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Short communication

Influence of forming methods on the microstructure of 3Y-TZP specimens

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Abstract

Nanosized 3Y-TZP powders with particle size of 10–40 nm were formed by gelcasting, dry pressing and cold isostatic pressing. The influence of particle size as well as forming methods on the microstructure and mechanical properties of specimens were investigated. Both SEM images and the analysis on pore size distribution reveal that the gelcast sample possessed more homogenous microstructure. 3Y-TZP powders with particle size of 10 nm have been gelcast with green density as 37.5% of theory and sintered density as high as 96% was achieved. Its fracture toughness was up to 11.9 MPa $m^{1/2}$ and the hardness value HV_{10} is of 15.2 GPa. The difference of microstructure and mechanical properties is explained in terms of the differences in grain size and the forming methods.

Keywords: B. Microstructure-prefiring; B. Microstructure-final; C. Mechanical properties; D. ZrO_2; Gelcasting

1. Introduction

Gelcasting is a well-recognized and alternative route for fabricating strong, complex shaped and machinable green ceramic bodies. The process consists of dispersing a ceramic powder in a solution containing organic monomers, casting the suspension in a mold, and initiating a polymerization reaction to form a gelled body. Further steps include drying the body, removing the polymer binder via burnout, and sintering. There are vast investigations in each critical step after Omatete's invention [1] a decade ago. A wide variety of ceramic materials including silicon nitride [2], silicon carbide [3] and zirconia [4] have been gelcast after initial detailed studies of alumina gelcasting [5]. Recently, a considerable research effort was undertaken to find less toxic monomers to replace acrylamide [6,7]. Also, the process has been extended to powder metallurgy and porous materials [8,9].

There is a lot of work that has been carried out in the following aspects [10,11] such as how to raise the solid content as high as possible, evaluate the dispersants to characterize the rheological properties of slurries, avoid cracking and warpage during drying. It was noted that the gelcast materials seemed to have homogenous microstructure. However, studies on effect of forming methods on the microstructure evolution are relatively scarce [12,13]. Nanometer-sized particles have attracted growing interest in the past decade because material properties change drastically resulting from the grain size reduced to nanometer scale. For example, using nano particles as starting materials leads to significantly lower sintering temperature and higher mechanical strength of ceramic components due to improved homogeneity and controlled particle size distribution. Anyhow, there is relatively less research on gelcasting process of nanosized ceramic powder [14] due to the difficulty in getting high solid content suspensions. This paper reports gelcasting of nano-sized 3Y-TZP powders. Another two forming methods dry pressing and cold isostatic pressing are employed to compare the influence of forming methods on the microstructure of the specimens.

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2. Experimental procedure

2.1. Starting materials and slurry preparation

Yttria stabilized tetragonal zirconia polycrystals containing 2.8 mol.% yttria were prepared by co-precipitation method using zirconium oxychloride and yttrium chloride as starting materials and ammonia solution as the precipitation medium. The precipitates were then dried at 120 °C overnight and calcined at 450, 700, and 900 °C for 2 h, respectively. Table 1 summarizes the physical properties of these powders. Poly (acrylic acid) with molecular weight as 5000 was used as dispersant. A certain amount of zirconia powder was mixed with water and dispersant. pH of the suspension was adjusted to around 9 by adding ammonia into it. The suspension was transferred into a plastic bottle, which was loaded with zirconia grinding media, and then agitated by a tarbomixer for 24 h before gelcasting.

2.2. Green body preparation

Green compacts were uniaxially pressed or cold isostatically pressed at 200 MPa for 30 min without any binders. Gelcast samples were produced from suspensions containing monomer of acryamide and *N*, *N*′-methylenbisacrylamide with ammonium persulfate as initiator and tetramethylendiamine (TEMED) as catalyst. After demolding, the wet green bodies were dried up to constant mass. All green compacts weight around 3.0 g with diameter ranged from 15 to 20 mm. All the samples are sintered at 1500 °C for 2 h.

