Direct Ink Writing of Cellulose - plasticized Aqueous Ceramic Slurry for YAG Transparent Ceramics

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Abstract

Additive manufacturing based on direct ink writing (DIW) opens a novel means to prepare transparent ceramics, which can comprise of both complex structures and multiple functional phases. However, there still remains a vital challenge to obtain a stable and printable aqueous ceramic slurry with high solids loading, which is important for forming high quality transparent ceramics. Therefore, we report a fabrication method by using celluloses for enhancing the plasticity of the aqueous YAG ceramic slurry with high solids loading up to 52 vol. %, by which both of the printability of ceramic slurries and the optical quality of transparent ceramics have been considerably improved. In the example, the in-line transmittance at 1064 nm for a 1.2 mm thick YAG ceramic can approach about 81.5%. This research provides a facile DIW method for preparing transparent ceramic from water - based slurry.

1 Introduction

Transparent YAG ceramics are being developed for military, medicine, information, environment and scientific research fields [1, 2] due to their excellent optical and thermomechanical properties. In recent years, the mold-less production of ceramics by additive manufacturing (AM) has attracted the increased interests in the field of advanced ceramics, since AM allows for rapid fabrication of complex ceramic 3D structures with fine features [3–7]. So far, there have been different AM techniques under consideration, such as stereolithography [8–10], laser direct deposition [11, 12], and direct ink writing (DIW) [13–18]. Wherein, DIW represents one most straightforward scheme for controlling the spatial distribution of the material ingredients, and therefore for the fabrication of multi - component and complex structured ceramic parts [14, 16].

For the DIW fabrication of transparent ceramics, there are rigorous requirements for tuning the rheological properties of the ceramic slurry. For example, the slurry should have good flowability for being extruded continuously and uniformly from the narrow nozzle. Upon extrusion, the slurry should rapidly develop a high enough yield strength to resist shape deformation or collapse [19–21]. Although, Jones et al. [14] and Zhang et al. [13] produced transparent ceramics by DIW using slurries, the ceramic slurries used so far only had a solids loading of less than 40 vol. % due to much organics that limited the further increase of the solids loading. Moreover, too much organics will cause defects such as cracks in green bodies during debinding. As a result, a low density of the green bodies can only be obtained, and a cold isostatic pressing is the necessity for the densification to offer higher optical quality [14].

Inspired by extrusion molding, we propose that ceramic slurries with plasticity are suitable for DIW process. The initial way to improve the plasticity of ceramic slurries is to add clay[22–24]or other additives. For the transparent ceramics, the introduction of impurity ions should be maximally avoided, and therefore the organic additives such as cellulose are more suitable to be considered [25–28] because that can be completely removed via heat treatment. Furthermore, cellulose can effectively adjust the free water content in the slurry by forming hydrogen bonds with water molecules, which means it is highly hygroscopic [29]. Even more specifically, the contact between cellulose and water produces a rapid

swelling in crystalline regions, as caused by the chemical adsorption of water in the amorphous region of cellulose and the physical adsorption of water by the pore structure. Besides, cellulose molecules are arranged in chains and can act as a lubricant between ceramic particles [29], which reduces the friction between particles, as shown in Fig. 1. In conclusion, cellulose increases the plasticity of the slurry by reducing the free water content and lubricating effect, which plays a similar role to the clay [22–24].

In this work, transparent ceramic slurry with high solids loading was first prepared, then hydroxyethyl cellulose (HEC) was used to adjust the plasticity of the slurry to meet the needs of DIW. Their effects on the viscosity and the shape retention of the slurries were investigated. Also, the influences of the solids loading on the density of green bodies, grain size and optical properties of the ceramics were studied.

2 Experimental

2.1 Materials

Commercial Al_2O_3 (99.99 wt. % purity, Taimei Chemical Co., Ltd, Japan) and Y_2O_3 (99.99 wt. % purity, Jiahua Advanced Material Resources Co., Ltd, Jiangyin, China) powders were weighed according to the stoichiometric ratio of $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG). MgO and tetraethyl orthosilicate (TEOS, Sigma - Aldrich, 99.999%) were added as sintering additives. The powders were ball milled in anhydrous ethanol for 12 h. The slurry was dried in oven for 24 h and sieved through an 80 - mesh grid. The sieved powder was heated at $2^\circ\text{C}/\text{min}$ to 800°C and held there for two hours to remove the organics. The calcined powder was then sieved once through an 80 - mesh grid. CE - 64 [30] (Dolapix CE - 64, Zschimmer-Schwarz-Germany) was added as a dispersant, hydroxyethyl cellulose (denoted as HEC, Shanghai Macklin Biochemical Co., Ltd., 3400–5000 mPa·s, China) as a thickener, glycerin (Sinopharm Chemical Reagent Co., Ltd., China) as a lubricant. The dispersant, powder, HEC and glycerin were added to the deionized water in sequence and ball milled for 1 h.

