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Materials Extrusion for Dense Ceramic Additive Manufacturing with Sol-gel Al_2O_3 Feedstock

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A novel strategy for highly dense additive manufacturing using a sol-gel-based ceramic slurry without polymeric additives is presented. Alumina, which is the most widely used fine ceramic, was chosen as a representative ceramic material. The proposed sol-gel solution enabled a high solid loading of approximately 50 vol. % without any polymeric dispersant while satisfying the requirements for material extrusion process, such as extrudable viscosity (< 100 Pa.s) and self-sustainable yield stress.The as-printed green body possessed high alumina content and 66% of theoretical density, which was higher than that obtained via the conventional molding methods. A reduced linear shrinkage of less than 16% and a high density of 99.5% of the theoretical value were also achieved. This research would present a practical strategy for ceramic additive manufacturing as an emerging fabrication process.

1. Introduction

Additive manufacturing (AM), which has been highlighted over the decades in both the academic and industrial sectors, is expected to become an essential part of the manufacturing process and lead to manufacturing innovations in various industries. The ceramic industry is one of the most promising areas for adopting the AM process because of its potential to materialize advanced ceramics with complicated structures, overcoming their intrinsic low processability and high processing costs.

One of the major problems that limits the use of ceramic AM for dense and monolithic structures is its high shrinkage ratio.In previous studies, ceramic components fabricated through the AM process reported a high linear shrinkage after sintering, regardless of the ceramic material. To form a the 3D-printed ceramic green body, the suspensions for ceramic AM must comprise a high organic content, thereby requiring the ceramic content to be relatively low (<50 vol. %), resulting in high shrinkage post-sintering. This high shrinkage can cause severe distortion and critical defects, such as cracks, and even failure in the final product, which is a fundamental problem in industrial applications.

In this research, Al_2O_3sol-gel composite slurry (SGC) was elaborately designed based on the physicochemical properties analysis to develop optimized feedstocks without polymeric binders for the dense ceramic three-dimensional (3D) printing with a material extrusion (ME) process.ME AM for ceramics has considerable industrial applicability with the advantages of wide material selectivity and high variability of process control. For instance, lithium-ion battery components, the 120 mm high zirconia structure, and yttrium oxide-stabilized zirconia were printed using ME AM. However, the use of ME AM technologies has been limited owing to the inevitable use of polymeric components in feedstocks. Herein, a polymer-free slurry was developed to overcome the aforementioned disadvantages and achieve the requirements for high-density ceramic with ME AM (**Fig. 1**).

2. Materials and methods

2.1 Materials

Aluminum nitrate nonahydrate[$Al(NO_3)_3{\cdot}9H_2O$, 98.0%, Samchun Pure Chemical Co. Ltd., Korea) was dissolved in deionized water to near its saturation point (70 g/100 ml H_2O). Urea (98.0%, Daejung Chemical Co., Korea) was added until the molar ratio between $Al(NO_3)_3{\cdot}9H_2O$ and urea was 1:2.5. After the reagents were completely dissolved, the solution was aged in an airtight oven at 95 °C for 6 h. The aging proceeded under humid conditions to eliminate the excessive evaporation of the solvent water. The aged sol-gel solution was degassed in a vacuum desiccator for 30 min at24 °C. A part of the prepared solution was subjected to further heating at 95 °C overnight, resulting in a transparent alumina gel (AlO-gel) for further analysis.

Corundum powder (AHP-200, 0.4 μm, Nippon Light Metal Co. Ltd., Japan) was added into the sol-gel solution based on the designated volumetric fraction of the final Al_2O_3 SGC. Citric acid was added to the Al_2O_3 SGC at approximately 0.1 wt.% of the alumina powder to increase the wettability of the alumina powder and lower the viscosity of the Al_2O_3 SGC. The mixture was first ball-milled overnight for the initial wetting of the powder and homogenized and degassed using a planetary mixer for 5 min.

2.2Printing process

The layer-wise curing print (LCP) was performed using a ram-head type DIW 3D printer (Foodbot, Ohsung System Co. LTD., Korea) with a customized plate heater and a heat bed add-on. The plate heater comprised of a polyimide heater mat (RS Components, United Kingdom) and an aluminum plate, linked with the z-axis frame of the 3D printer, maintaining a uniform distance (3 mm) from the top of the printed object. The 3D models for printing were prepared using a commercial computer-aided design software in the form of .STL files and “sliced” using an open-source slicing software (Cura 4.0.0, open-source), resulting in a G-code output.

Al_2O_3SGC was deposited on the silicon wafer attached to the heat bed, while the temperatures of the plate heater and PCB heat bed were maintained at 70 °C and 53 °C, respectively. After the LCP, the printed green bodies were fully dried in an oven at 50 °C for 12 hours and detached from the silicon wafer substrate.

