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Short communication

Microstructure and bending strength of 3Y-TZP ceramics by liquid-phase sintering with CAS addition

Yi-hai Sun[a b,*], Yu-feng Zhang[a], Jing-kun Guo[a]

[a]*Engineering Research Center for Structural Ceramics, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Rd., Shanghai 201800, China*

[b]*Epcos (Zhuhai FTZ) Co., Ltd. Hongwan, Wanzai District, Zhuhai Free Trade Zone, Zhuhai, GuangDong 519030, China*

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Abstract

3Y-TZP have been fabricated via liquid phase sintering at 1300–1450 °C by adding different weight ratios of CAS glass (CaO–Al_2O_3-SiO_2) additive. Sintering behaviour, microstructure and flexural strength as a function of sintering temperature and sintering aid were investigated. The experiment results showed that with 1 wt.% CAS additive and sintering at 1400 °C, the bending strength of 3Y-TZP is 950±40 MPa, and the grain size of 3Y-TZP is very fine, about 0.2 μm. It was found that the fine grain size is the main reason of the high bending strength of the materials.

Keywords: A. Sintering; B. Grain size; B. Microstructure; 3Y-TZP

1. Introduction

Tetragonal zirconia polycrystals (TZP) [1] with 3 mol% of Y_2O_3 (3Y-TZP) have been investigated and used widely, because of their good mechanical properties. These kinds of ceramics are usually fabricated via solid-state sintering at high temperature (e.g. ~1550 °C) [1,2], while it is a very expensive fabrication method and will inevitably increase the production cost limiting their utilization. Sometimes, in order to lower the sintering temperature, additives are deliberately introduced. Many studies have been reported in the literature concerning the effects of additives on sintering, e.g. Fe_2O_3 [3,4], SiO_2 [5], $A1_2O_3$ [3,6,7], Bi_2O_3 [8–10] or B_2O_3 [11]. Radford and Bratton [3] reached a density of 81% theoretical density when yttria stabilized zirconia (YSZ) was sintered at 1280 °C for 3 h. Introduction of 5 mol% Fe_2O_3 increases this density by about 10–91.5%, while 1 mol% $A1_2O_3$ gives an increase of 6.5%. The addition of 1–3 mol% Bi_2O_3 [8] lowers the sintering temperature from 1600 to 1080 °C while resulting ceramics have a comparable density (92–95%) and the grain size decreases from 90 to 5 μm. In addition, Buchanan and Sircar [11] got a relative density of 95% via liquid phase sintering at 1200 °C, adding B_2O_3 additives in 13 mol% calcia full-stabilized zirconia (l3Ca-FSZ).

In most cases, the presence of additives resulted in improved densification of the ceramics via liquid-phase sintering. However, these improvements in sintering were generally obtained at the huge expense of mechanical properties. The degradation in mechanical properties was attributed to the accumulation of silicate grain-boundary phases. In this paper, a series of 3Y-TZP samples have been prepared using different amounts of CAS glass as sintering additive. It was found that with 1 wt.% of CAS, sintered TZP ceramics with a high bending strength, relative density above 98%, and grain size of 0.2 μm have been obtained via liquid-phase sintering at 1400 °C.

2. Experimental procedure

2.1. Preparation of CAS glass powder

The calcium aluminosilicate (CAS) glass powder was prepared by milling a mixture of $CaCO_3$, SiO_2 and Al_2O_3 for 24 h, then melting at 1500°C for 4 h and quenching it in cold water. Clear transparent glass was obtained. This glass was crushed in a mortar and

* Corresponding author.
E-mail address: dennis.sun@epcos.com (Y. Sun).

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reduced to <1 mm, after which it was milled for 72 h with 3 mm diameter and 5 mm high purity ZrO_2 balls and sieved with a 120 mesh screen. Distilled water was used as the milling dispersant medium for preventing crystallization. The powder was characterized by X-ray diffraction to ensure that it was amorphous.

2.2. Materials processing

High purity commercial 3Y-TZP and CAS glass powders were used as raw materials coded as A, B, C, and D containing 1, 2, 3, and 5 wt.% CAS, respectively. The main impurities gained by chemical analyses (inductively coupled plasma, ICP spectroscopy) are shown in Table 1. The particle size distribution of 3Y-TZP was analyzed by Mastersizer 2000, as shown in Fig. 1. The TZP powder and CAS glass powder were mixed in distilled water via ball milling for 24 h, using an alumina jar and high-purity ZrO_2 balls, then dried and sieved through 120-mesh screen. After adding PVA and sieving through a 40-mesh screen, the mixtures were pressed uniaxially to rectangular bars at 60 MPa and cold isostatically pressed at 250 MPa. Then the green compacts were pressurelessly sintered at 1250–1400 °C in a $MoSi_2$ furnace for 2 h and furnace cooled.