2.2 3D printing and sample preparation

After degassed, the prepared ceramic slurry was loaded into a syringe, and then printed on a glass substrate by a home - made DIW 3D printer, consisted of a three - axis gantry stage with a multi - axis motion controller. The stage's linear positioning accuracy was $\pm 5\ \mu\text{m}$ with feedback resolution of $1\ \mu\text{m}$. All movements were programmed in C#. The printing speed is 3 mm/s, the inner diameter of the needle is 0.52 mm, and the layer thickness is 0.35 mm. To control the drying process, the printed wet body was placed in a constant temperature and humidity chamber for drying. The dried green body was heated in a muffle furnace at $1^\circ\text{C}/\text{min}$ to 800°C for debinding. Then the samples were vacuum sintered in a vacuum furnace at 1700°C for 6 h.

2.3 Characterizations

The rheological properties of the slurry were characterized by a rotational rheometer (Haake Viscotester iQ Air, Thermo Electron GmbH, Germany), a flat plate with the diameter of 20 mm was selected, and the

temperature of the test platform was controlled to be constant at 25°C. The densities of the green bodies and ceramics were measured according to the Archimedes principle. The microstructure of the ceramics was observed by scanning electron microscope (TM3000, Hitachi, Japan). The average grain size of the ceramics was estimated on the SEM micrograph by the linear intercept method. Mean grains size was estimated over at least 100 grains to ensure good measurement reliability. Each grain is approximately spherical, and the true average grain diameter G can be expressed as a function of the average apparent grain size g obtained from the SEM micrograph [31]:

$$G = \frac{\sqrt{6}}{2} g$$

The in-line transmittance of polished ceramics with a thickness of 1.2 mm was measured by an ultraviolet-visible spectrophotometer (V – 770, JASCO Corporation, Japan).

3 Results And Discussion

Figure 2a shows the effect of CE – 64 content on the viscosity of the slurries with 50 vol. % solids loading. With the increase of CE – 64 content, the viscosity of ceramic slurry shows a trend of first decreasing and then increasing. This can be explained that with the increase of dispersant content, the electrostatic repulsion between ceramic particles increases and the slurry viscosity decreases. When the content of dispersant is higher than an upper limit, the excess dispersant increases the ionic strength of the slurry, which compresses the electric double layer and reduces the electrostatic repulsion between particles. Thus, an optimal dispersant content of 0.6 wt. % relative to the powder mass fraction has been found in our work.

In order to study the effect of the cellulose on the slurry, the viscosity before and after adding cellulose to different solids loading were compared, as shown in Fig. 2b. The results show that for slurries with different solids loading, the viscosity increased by dozens or even hundreds of times after adding the celluloses. For example, the viscosity of 50 vol. % solids loading slurry without adding cellulose at 100 s^{-1} was only about $0.14 \text{ Pa}\cdot\text{s}$; but the viscosity significantly increases up to $11.39 \text{ Pa}\cdot\text{s}$ just after adding about 0.5 wt. % cellulose. When the slurry has a solids loading of 54 vol. %, shear thickening was observed after adding cellulose, and its viscosity was too high to be used for writing. The thickening effect of cellulose on the ceramic slurry is mainly achieved through swelling [29, 32]. On the one hand, hydrogen bonds are formed between cellulose and water molecules. The chemical adsorption of water in the amorphous region and the physical adsorption of water in the pore structure restrict the movement of free water in the slurry. On the other hand, cellulose increases in volume due to swelling, squeezing the ceramic particles to reduce the distance between them, thereby increasing the viscosity of the slurry.

The printability of the slurry after modified with cellulose has been significantly improved, as shown in Fig. 3. It can be seen that for the slurries with different solids loading, when the amount of cellulose as added was low, the phenomenon of drippage or slumping after extrusion was observed. The reason is

that the flow point of the slurry is too low, as shown in Fig. 3 (a), (b), (e), (f) and (i). After the pressure was unloaded, the slurry dropped under its own residual elastic force and gravity. Although the slumping slurry did not drip, as shown in (c) and (j), the volume flow rate during extrusion was unstable, and some of the slurry flowed slowly after the pressure was released, resulting in excessive volume flow rate during normal pressurization. A slurry with a suitable amount of cellulose had a suitable flow point, good printability, and clear lines after extrusion, as shown in (d), (g), (h) and (k). For the slurry with much higher cellulose addition, the bubbles in the slurry were difficult to be removed and the intermittent appearance of bubbles during extrusion caused defects on the green body and, as shown in (l).

