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Sintering behavior and mechanical properties of injection-molded zirconia powder

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Abstract

Compared to normally continuous sintering at 1500 °C for 30 min, a novel two-stage sintering by firing the sample at 1500 °C for 5 min and then rapidly cooling down to 1300 °C for 10 h was proposed to investigate sintering behavior and mechanical strength of injection-molded yttria-stabilized zirconia (Z3Y). The injection-molded Z3Y feedstocks were prepared from the mixture of Z3Y powder and organic polymers with different solid content from 75 to 82 wt.%. The effect of sintering process on the microstructure evolution, physical characteristics and mechanical strength of molded Z3Y samples was investigated. It was found that bulk density and mechanical strength increases with solid content from 75 up to 82 wt.% in both sintering processes. X-ray diffraction (XRD) analysis shows that the industrial Z3Y samples consist of monoclinic and tetragonal phase, and the relative intensity ratio of tetragonal to monoclinic phases is almost independent of sintering process. Experimental results further demonstrate that a denser microstructure with finer grains was obtained with the two-stage sintering. Enhancement of bending strength (1078 MPa) due to the two-stage sintering process by a factor of four times in comparison with that (295 MPa) fired with normal sintering process has been obtained in the injection-molded Z3Y with the solid content of 82 wt.%. The enhanced bending strength is primarily attributed to more dense and fine-grain microstructure but not to tetragonal phase effect. Similar enhanced effect is also applied for the tetragonal zirconia polycrystals (TZP).

Keywords: A. Sintering; A. Injection molding; C. Mechanical properties; D. Zirconia; Z3Y

1. Introduction

Injection molding is one of the interesting processing techniques for making fine ceramics in the past two decades. These ceramics, including alumina, zirconia, and silicon nitride, are fabricated by this technique for performance applications, such as ceramic turbines or ferrules [1]. The technique offers the opportunity for mass production of ceramic parts with complicated shapes combined with the advantages of dimensional reproducibility and near-net-shape formation [2]. The process usually involves compounding the fine ceramic powder with a blend of polymers or wax in the solvent, such as toluene [3]. The organic binders embedded in the molded green parts have to be subsequently removed via thermal pyrolysis or solvent detracting prior to sintering [4].

A number of workers have investigated the properties of powder formula to improve the mechanical properties. Witbreuk and De With [5] investigated that the mechanical properties and microstructure of Y-tetragonal zirconia polycrystals (Y-TZP) ceramic under various controlled parameters. Edirisinghe et al. [6] studied the flow properties of different ceramic injection formulations. The influence of powder formula and processing parameters on microstructure of molded ceramic samples has been widely investigated [7–9]. The formulation and rheological properties of feedstocks containing a submicron-sized zirconia powder were studied by Okada et al. [10] showing that solid content has a strong influence on the viscosity. Although the powder formula and processing control have played an important role in the mechanical properties of molded ceramic parts, the subsequent processing parameters especially sintering control should be highly emphasized.

Zirconia is well-known high-temperature and high-strength material for structural applications [11]. Commercial zirconia powder is usually characteristic of partially stabilized zirconia (PSZ) which is a duplex structure ceramic, i.e. with a microstructure of tetragonal and monoclinic phases [12]. Although TZP possesses bending strength as high as ∼1000 MPa that is much better but more expen-

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sive than PSZ, it tends to induce phase transformation of tetragonal into monoclinic during sintering, depending on composition, sintering temperature, and grain size [13]. Since zirconia exhibits such high-mechanical strength and high-fracture toughness, zirconia was widely used for injection molding. However, many studies have focused on the development of powder formula and injection processing of injection-molded zirconia [3–8,14]. No further investigation was focused on the sintering behavior of injection-molded ZrO_2 samples.

Sintering is the process whereby the interparticle pores in a compact material can be eliminated by atomic diffusion driven by capillary forces [15]. However, the capillary driving forces for sintering (involving surface) and growth (involving grain boundaries) are comparable in magnitude. If the final-stage grain growth can be suppressed by exploiting the difference in kinetics between grain-boundary diffusion and grain-boundary migration, this variation can be controlled and tuned through heating schedules [16,17]. Consequently, although industry-grade ceramic powder was used, such a process should facilitate the cost-effective preparation for practical applications.

