

## 3D Printing of ZrO<sub>2</sub> Ceramic using Nano-zirconia Suspension as a Binder

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**Keywords:** 3D-printing, ZrO<sub>2</sub>, nano-zirconia suspension, sintering shrinkage, mechanical properties  
**Abstract.** 3D printing is applied to fabricate complex structure green ceramic parts rapidly. In this study, ZrO<sub>2</sub> ceramic were fabricated by 3D printing and sintering operation. In the 3D printing process of ZrO<sub>2</sub> green bodies, zirconia/polyvinyl alcohol (PVA) mixture was chosen as a precursor powder material, while nano-zirconia suspension as a binder. Green bodies were sintered at 1400 °C for 2 hours. The effect of nano-zirconia suspension content on physical and mechanical properties of fabricated ZrO<sub>2</sub> ceramic bodies was studied. It was found that the increment of binder content from 50% to 125% would result in an increase of relative density of green bodies. Also, it gives an increase of relative density and bending strength of the sintered bodies and a significantly decrease of linear shrinkage of sintered bodies.

### Introduction

ZrO<sub>2</sub> ceramic is a high performance ceramic material with a wide large of applications as cutting tools, refractory, insulator or high temperature filtering due to their excellent high strength, toughness, hardness and chemical stability at high temperatures [1-4]. Usually, the fabrication of molds for complex shaped ZrO<sub>2</sub> ceramic green parts using slip casting, gel casting, injection molding powder metallurgy or machining is labor-intensive and time-consuming [5].

In last two decades, additive manufacturing (AM) techniques have been proposed for fabricating complex shaped molds to rapid forming ceramic parts. Nowadays, the study of AM is focused on directly rapid forming ceramic parts due to their industrial applications. Three AM techniques of fabricating ceramic parts are the mainstream: stereolithography apparatus (SLA), selective laser sintering (SLS) and three dimensional printing (3DP). Among these AM techniques, 3DP is a novel and unique method that binder solution is locally applied on a powder layer by inkjet printing technology to bond the powder. It has several advantages, such as small equipment investment and low operation cost [6-8]. Thus, 3DP is more suitable for rapidly forming ceramic parts.

At present, 3DP was used to fabricate complex shaped ceramic of Al<sub>2</sub>O<sub>3</sub>/Cu-O [6], Ti<sub>3</sub>SiC<sub>2</sub> [9], TiAl<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> [10], et al. However, because of low density, the 3D printed ceramic green bodies have large sintered shrinkage rate [11-14], which could result in difficulties to control the dimensional accuracy of 3D printed ceramic parts. In order to decrease sintered linear shrinkage of ceramic parts, it is desirable to develop a novel and effective method to improve the density of 3D printed ceramic green parts.

In this work, zirconia/polyvinyl alcohol (PVA) mixture is chosen as a precursor powder material and nano-zirconia suspension as a binder. ZrO<sub>2</sub> ceramic samples were prepared by 3DP and sintering operation. The effects of binder content on the properties of sintered samples were investigated.

### Experimental

**Materials and Preparation.** Zirconia powder (Jiangxi Fanmeiya Materials Co., Ltd., China) was used as the raw material. This powder has a mean diameter 1.23 μm (MS2000, Malvern Instruments, UK), and a BET surface area of 7.52 m<sup>2</sup>/g (SSA-3600, Builder, China). The powder blend was prepared from ZrO<sub>2</sub>, polyvinylpyrrolidone powder (PVP, Chengdu Kelong Chemical Co., Ltd., China)

and polyvinyl alcohol powder (PVA, Chengdu Kelong Chemical Co., Ltd., China) with the ratio of 100:3:3. The powder blend was mixed in absolute ethyl alcohol by using ball milling for 2 h, and then dried at 60 °C. After dry ball milling in a tumbling mill, the powder blend was sieved through 150 mesh before printing. 10wt.% nano-zirconia suspension with 1.6 mPa s viscosity and 38.9 mN/m surface tension was chosen as a binder (Xuan Cheng Jing Rui New Material Co., Ltd., China).

**Specimens Preparation.** 3D-Printing was carried out in a self-developed 3DP machine using an Epson piezoelectric printer head. The mechanical structure is shown in Fig. 1. During the process, the temperature and humidity of building box were remained at  $50 \pm 2$  °C and  $10 \pm 3\%$  RH, respectively. The ceramic specimens ( $6 \text{ mm} \times 8 \text{ mm} \times 80 \text{ mm}$ ) were printed using a layer thickness of 0.1 mm and a binder content of 50%, 75%, 100%, 125%, respectively. The printed specimens were left in the building box for 1h before being taken out from the machine and then remove the unbounded powder. The printed bodies were sintered at 1400 °C for 2 h.

