μm.

1. Introduction
Additive manufacturing (AM) is extensively used in polymers for prototyping due to the flexibility in shaping [1–5]. Recently, interest has also been seen for 3D printing of ceramic and metals [6–10]. Conventional shaping of traditional and advanced ceramics proceeds through a series of operations from powder processing to shaping using expensive die or molds followed by sintering. These components are generally machined to achieve the final dimensions. Stereolithography (SLA) [11–13], binder jetting [14–17] and extrusion of ceramic pastes [18–20] are the 3D printing processes presently explored for ceramic shaping. As the current study is based on extrusion of alumina paste similar to fused deposition modeling shear thinning or pseudo-plastic behavior of the paste through proper selection of binder and plasticizing agents is critical [21–23]. Further, nozzle dimensions, self-standing distance of the extrudate, printing speed and interaction of the surface with the extrudate are found to have an effect on the process or printed parts. Filling patterns such as rectilinear, aligned rectilinear, concentric and filling angle is found to have minimal effect on the density and mechanical properties of the printed part.

In the present study, alumina powder was subjected to XRD analysis to assess the phase purity and Dynamic Light Scattering (DLS) for particle size analysis. Varying concentrations of binder and water were added to the mix which was subsequently kneaded for 30 minutes under vacuum in a high shear blender. The homogeneous paste thus made was characterized by rheological properties with respect to shear rates and extrusions were carried out with the paste having the shear rate exponent, n = 0.67. A ram type 3D printer was used to print the paste through a nozzle with 1.0 mm diameter and varying L/D ratio of 10–25 with L/D of 25 found to be the optimum. Desirable self-standing distance was found to be 1.25 ± 0.25 mm and is optimum for the current nozzle dimensions. The effect of filling pattern and filling angle are found to be negligible for printed parts. Green density of the dried samples was determined and was subjected to binder removal followed by sintering at 1650°C. The samples were subjected to microstructural characterization which correlates well with the density and hardness of the samples.

2. Experimental procedures
Alumina powder procured from commercial source (Rohini Industries, Pune, India) was characterized by X-Ray Diffraction (D8-Brucker, Germany) for phase identification and Dynamic Light Scattering (DLS) (Nanosizer, Malvern Instruments Limited, UK) for particle size and distribution analysis. Alumina powder was...
blended with 0.25–0.75 wt% of methyl cellulose (MC) (Loba Chemie, Mumbai, India) as binder and 35–39% of water by weight of the powder and the mixture was kneaded in a high shear blender for 30 minutes to form cohesive dough. The rheological behavior of all the pastes was determined with respect to shear rate to assess the flow properties of the paste using rheometer (MCR 51, Anton Paar, Austria).

A ram 3D printer was used for the printing of the specimens. SS 316 nozzles with 1 mm diameter with varying length of 10, 15 and 25 mm were fabricated and specimens were printed at printing speed of 5–6 mm/s. Optimum self-standing distance was obtained by varying the distances from 0.5 to 2 mm. Glass plate, aluminum foil and plaster of paris were used as substrates for printing of extrudate. Additionally, three filling patterns such as rectilinear, aligned rectilinear, concentric pattern and filling angles of 30, 45, 60, 90° are also investigated. All the parameters are correlated with green density after drying. All the printed and dried samples were subjected to binder removal followed by sintering at 1650° C for a dwell time of 1 hour in high-temperature furnace (Deltech, USA). The alumina powder used in the current study is of 99.9% purity with no sintering or grain refining agent present in it. As reported in our earlier studies [24], the sintering temperature of 1650° C is found to yield sintered density (~98-99%) close to theoretical density.

The samples were also characterized for density by Archimedes principle (ASTM B962), microstructure of the etched ceramo-graphically polished surface by FESEM (Gemini 500, Carl Zeiss, Germany) and hardness by Vickers indentation method (ASTM C1327) followed by grain size measurement by linear intercept method.

3. Results and discussion

Figure 1(a) and (b) shows the powder XRD pattern and the particle size distribution of the alumina powder, respectively. XRD pattern of alumina powder clearly exhibits α-alumina phase and the particle size distribution of the powder is indicating the average particle size of 330 nm.