2.3. Characterization of materials

Bulk density was measured by the Archimedes method. Phase composition was analyzed by XRD. The sintered samples were polished and etched. The etched surface was examined by scanning electron microscopy (SEM) to investigate the Y-TZP grains. Rectangular bars for bending strength tests (3 mm×4 mm in cross section and 35–45 mm long) were cut, and three-point bending strength measurements were carried out with an inner span of 30 mm and a crosshead speed of 0.5 mm/s at room temperature using an Instron-l195 Universal Test Machine. At least five specimens were tested per composition. Fracture toughness, K_{IC}, was determined using an indentation technique with a Vicker indenter. By measuring the length of cracks that developed in 20 kgf and a holding time of 20 s, K_{IC} was evaluated [12]. With each specimen, at least five indentations were measured.

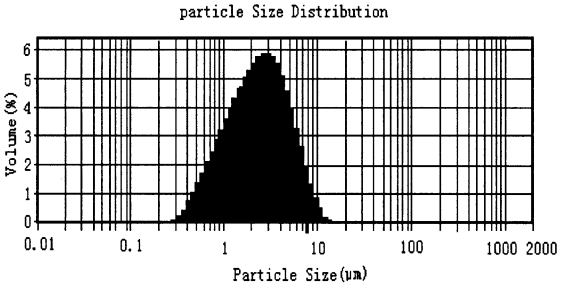

Fig. 1. Particle size distribution of the original Y-TZP powder.

3. Results and discussion

3.1. Sintering behaviors of 3Y-TZP

The relative densities of samples A–D sintered between 1300 and 1450 °C are shown in Fig. 2. It was found that at 1300 °C, the relative density of sample A is only 95.4%, but that of sample D is 99.4%. The relative densities of the samples increased with elevating the sintering temperatures. At 1300 °C, the densities of the samples started to increase rapidly. The relative densities of the samples reached after sintering to 1400 °C reaches higher than 98%, which appeared to the optimal sintering temperature, since higher temperature did no more increase the densities.

With CAS additive, the sintering temperature of samples could be effectively lowered. This was due to the change of sintering behavior of the samples. Liquid phases would be generated in sintering process when CAS is added, and the sintering behavior was changed from solid-phase sintering to liquid-phase sintering. Liquid phases that generated in the sintering process influences the compactness of the Y-TZP in two aspects

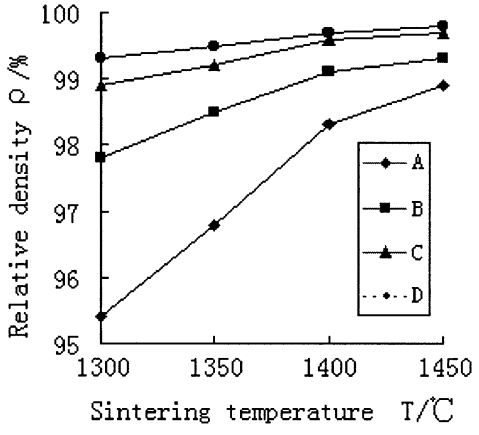

Fig. 2. Relative density as a function of sintering temperature.

Table 1
Chemical composition of Y-TZP powder

	Y_2O_3	SiO_2	Fe_2O_3	Na_2O	TiO_2	Cl^-	H_2O (110 °C, 2 h)
Content (wt.%)	5.4±0.2	<0.005	<0.005	<0.01	<0.001	<0.01	1.10

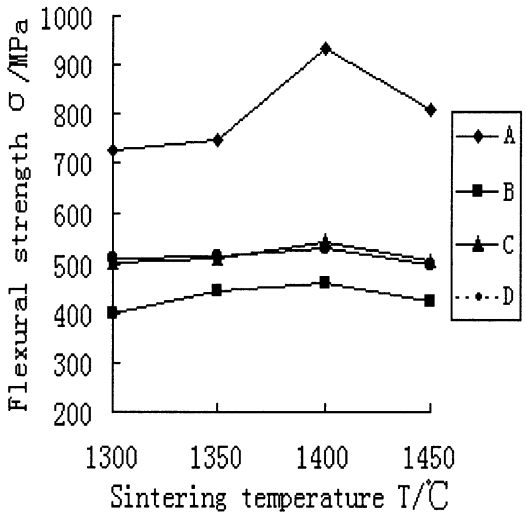

Fig. 3. Flexural strength of Y-TZP as a function of aid content and sintering temperature.