3. Results

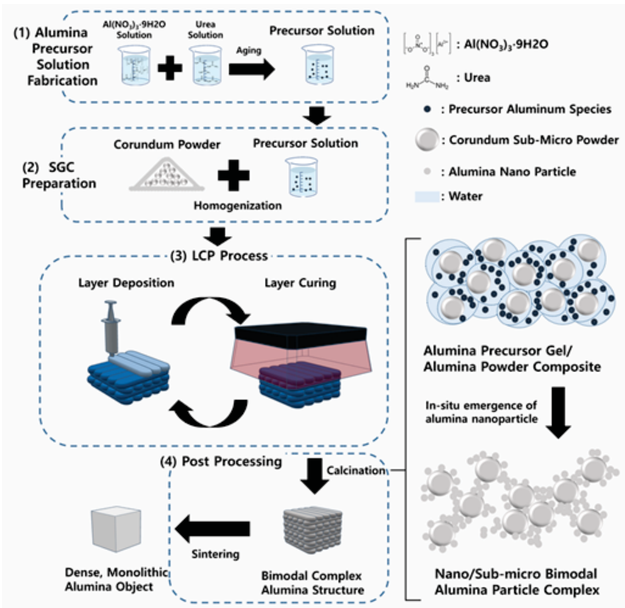

Fig. 1 Schematic diagram illustrating (1) fabrication of alumina precursor solution containing $Al(NO_3)_3{\cdot}9H_2O$, (2) preparation of Al_2O_3 SGC, (3) LCP process for green body fabrication, and (4) post-process with the evolution mechanism of Al_2O_3 SGC.

3.1 Rheology characterization for SGC

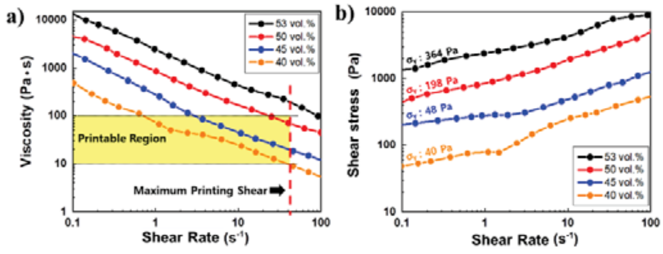

Fig. 2Rheology characteristics of Al_2O_3SGC with different alumina powder contents.

The extrudable condition determined from moderate viscosity condition (10–100 Pa.s) and a maximum shear rate of this DIW system (up to 32 s^{-1}) is the yellow region denoted in **Fig. 2(a)**.Theslurries with the powder content between 40, 45, and 50 vol. % satisfied that condition and exhibited suitable extrudability for the DIW printing process.**Fig. 2(b)** shows the shear stress as a function of the shear rate and yield stress for each Al_2O_3 SGC. The shear stress of the Al_2O_3 SGC increased with an increase in the powder content in the Al_2O_3 SGC, regardless of the shear rate. According to the rheological properties, the 50 vol% is the highest solid fraction with printability. Al_2O_3 SGC with 50 vol.% powder content was chosen as the feedstock for the printing process.

3.2Structures of 3D-printed Al_2O_3 SGC

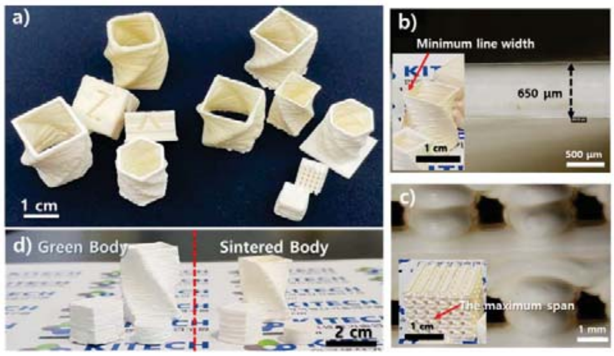

Fig. 3 Representative structure and details of 3D-printed Al_2O_3SGC fabricated using the LCP process.

Fig.3 shows a photograph of the representative 3D-printed Al_2O_3 SGC objects fabricated using the LCP process after sintering with different feature sizes. It is noticeable that every printed object, including bulk and monolithic structures, was sintered without any distortion or cracks. In conventional ceramic 3D printing, bulk, monolithic structures without cracks are difficult to achieve owing to the large shrinkage and complexity in the stress-free debinding process.

3.3Mechanical properties of 3D-printed Al_2O_3 SGC

The hardness and flexural strength of the sintered 3D-printed Al_2O_3 SGC object using the LCP process were measured to be 17.5 ± 0.9 GPa and 397.0 ± 16.8 MPa, respectively, which were compatible with the values of commercially available alumina (hardness 17.5 GPa; flexural strength 400 MPa; AO601, KYOCERA Co., Japan).

3. Conclusions

The sophisticated ceramic feedstock design which could materialize the practical ceramic AM process was demonstrated. The proposed approach with sol-gel based inorganic binders in the feedstock was more economical than the established ceramic AM process using polymeric constituents by eliminating the debinding process. Moreover, with a high density and comparable mechanical properties to a commercial product of 3D printed objects, it could meet the requirements for ceramic products in the industrial sectors. A notable feature of this material design is that it could be extended to other materials, not only a single ceramic material but also multi-ceramic composites or metal-ceramic compositions, through adjustable sol-gel solutions. Consequently, this study has proven to be a feasible approach for ceramic AM, and further researches applying this methodology to other functional ceramics or composite materials would be conducted in the future.

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