3.1. Rheological properties of the paste

Alumina with a mixture of 0.25 wt% of MC and 35 wt% of water formed homogeneous cohesive dough after kneading for 30 minutes, however, mix with 0.50 and 0.75 wt% of MC have resulted in visible segregation. On gradual addition of water to 37 wt% and 39 wt%, to the mix with 0.50 and 0.75 wt% of MC respectively have resulted in the gradual disappearance of the agglomerates forming cohesive dough. Plot of apparent viscosity vs shear rate data is shown in Figure 2(a). It is evident from the plot that, the viscosity decreases with shear rate suggesting a non-Newtonian behavior. A Power Law Model, \( \eta = m \cdot \gamma^{n-1} \) can be applied for analyzing such behavior, where \( \eta \) is the viscosity, \( m \) is the consistency constant, \( \gamma \) is the shear rate and \( n \) is the shear rate exponent or power law index, proposed by Ostwald de Wale [25] for the pseudo-plastic polymeric materials. A plot of ln(\( \eta \)) vs. ln(\( \gamma \)), shown in Figure 2(b), shows a linear relation with acceptable fit. Though all mix have formed homogeneous cohesive dough the shear rate exponent (n) was 0.67, 0.88 and 0.93 respectively with increasing concentration of MC.

Pseudo-plastic or shear thinning behavior of alumina paste used for the 3D printing process dictates the properties of 3D printed parts within the pre-designed tolerances of the parts after shaping. In order to have easy flow of the paste, under the application of the shear while printing a lower the viscosity of the paste is desirable. However, for the retention of the shape after printing a higher viscosity is advantageous [26]. The parts also must have adequate handling strength to maintain the shape until drying and subsequent also further post-heat treatment process. In view of this, paste with the shear rate exponent (n) of 0.67 and minimum additives with respect to binder (0.25 wt%) and water (35 wt%) is desirable.
3.2. 3D printing of alumina parts

The block diagram of 3D printer used in the present study is shown in Figure 3. The printer is equipped with a ram type extruder with a cylinder and piston fitted with an interchangeable nozzle. 3D printing process involves the flow of the paste through a barrel which stores the mix, a cone at the end channelizes the flow of paste into a nozzle of the diameter typically 22 times smaller than the diameter of the barrel and the details of the actual system assembly is shown as an inset image in Figure 3. During this process the paste is compressed within the barrel which peaks up a load to overcome the initial resistance and starts flowing as extrudate through the nozzle and printing occur at the preset control printing parameters.

3.3. Printing speed

Alumina parts are 3D printed at various printing speeds. It was observed that a printing speed of > 6 mm/s leads to overflow of the paste and results in the formation of the component beyond the pre-designed layer tolerance. Further the extended duration of printing and loss of moisture are the undesirable results when the speed is < 5 mm/s as it causes layer to layer inhomogeneity. An optimum printing speed was determined by considering the required accuracy in the final part and the desired printing time.

![Figure 3. Block diagram of the ram extrusion-based 3D Printing process.](image)
speed of 5–6 mm/s is identified to provide desirable results with respect to pre-designed layer tolerance.

3.4. Effect of L/D ratio of the nozzle on printed samples

Nozzle with L/D ratios of 10, 15 and 25 and the green densities of 3D printed samples are shown in Figure 4. Length-to-diameter ratio (L/D ratio) of 10 and 15 has shown an identical green density of 2.10 g/cc; however, the green density has shown a marginal increase to 2.14 g/cc at an L/D ratio of 25. The relatively high-density values can be attributed to the additional wall shear and intermixing of the paste due to the increased length of the nozzle leading to a better homogeneity of the paste.

3.5. Effect of self-standing distance of extrudate

Self-standing distance of the extrudate is illustrated in Figure 3 and is found to have a significant influence on the retention of the shape of the part.

The effect of self-standing distance on the dimensional tolerance is represented in Figure 5. At a distance of 0.5 and 0.75 mm the surface of the extrudate layer was smeared and part was printed...
out of the tolerance limits. When the self-standing distance is increased to 1 mm and 1.5 mm printed, extrudate is found to maintain the designed layer thickness and the printed parts were well within the tolerance limit. Further, the self-standing distance beyond 1.5 mm, the extrudate was overhanging and deviated from the designed print path with discontinuities throughout the printed parts.