Since the process of DIW is accumulation of ink printing layer by layer, it may leave printing marks (knot lines) unique to additive manufacturing in the green body, which is detrimental to the dense structure. The scanning electron microscope was used to observe the microstructure of the green body with different solids loading, as shown in Fig. 4. The results show that for the inks prepared with different solids loading slurries, the green bodies have a relatively complete and dense structure without obvious printing marks. Compared with the green bodies prepared from 50 vol. % and 52 vol. % solids loading slurries, the counterpart from a 48 vol. % solids loading slurry has a small amount of large pores. Table 1 shows the bulk density and relative density of the green bodies prepared from different solids loading slurries. With the solids loading increased from 48 vol. % to 52 vol. %, the bulk density of the green body increased from 2.558 g/cm³ to 2.615 g/cm³. It can be seen that the relative density of the green body formed by direct ink writing can be up to about 57.5%, which is higher than that by cold isostatic pressing after dry pressing of the same powder (about 56.1%).

Table 1
Bulk density and relative density of green bodies prepared by DIW.

Solids Loading/vol. %	Bulk Density/g·cm ⁻³	Relative Density/%
48	2.558	56.2
50	2.561	56.3
52	2.615	57.5

The influences of the ceramic microstructure on optical quality were studied. The results in Fig. 5 show that as the solids loading increased, the grain size of the ceramics increased. For example, with the solids loading increased from 48 vol. % to 52 vol. %, the grain size of the ceramic increased from 9.3 μm to 13.5 μm. The increase in solids loading of the slurry increases packing density of particles in the green body, so the densification rate and grain growth rate are faster at the same sintering temperature. However, a small number of pores were found in the ceramics prepared with 48 vol. % and 50 vol. % slurries, while few pores were found in the 52 vol. % sample. With the increase of solids loading, the packing density of ceramic particles is higher, which is more conducive to the densification process.

Transparent ceramics were obtained after vacuum sintering at 1700°C for 6 hours. Figure 6 shows the in-line transmittance of ceramics (1.2 mm thick) prepared from different solids loading slurries after

polishing. In-line transmittance of the ceramics slightly increased with the increase in solids loading from 48 vol. % to 52 vol. %. It fell in our expectation that the ceramic prepared from 52 vol. % solids loading slurry have the highest in-line transmittance of about 81.5% at the wavelength of 1064 nm, which is almost close to the theoretical transmittance of YAG ceramics. We also noticed that the relatively lower transparency in the short wavelength region was ascribed to the small amount of residue pores shown in Fig. 5.

The present works of direct ink writing YAG transparent ceramics are compared from slurry system, solids loading, optical quality, etc., as shown in Table 2. It can be seen that the use of slurry with high solids loading and low organic content can effectively increase the density of green bodies without cold isostatic pressing, thereby further improving the optical quality of the ceramics.

Table 2
Slurry system and preparation method used for DIW of YAG transparent ceramics.

	Zhang [13]	Jones [14]	This work
Slurry System	Aqueous	Organic	Aqueous
Organic Content (wt. %)	4–6	20–55	1.5
Solids Loading (vol. %)	36	30–45	52
Relative Density of Green Body (%)	-	45	57.5
Cold Isostatic Pressing	×	√	×
Hot Isostatic Pressing (HIP)	×	√	×
In-line Transmission at 1064 nm (%)	70 (1.45 mm)	Optical Scatter < 3%/cm	81.5 (1.2 mm)

4 Conclusion

Cellulose was used for modifying the printability of water-based ceramics slurries during the DIW process. By adjusting the amount of cellulose added and the solids loading, the rheological properties of the slurries were adjusted. Then, YAG ceramic slurries suitable for DIW were obtained. The results show that the obtained green body has structural integrity and high relative density, up to about 57.5%. Therefore, transparent ceramics were successfully obtained by vacuum sintering at 1700 °C for 6 h. After polishing, 1.2 mm thick YAG ceramic from the slurry with 52 vol. % solids loading had good optical quality, and the in-line transmittance at 1064 nm was up to 81.5%.

Declarations

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Figures

Figure 1

Schematic diagram of cellulose swelling (a) Structure of cellulose before swelling (b) Thickening effect of cellulose swelling (c) Hydrogen bonding between cellulose chains after swelling.

Figure 2

Effect of (a) CE - 64 and (b) HEC contents on slurry viscosity.

Figure 3

Extrusion morphologies of slurries modified with different cellulose additions (Inset of l: defects)

Figure 4

SEM images of green bodies prepared by slurries with different solids loading.

Figure 5

SEM microstructure images of polished and thermal etched ceramics surfaces from different solids loading slurries (Under different magnification).

Figure 6

In-line transmittance of the 1.2 mm thick polished YAG ceramics from different solids loading slurry.