Preparation and performance of binder jetting porous alumina ceramic

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Abstract: This study examines the effects of zirconium basic carbonate (ZBC) added to alumina powders on the mechanical behavior of binder jetting porous alumina ceramic. ZBC powder is easily decomposed to form zirconia particles and then is deposited in the interparticle void spaces. Green alumina samples were obtained with different ZBC contents of 0~8 wt%. The density, linear shrinkage, bending strength, and microstructural evolution of ceramic parts were analyzed and categorized in different ZBC contents. Results showed that the formation of zirconia particles was dominant and improved the performance of sintered samples. Sintering at 1450°C resulted in a denser Al2O3 part with a comparable bending strength of 75.2 MPa and an accessible linear shrinkage of 10% for the ZBC content range of 0 to 6 wt%. At ZBC content of 8 wt%, the gas generated by ZBC decomposition reduced the sintering density. Therefore, adding 6 wt % ZBC content is the optimal choice for binder jetted porous alumina ceramic.

1. Introduction
Ceramic materials have been applied in various fields of the manufacturing industry, especially in aerospace and biological medicine [1, 2]. Due to the brittleness and hardness of ceramic materials, especially in the complex geometry of ceramic parts, the manufacturing of ceramic materials is complicated. The traditional alumina ceramic manufacturing process is tedious and time-consuming, which is caused by the level of experience required in alumina ceramic manufacturing, the complexity of 3D shapes, and the possible waste of materials [3, 4]. Because of the potential application of binder jetting, the new method of printing 3D parts in layers has been extensively studied [5].

Binder jetting is a computer-controlled technology that fabricates three-dimensional parts by binder jetting of droplets through printhead nozzles onto a powdered substrate [6, 7]. The precise location and micron size of droplets after jetting can be achieved by thermal excitation or piezoelectric effect [8, 9]. Compared to other additive manufacturing of ceramic materials, Binder jetting ceramic part has particular characteristics, including material availability and cost savings. As long as the raw materials are powder, there is no need to post-process into the slurry or other shapes. Sintering [10] or infiltration processes [11] can be used as a post-treatment to increase the ceramic strength. In this case, dispersed nanoparticles in binder [12, 13] and solid binder particles [14] in the raw material undergo significant curing and thus provide continuous bonding strength during the sintering.

The selection of particle densifier is essential when the binder is jetted, which directly affects the sintered density and bending strength [15-17]. In this study, the binder jetting process was used to manufacture porous ceramic parts by selectively depositing the binder in layers onto a powder bed. Different proportion of zirconium basic carbonate (ZBC) was mixed with alumina powders to promote
the quality of the porous ceramic parts. The purpose of this work is to investigate the effect of ZBC content in the alumina powder on mechanical performance and microstructure evolution of the ceramic parts. The reformed ZrO$_2$ particles decomposed by heating ZBC were deposited on the surface or the interstice of the Al$_2$O$_3$ particles to increase the mechanical performance for the final ceramic parts.

2. Experimental

2.1. Raw materials
Al$_2$O$_3$ powder with $d_{50} = 1 \mu m$, $\geq 99$ wt.% purity was purchased from Jiangxi Farmeiya Materials Co., Ltd., China, as an initial powder for the binder jetting process. 5 wt.% inorganic colloidal liquid (TW504226Y, Chengdu Kelong Chemical Co., Ltd., China) was dissolved in distilled water as a prearranged binder. The chemical composition of inorganic colloidal liquid was sodium silicate (Na$_2$O•3.2SiO$_2$), phosphate, and few organic additives. 0~8wt% zirconium basic carbonate powder (ZrOCO$_3$·nH$_2$O, ZBC, Jiangxi Kingan Hi-tech Co., Ltd, China, Purity, ZrO$_2 \geq 40.0\%$, $D_{50} = 6.8 \mu m$) as a densifier was mixed in the starting powder. The inorganic powder (TW504226F) as a liquid/solid binder was also blended with Al$_2$O$_3$ powders as starting powder. The mixing ratios of the starting powders are shown in table 1.

| Powder | Al$_2$O$_3$ (wt%) | ZBC (wt%) | Inorganic powder(wt%) |
|--------|----------------|-----------|----------------------|
| A      | 99             | 0         | 1                    |
| B      | 97             | 2         | 1                    |
| C      | 95             | 4         | 1                    |
| D      | 93             | 6         | 1                    |
| E      | 91             | 8         | 1                    |

2.2. Binder jetting process
The hub model sample (figure 1) and bar-shaped sample with dimensions of $6 \times 8 \times 80$ mm were fabricated by a self-developed 3D printer. According to our previous research [18], the optimized printing parameters are as follows: a 0.1mm layer thickness, a 00% binder saturation, and a roller actuation. After printing, parameters of 2h and 120 °C were set in the drying oven to strengthen the green parts. Then, green parts were removed from the surrounding powder by carefully brushing with a pressurized airflow. The green density of printed parts was measured by an electronic balance device. Finally, the green parts were heated to 1450 °C and held for 2h to sinter in the air. The schematic diagram of the printing and post-treatment process is shown in figure 2.