2.3. Measurement of properties

The pore size distributions of green specimens were measured on Pore sizer 9320 (Micromeritics, USA). The microstructure was characterized by the analysis of fractured surfaces using scanning electron microscopy (ESEM, XL30, Philip Co.). Archimedes method was used to measure the sintering density. Both hardness and fracture toughness were measured using a Vickers indenter (Akashi-A). The fracture toughness (K_{1c}) was calculated from the crack half-length and hardness.

Table 1
The properties of three powders calcined at different tmeperatures and their slurries

	No. 1	No. 2	No. 3
Calcined temperature	450 °C	700 °C	900 °C
SSA (m^2/g)	81.9	48.1	18.3
Grain size /nm (by BET)	6.0	10.4	27.3
Grain Size/ nm (by TEM)	10.0	24.1	36.8
Solid content of suspension (vol.%)	23.4	32.7	34.8
Amount of the dispersant (wt.%)	4.2	4.0	3.7

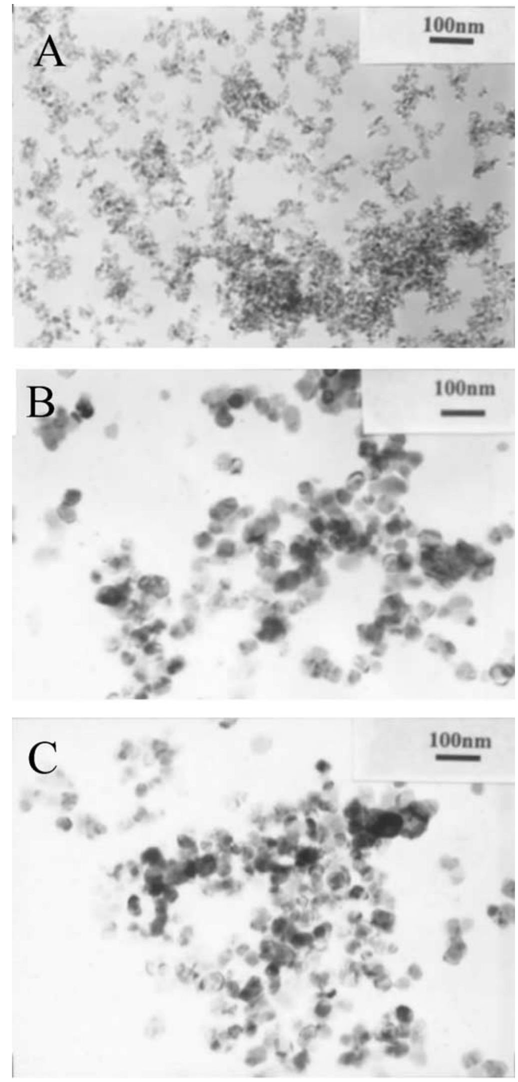

Fig. 1. TEM images of 3Y-TZP raw powders calcined at three temperatures. (A) 450 °C, (B) 700 °C, (C) 900 °C.

3. Results and discussion

Fig. 1 shows TEM micrographs of three powders used in this study. Their physical properties and the highest solid content of the suspension are listed in Table 1. Detailed investigation of the particle size on the rheological properties could be found in our published paper [15]. The highest solid content of the suspensions is closely related with the powder properties. With the increasing of particle size and decreasing of the specific surface areas, the solid content of the suspension can rise sharply. Solid content of the slurries were up to 23.4, 32.7, and 34.8 vol.% corresponding to the powder calcined at 450, 700, and 900 °C, respectively.