[13]. First, in the initial stages of sintering, the liquid phase could exert a significant capillary pressure capable of pulling the particles together. And in case that the liquid phase wetted the particles, it could envelop and collapse the pores, resulting in densification. Second, since the solid was to some extent soluble in the liquid [7], then the liquid phase also could aid densification by providing a rapid diffusional path-way between the particles in which mass transfer occurred by a dissolution–reprecipitation mechanism. With little amounts of CAS additive, the effect of the liquid phase was not very significant, and the densification process was very slow. The lowered viscosity of the liquid phase as the result of sintering temperature rising accelerated material transfer. Therefore, the relative density of these samples increased quickly with elevating the sintering temperatures. With large amounts of CAS additive, the liquid phase amount was higher even at low temperature, and hence higher densities were obtained. It was no longer needed to raise the sintering temperatures because the density will not significantly increase since much liquid phase was already presented.

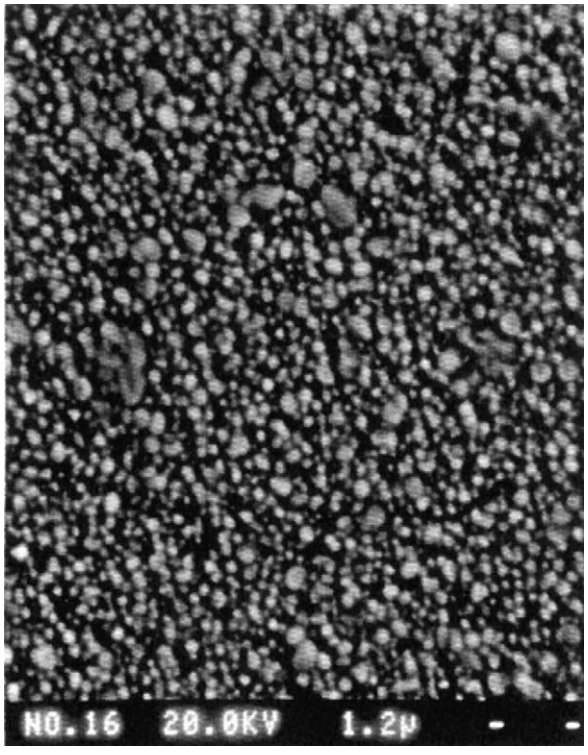

Fig. 4. SEM micrograph of fracture surface of Y-TZ (1400 °C, with 1 wt.% additive).

3.2. Bending strength

Fig. 3 shows the bending strength of 3Y-TZP as a function of the sintering temperature and aid content. The bending strength increased with increasing sintering temperatures at lower sintering temperature, which was in agreement with the variation trend of samples density, and reached its ultimate sintered density at 1400 °C. If sintering temperature was still raised, the bending strength would no longer increase because the relative density is almost 100%. Due to overburning, high sintering temperature reduced the samples' bending strength. Fig. 3 also demonstrates that CAS adding is disadvantageous to bending strength. Therefore, additive contents should be constrained under the condition that satisfied sintering demand.

Fig. 4 shows a SEM micrograph of polished surface. This microstructure determined the high bending strength of Y-TZP. The average grain size is about 0.2 μm, which nears to the critical grain size of martensite transformation of 3Y-TZP. It was found in the XRD pattern (Fig. 5) that there was little tetragonal phase transformed to monoclinic phase. Therefore, the superfine grain size is the main reason that leads to high bending strength of this material. For ceramics, the

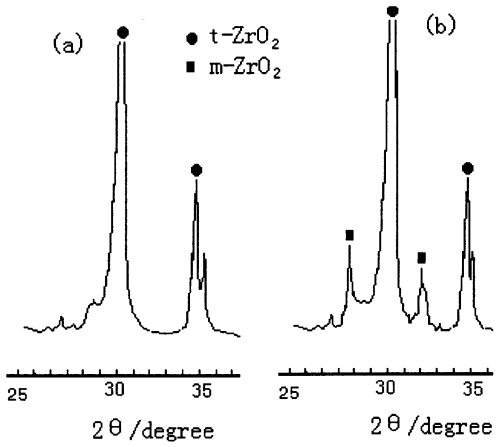

Fig. 5. XRD patterns of polish surface and fracture surface of Y-TZP with 1.wt.% addition (pattern a is polished surface).

relation between grain size and bending strength can be expressed in Hall–Petch equation [14]:

$$\sigma_f = \sigma_0 + kd^{-1/2}$$

where σ_0 is the bending stress of unit crystal of infinitely great, k is a coefficient, d is the grain size. According to this equation, the bending stress increased with decreasing grain size. Therefore, although the effect of phase transformation is not obvious in these samples, the bending stress is still high owing to their superfine grain size. The bending stress of sample A can reach to 950±40 MPa sintered at 1400 °C

4. Conclusions

1. Liquid phase sintering at low temperature could be realized through adding CAS to Y-TZP. The relative density was higher than 98% when the sintering temperature was more than 1400 °C.
2. Y-TZP samples had high bending stress owing to their superfine grain size, resulting from low sintering temperature. Bending strength of Y-TZP samples with 1% CAS and sintered at 1400 °C reached to 950±40 MPa.

Acknowledgements

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