### 3.6. Effect of type of substrates

Substrate surface on which the parts are printed is also found to have an influence on the properties of the printed parts. Among various substrates experimented in the current study, the plaster of paris (POP) holds the first layer of the extrudate by providing better adherence due to its inherent porosity related capillary action which absorbs the water from the extrudate leading to non-uniform drying and intermittent cracking of samples while drying. Glass plate as substrate for printing of extrudate, the first layer does not adhere properly leading to occasionally minor displacement of the subsequent layers. In the case of the metallic surface or an aluminum foil placed on glass plate, MC binder interacts chemically with the metal surface and holds the first layer [27] of extrudate without deformation. This helps in building the subsequent layers according to the predesigned model. Further, on exposure of MC to drying temperatures gradually releases the extrudate due to polymerization and gelling.

### 3.7. Effect of filling pattern and filling angle

The filling patterns namely rectilinear, concentric and aligned rectilinear are experimented in the current study and the typical filling patterns are shown in Figure 6(a–c). It is evident from Table 1 that the duration of printing as well as the average green density of the printed samples are similar and no significant effect on filling pattern is observed. Experiments were also conducted to study the effect of filling angle on the rectilinear filling pattern and the angle was varied from 30° to 90°. A schematic of the filling angles used for printing of specimens is shown in Figure 6(d). Green density of the alumina samples is shown in Table 1 signifies the minimum effect on density values.

### 3.8. Properties of sintered alumina parts

Table 2 depicts the optimum conditions desirable for printing. Sintered density, grain size and hardness of the alumina parts printed at optimum condition are shown in Table 3. The 3D printed samples at optimum conditions in green and sintered stage are shown in Figure 7(a) and (b) respectively. Further, the microstructure of the sintered sample

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**Table 1.** Properties of printed samples with rectilinear pattern with different filling angles.

| Properties     | Filling pattern |                | Filling angle (Rectilinear) |
|----------------|-----------------|----------------|----------------------------|
|                | Rectilinear     | Concentric     | Aligned rectilinear       |
| Green density (g/cc) | 2.03 ± 0.04 | 2.04 ± 0.06 | 2.08 ± 0.06 | 2.03 ± 0.07 | 2.02 ± 0.08 | 2.03 ± 0.06 | 2.00 ± 0.06 |

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**Figure 6.** Schematic of fill patterns (a) Rectilinear, (b) Concentric and (c) Aligned rectilinear with (d) fill angles of 30°, 45°, 60° and 90°.
Table 2. Optimum parameters for 3D printing alumina parts.

| S. No | Parameters                  | Optimum values |
|-------|-----------------------------|----------------|
| 1     | Printing Speed (mm/s)       | 5–6            |
| 2     | L/D ratio                   | 25             |
| 3     | Self-standing distance (mm) | 1.25±0.25      |
| 4     | Filling angle (°)           | 90             |
| 5     | Filling pattern             | Rectilinear    |
| 6     | Substrate                   | Aluminum foil  |

Table 3. Properties of sintered alumina specimens.

Properties of sintered alumina specimens

| Property                      | Value |
|-------------------------------|-------|
| Sintered density (g/cc)       | 3.88  |
| Average grain size (μm)       | 9.68  |
| Hardness (GPa)                | 16.5  |

Table 4. Properties of sintered alumina specimens.

| Properties                     | Value |
|--------------------------------|-------|
| Sintered density (g/cc)        | 3.88  |
| Average grain size (μm)        | 9.68  |
| Hardness (GPa)                 | 16.5  |

4. Conclusions

Out of the various printing parameters studied, printing speed and self-standing distance have been found to be most critical. Substrate surface and chemistry are found to have a prominent effect on dimensional tolerance. Filling angle and filling patterns have shown only negligible effect. Optimum parameters used for printing are summarized in Table 2.

3D printed and sintered samples are found to exhibit a density of 3.88 g/cc (97% of theoretical density). Samples have shown a hardness of 16.5 GPa. Microstructure of the sample has shown average grain

Figure 7. 3D Printed alumina samples at optimum conditions (a) Green and (b) Sintered samples.

Figure 8. Microstructure of the alumina sample.
size of ~9.68 μm correlating well with the density and hardness values.

**Disclosure statement**

No potential conflict of interest was reported by the author(s).

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