For ZrO_2, traditionally, a normal sintering schedule is employed to heat the powder compact at a certain rate, holding it at the highest temperature, such as 1500–1550 °C, until the maximum density is reached. The grain size of the ZrO_2 samples increases continuously with the density and the abnormal growth probably occurs in final-stage sintering. In this condition, even though sub-micron yttria-stabilized zirconia (Z3Y) powder with tetragonal phase was used, the mechanical strength would be reduced. Therefore, in this study, in contrast to conventional sintering process, a two-stage sintering method was adopted in the sintering schedule to control the microstructure with fine grains. The molded Z3Y samples were first heated to a higher temperature to achieve an intermediate density, then cooled down and held at a lower temperature for a longer time until it is fully dense without further grain growth. The sintering behavior and mechanical properties of molded Z3Y with different ZrO_2 solid content will be focused and compared between the conventional and two-stage heating process in this work.

2. Experimental procedure

2.1. Materials and processing of injection molding

A commercially available Z3Y ceramic powder, containing 5.24 wt.% (~3 mol%) Y_2O_3 with an average particle size of 0.27 μm, was used in this study. The organic binder system contains polyvinyl butanol (PVB) resin and dibutyl phthalate (DBP). The organic binder was mixed with PVB and DBP in 60:40 weight ratios in the poisonous ethylene alcohol (denoted as EtOH). After the binders were mixed, the Z3Y powder with the weight fraction (i.e. solid content) of 75, 80, and 82% was mixed and then kneaded together in a high-shear extruder. The solid content was defined as follows:

$$\text{Solid content} = \left(\frac{\text{Z3Y powder weight}}{\text{Z3Y powder weight} + \text{organic weight}}\right) \times 100\%$$

The extruded pellets are in cylindrical shape with 3 mm in diameter and 2–4 mm in length. The fully plasticized feedstock was tested in the capillary rheometer (SHIMAZU C-550 FC) to measure the suspension viscosity at a temperature range of 135–145 °C. The relationship between shear rate and viscosity was used a reference for the subsequent molding process. The pellets were injection-molded by Arburg 270M with an injection pressure of 680 bar at 140 °C.

2.2. Debinding and sintering

The heating profile, used for binder removal, follows the two stages. The molded samples were first heated to 100 °C with 2 °C/min, and thereafter to 600 °C with 10 °C/h and furnace cooled. After debinding, the molded Z3Y samples were sintered by normal continuous sintering and two-stage sintering process. For normal sintering, the samples were sintered at 1500 °C for 30 min at a heating rate of 10 °C/min. On the other hand, for two-stage sintering, the samples were heated to 1500 °C for 5 min and then rapidly cooled down and held at a lower temperature of 1300 °C for 10 h during which a fully dense microstructure composed of fine grains was obtained.

2.3. Characterization

To determine the debinding temperature, thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed. The crystal phase of the sintered Z3Y samples was determined by X-ray diffraction (XRD) on Rigaku X-ray diffractometer. For surface microstructure, after polished and then thermally etched at 1300 °C 2 h to delineate grain boundaries, the as-sintered Z3Y was observed using JEOL JSM-5600 scanning electron microscopy (SEM). The average grain size was measured from SEM micrographs after Medelson [18]. The bulk density of the Z3Y samples was measured by the Archimedes's method. The bending strength was measured with a universal testing machine, using three-point bending with a 30-mm span (bend bars of 3 mm × 4 mm × 40 mm) and a crosshead speed of 9×10^{-6} m/s.