![Figure 1.](image_url) Figure 1. Photograph of the hub model sample fabricated by inorganic colloid binder.
2.3. Characterization

The particle size distribution of prepared powder was determined by a laser size detector (MS3000, Malvern Instruments, UK). The relative density was measured by the Archimedes’ method, and shrinkage of the sintered parts was calculated by three-dimensional measurements. The three-point bending strength of the ceramic parts was tested using MTS810 universal machine with a displacement speed of 0.05 mm/min. The microstructures of the printed parts were looked at by ESEM (Quanta 200, FEI, Netherland). The surface of ceramic parts for SEM analysis was sputtered with carbon.

3. Results and discussion

The mixing process is performed to create agglomerates and thoroughly mixed by using a planetary ball mill at 450 rpm for 1 h. The particle size distribution of starting powder and mixed powder with 6 wt% ZBC content was shown in figure 3. The particle sizes of mixed powder with 0~8 wt% ZBC content did not change significantly. Then, mixed powders were sieved to less than 56 μm in size using different mesh screens.

As shown in figure 4, the green density with different ZBC content is basically the same, and the sintering density increases with the ZBC content. This is because the micro-sized ZrO₂ particles generated by thermal decomposition of ZBC fill the interspace between alumina particles and then inhibit the growth of alumina particles. However, the sintering density decreased when the ZBC content exceeded 6 wt%. At the ZBC content of 8 wt%, the gas generated by ZBC decomposition will reduce the sintering density. Therefore, adding 6 wt % ZBC content is the optimal choice.
**Figure 4.** Green and sintered densities at different ZBC contents.

| Sample | Bending strength (MPa) | Shrinkage in X/Y/Z axis (%) | Porosity (%) |
|--------|------------------------|----------------------------|--------------|
| A      | 60.5                   | 9/8/23                     | 54.1         |
| B      | 62.1                   | 7/9/17                     | 50.5         |
| C      | 68.5                   | 7/8/14                     | 46.1         |
| D      | 75.2                   | 6/5/10                     | 40.4         |
| E      | 67.1                   | 11/10/26                   | 45.5         |

Table 2 lists the results of the mechanical performance of sintered samples with different ZBC contents. As expected, at an increasing ZBC content, a higher newly formed ZrO₂ content correlates to smaller linear shrinkage. All directions have suffered shrinkage, and the higher linear shrinkage of axis was caused by printing layer upon layer. The samples with 6 wt% ZBC content show a higher bending strength and lower shrinkage. When the addition of ZBC is 8%, the gas generated by the decomposition of ZBC during sintering will largely occupy the space of the particles and form more pores than that of 6 wt% ZBC, which is not easy to be discharged, making the shrinkage more serious.

**Figure 5.** Microstructure of green and sintered Al₂O₃ ceramic with different ZBC contents (a) 0 (b) 6 wt % (c) 8 wt % (d) 0,1450 °C (e) 6 wt %,1450 °C (f) 8 wt %, 1450 °C.

Figure 5 shows the microstructural evolution of green and sintered Al₂O₃ ceramic with different ZBC.
content. As shown in figure 5, green bodies have more pores but possess a sufficient bond strength. Sintering at 1450 °C significantly increases the density and reduces partial porosity, resulting in a more homogeneous sample surface. The specific contact surface area among micro-sized ZrO₂ and Al₂O₃ particles was larger than that among Al₂O₃ particles. So samples with a higher ZBC content were more likely to combine with Al₂O₃ particles strongly in the sintering process. But 8 wt% ZBC sample was more likely to produce pore and cause larger shrinkage than lower ZBC content samples during the sintering. Therefore, adding the ZBC in moderation can reduce the number of pores and enhance the immersion of Al₂O₃ particles, thus improving the mechanical bonding.

4. Conclusions
ZBC powder, as a particle densifier, which easy decomposition is favorable for the formation of ZrO₂ particle, was developed for alumina ceramic in binder jetting. To determine the optimal content of ZBC, we analyzed the mechanical strength, shrinkage, density, and microstructure of green and sintered samples. In the range of ZBC content of 0-8 wt%, the highest mechanical strength of binder jetting alumina ceramics was obtained with the ZBC content of 6%wt. The green sample densities with different ZBC contents were basically the same. An increase in the bending strength was obtained by increasing the ZBC content, which implied that newly formed ZrO₂ particles deriving from thermal decomposition of ZBC could be deposited into interstices between particles and act as Al₂O₃ ceramic fillers/densifiers.

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