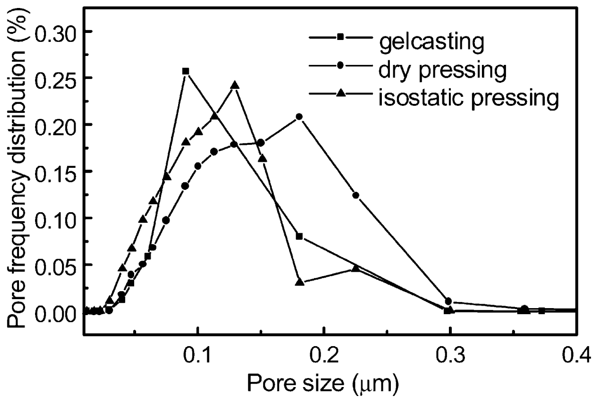

Fig. 2. Pore frequency distribution measured by mercury intrusion method using powder calcined at 450 °C.

Powders calcined at 450 °C were formed by three methods. Their pore size distributions of the green specimens are shown in Fig. 2. Among three of them, gelcast sample shows a narrow pore size distribution. The maximum pore size in the gelcast sample is smaller than 100 nm. Dry-pressed sample shows the broadest pore size distribution; a considerable amount of pore size is around 200 nm. There are two peaks for cold isostatically pressed sample, one is located at the position of 140 nm and another is located at the position of 220 nm. Fig. 3 shows the corresponded microstructures of the specimens. There is a clear distinction between the roughness of the surfaces of the dry pressed and isostatically pressed samples compared with the gelcast one. Large pores and agglomerates are found in the dry pressed and isostatically pressed samples, while very fine structure and homogenous distribution of the particles existed in gelcast body.

The relative densities of green and sintered specimens formed by gelcasting are listed in Table 2. The larger the particle size, the higher densities were obtained, since

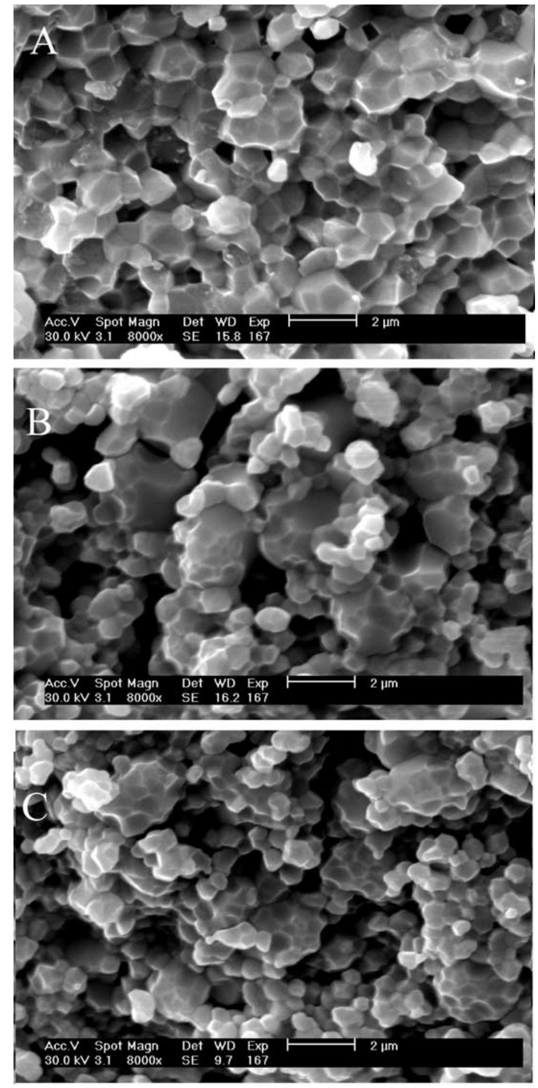

Fig. 4. SEM images of the fractured surfaces of sintered specimens formed by three methods, the starting powder is 3Y-TZP calcined at 450 °C. (A) gelcasting, (B) dry pressing (C) cold isostatic pressing.