3. Results and discussion

3.1. Physical characteristics of injection-molded Z3Y

The green density of injection-molded Z3Y was measured as a function of solid loading. As shown in Fig. 1, the green

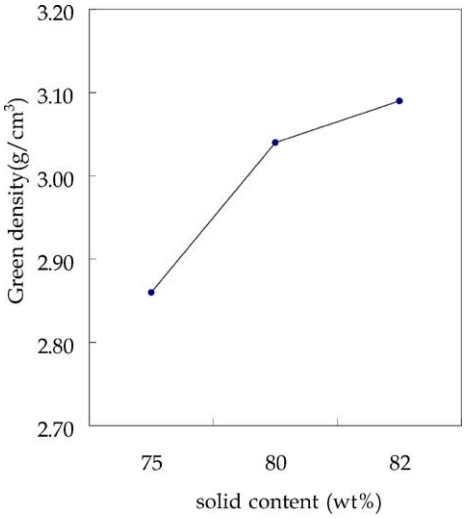


Fig. 1. Green density of injection-molded Z3Y varying with solid content.

density increases from 2.86 to 3.09 g/cm^3 with solid content from 75 up to 82 wt.%. Above that, it was found that the viscosity is too high for injection molding. Fig. 2 shows the XRD patterns of the molded Z3Y samples containing different solid content (75, 80, and 82 wt.%) sintered at 1500 °C for 30 min. It was found that the as-sintered samples consist of monoclinic and tetragonal phases and no apparent difference can be identified for the samples with different solid content. However, as the sample was first sintered at 1500 °C for a short time, such as 5 min, and then rapidly cooled down to 1300 °C and held for 10 h, the XRD patterns in Fig. 3 shows that the relative peak intensity of tetragonal to monoclinic phases was a little increased. In other words,

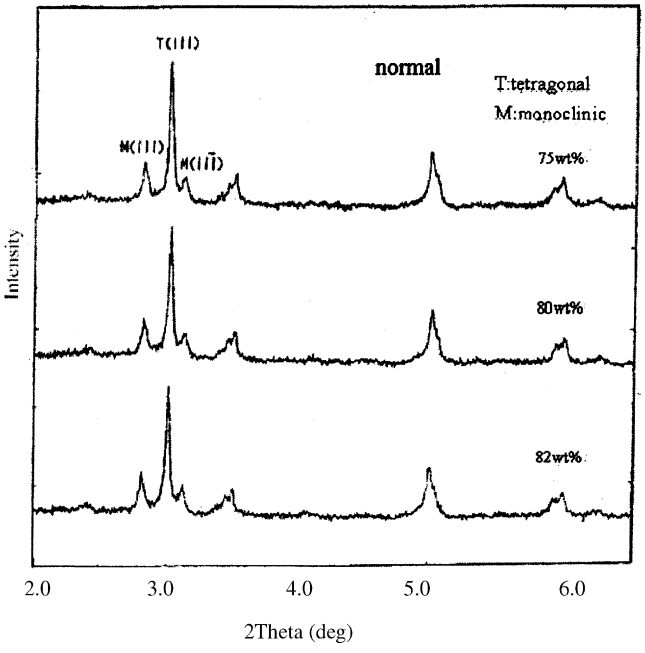


Fig. 2. XRD patterns of injection-molded Z3Y samples as a function of solid content sintered at 1500 °C for 30 min.

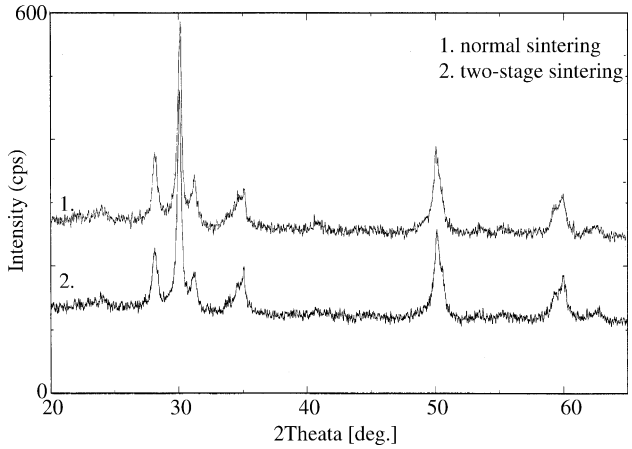


Fig. 3. XRD comparison of injection-molded Z3Y with 82 wt.% solid content fired with normal and two-stage sintering processes.