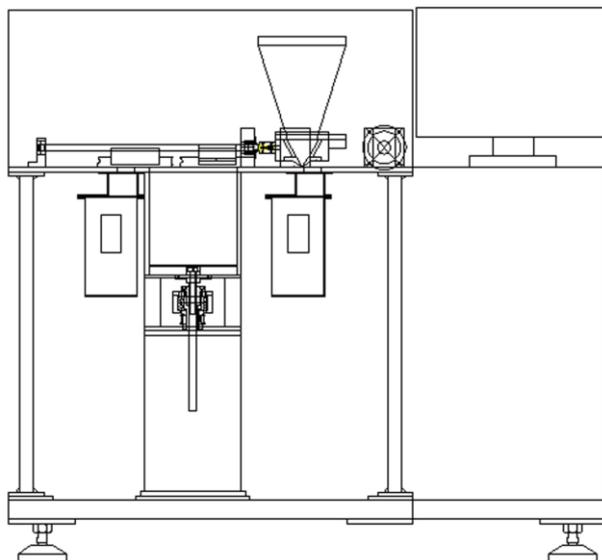


Fig. 1 The mechanical structure drawing of self-developed 3DP machine

**Characterization.** The relative density and linear shrinkage of zirconia sintered bodies were calculated according to dimensional measurement and Archimedes' principle. The microstructure of sintered bodies was performed using a scanning electron microscopy (SEM, Sirion 200, FEI). The three-point bending strength was determined using a MTS810 universal testing machine with a span of 30 mm and a punch displacement speed of 0.05 mm/min.

## Results and Discussion

**The Physical Properties of Sintered Zirconia Bodies.** To evaluate the relative density and linear shrinkage of the sintered zirconia bodies, a series of specimens was conducted to investigate the influence of these performance indicators on nano-zirconia suspension. The results are shown in Fig. 2 and Fig.3.

Fig. 2 shows the effect of binder content on the relative density of sintered bodies. The relative density is the ratio of the bulk density to the theoretical density. As can be seen, the relative density increases rapidly with the addition of binder content. As the binder content increases from 50% to 125%, the relative density increases from 75.2% to 86.8%. This results from the increase of the binder content which improved the amount of nanozirconia particles in the pores of zirconia powder layers. In turn, decreased the average pore size in the green bodies, thereby increased the relative density of sintered bodies.

The effect of binder content on the linear shrinkage of sintered bodies is shown in Fig. 3. As expected, higher addition of binder content in the powder layers results in a smaller linear sintered shrinkage. The linear shrinkage decreases from 22.3% at 50% binder content to 10.6% at 125% binder

content. It is common knowledge that the linear shrinkage of sintered 3D printed bodies is determined by the relative density of green bodies.

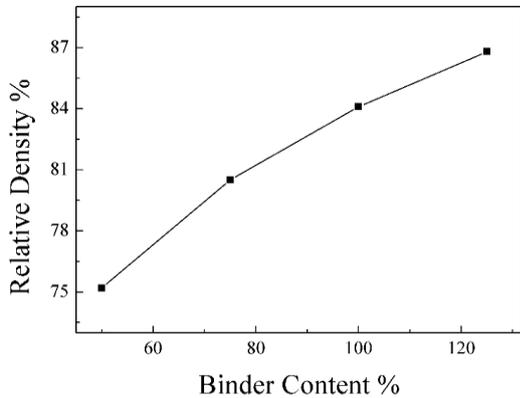


Fig. 2 The effect of binder content on the relative density of sintered bodies

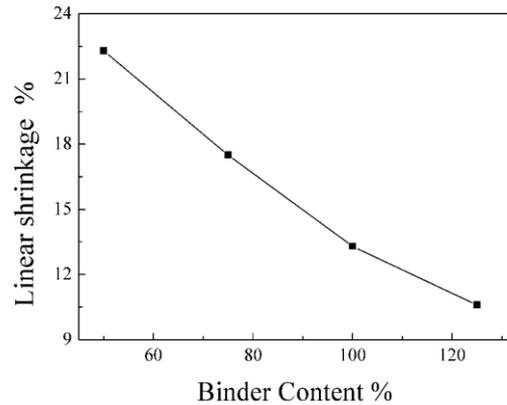


Fig. 3 The effect of binder content on the linear shrinkage of sintered bodies

Usually, the structure of 3D printed green body is loose and porous, and the linear shrinkage of sintered body is more than 30% [12]. So an increase of binder content would increase the relative density of green bodies, and also decrease the linear sintered shrinkage. In addition, smaller linear shrinkage would improve the dimensional stability of the parts.