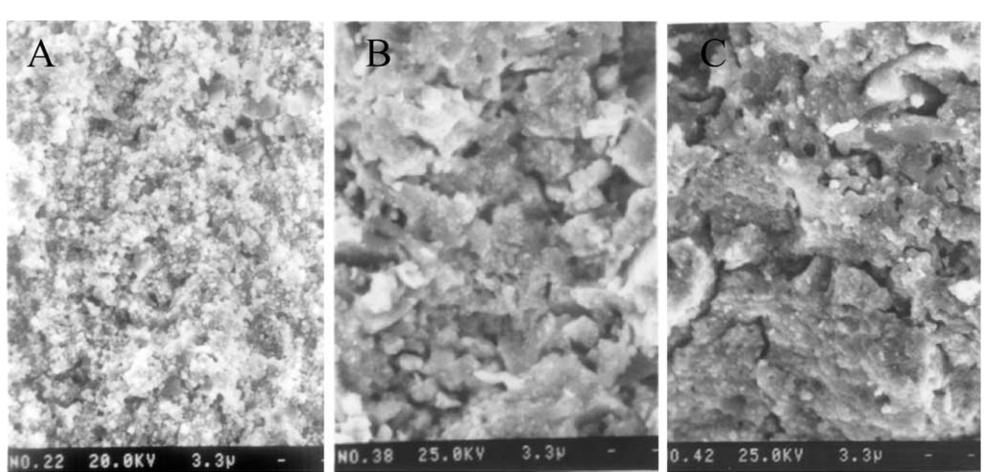

Fig. 3. SEM images of the fractured surfaces of the green specimens formed by three methods, the starting powder is 3Y-TZP calcined at 450 °C. (A) gelcasting (B) dry pressing (C) cold isostatic pressing.

Table 2
Relative green and sintered density of powders formed by gelcasting

Relative density (%)	Green bodies	Sintered bodies
No. 1	37.5	96
No. 2	40	98
No. 3	44	98

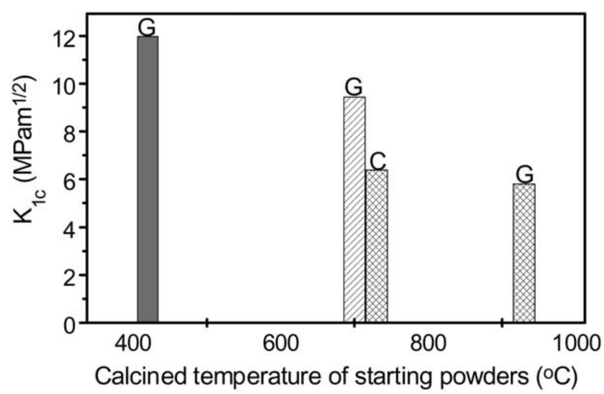

Fig. 5. The fractured toughness of gelcast (G) and cold isostatically pressed samples (C).

the specific surface area decreases sharply and it is favorable to get higher solid content suspensions, thus particles are closely packed after gelcasting.

The microstructures of sintered samples formed by three methods are shown in Fig. 4. The starting powders used are 3Y-TZP powders calcined at 450 °C (No.1 in Table 1). The relative density of the green bodies is 37.5, 35, and 38%, respectively for gelcasting, dry pressing, and isostatic pressing. The sintered density of the specimens is 96, 92, and 95.5%, respectively for gelcasting, dry pressing and isostatic pressing. The gelcast sample shows more homogeneous microstructure compared with dry pressed and cold isostatically pressed one. Fig. 5 shows the fracture toughness of gelcast samples by three different particle sized powders. Typical HV_{10} hardness value of 15.2 GPa was obtained and the fracture toughness was up to 11.98 MPa m$^{1/2}$ for specimens using powders calcined at 450 °C. The K_{1c} of cold isostatically pressed sample is also plotted for comparison, which value is about 50% lower than the gelcast one. The reason why low temperature calcined powder shows higher K_{1c} is not clear yet.

3. Conclusions

Gelcasting of nanosized 3Y-TZP was successfully carried out with three different calcined powders as starting materials. Gelcast zirconia shows a more homogenous pore size distribution and microstructure in comparison to dry pressed and cold isostatically pressed samples. The homogeneity in the microstructure leads to significantly higher fracture toughness of 11.9 MPa m$^{1/2}$ and hardness values of 15.2 GPa.

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