some of tetragonal phase can be partially retained during the thermal treatment. The thermal analysis of the molded Z3Y samples was performed. As shown in Fig. 4, the TGA shows three decomposition peaks and no further weight loss was detected over 500 °C. The three exothermal peaks correspond to the evaporation of EtOH and the decomposition of PVB and DBP. However, the DTA curve illustrates that there are two peaks. One smaller broad exothermal peak starts from 227 °C, and the other greater exothermal peak appears at 509 °C and ends at around 600 °C. However, no more weight loss was detected above 500 °C as evidenced from TGA. It implies that the exothermal peak should be probably associated with the shearing effects exerted on the fine ZrO_2 powder during the kneading. Therefore, the molded Z3Y samples were debinded at 600 °C instead of 509 °C according to DTA analysis.

Fig. 5 shows the bulk density of the molded Z3Y samples fired at 1500 °C for 30 min under normal sintering process. The data illustrate that the bulk density of the sintered Z3Y

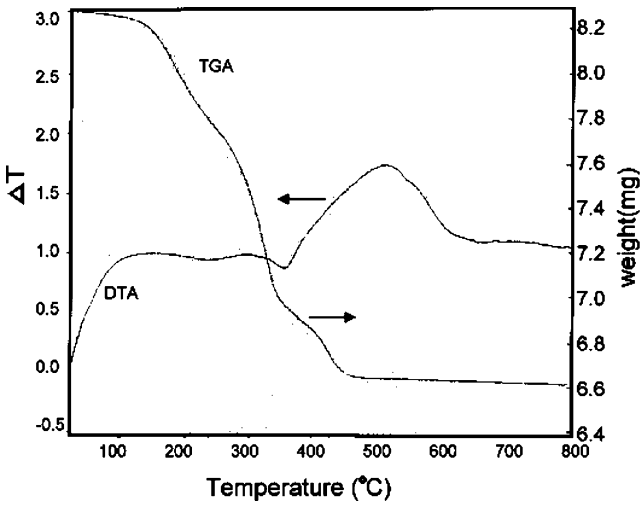


Fig. 4. DTA and TGA curves of Z3Y feedstock containing solid content of 82 wt.%.

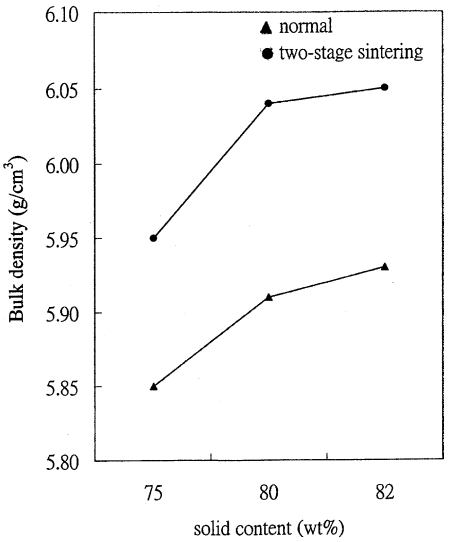


Fig. 5. Dependence of bulk density on solid content of injection-molded Z3Y under normal and two-stage sintering processes.

samples can be improved from 5.85 to 5.91 g/cm^3 by increasing solid content from 75 to 80 wt.%. Above that, the enhancement (5.91–5.93 g/cm^3) in the bulk density is only marginal with increasing solid content from 80 to 82 wt.%, implying that the available maximum solid content to improve bulk density is limited. The enhanced bulk density can corresponds to the water absorption. As shown in Fig. 6, the water absorption can be remarked reduced from 0.6 to 0.16% with increasing solid content from 75 to 80 wt.% under normal sintering process.