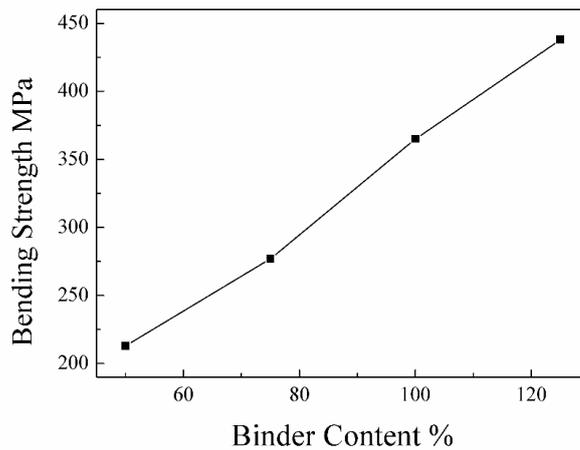


Fig. 4 The effect of binder content on the bending strength of sintered bodies

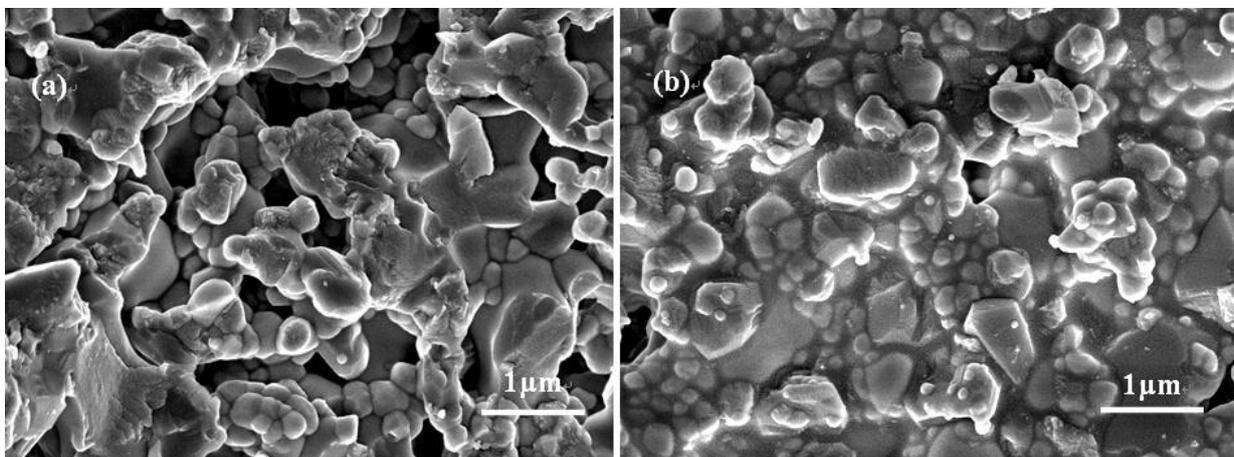


Fig. 5 Microstructures of sintered 3D printed zirconia bodies with (a) 50% binder content and (b) 125% binder content at 1400 °C

**The Bending Strength and Microstructure of Sintered Zirconia Bodies.** The bending strength of sintered zirconia bodies was determined by a MTS810 universal testing machine at different binder content. Results are shown in Fig.4. The bending strength is strongly affected by the binder content. It increases rapidly with an increase of the binder content from 213 MPa at 50% to 438 MPa at 125%. This is due to the change of the relative density of the sintered bodies. Generally speaking, higher binder content would improve the relative density of sintered bodies, and increased the amount of bonding bridge of unit volume of sintered bodies. Fig. 5 shows the microstructure of sintered zirconia bodies with (a) 50% binder content and (b) 125% binder content at 1400 °C. As seen, the amount of nano-zirconia particles was increased in the pores of sintered bodies, and the number of pores was sharply decreased. A high binder content can reduce the average pore size in the printed bodies, which can improve the sintering performance.

## Conclusions

Zirconia ceramic green parts were fabricated by 3D printing using nano-zirconia suspension as a binder. The effect of binder content on the relative density, linear shrinkage and bending strength of the bodies was investigated after sintering at 1400 °C. The relative density and bending strength were increase with the increase of nano-zirconia suspension, and the linear shrinkage was decrease. When the addition of binder content is 125%, the sintered bodies exhibits a relative density of up to 86.8%, linear shrinkage of up to 10.6%, and bending strength of up to 438 MPa. The microstructure of sintered bodies is revealed that the addition of binder content could improve the density of green bodies.

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