In sharp contrast, as the sample was sintered with a two-stage process (first heated at 1500 °C for a short time (5 min) to 1300 °C for 10 h), as shown in Fig. 5, it was found that the bulk density apparently increases from 5.95 to 6.04 g/cm^3. According to the reported theoretical density of tetragonal (6.10 g/cm^3) and monoclinic phases (5.56 g/cm^3) [19], the bulk density (6.04 g/cm^3) of the present Z3Y can be considered approximately to theoretical density (~100%

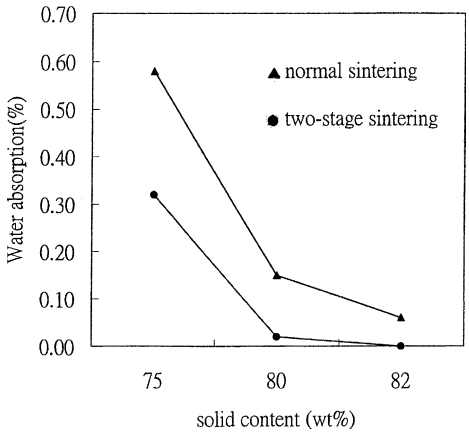


Fig. 6. Effect of solid content on water absorption of as-sintered Z3Y after normal and two-stage sintering.

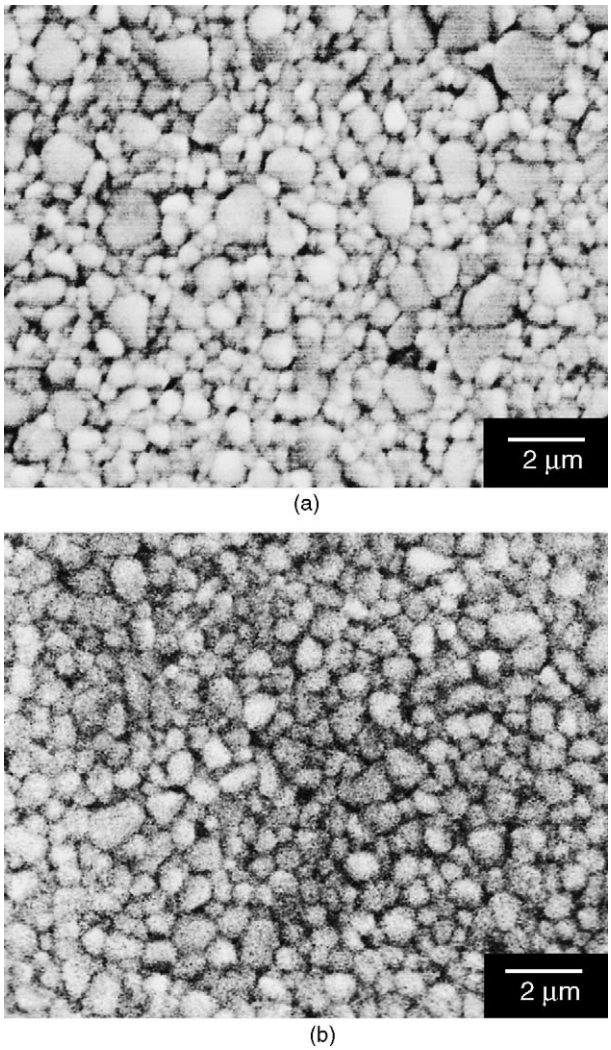
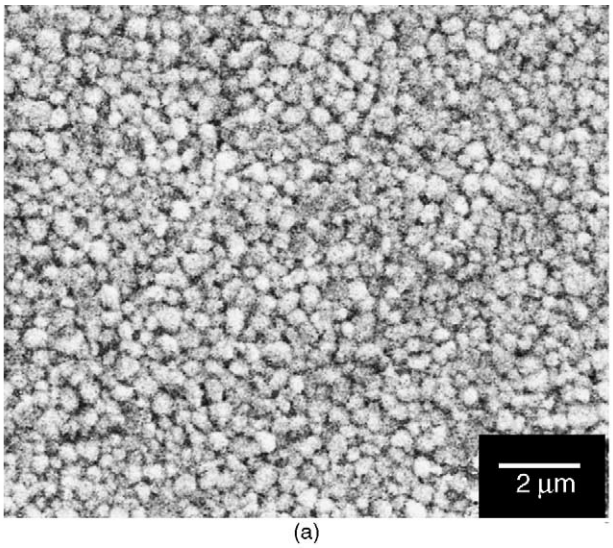


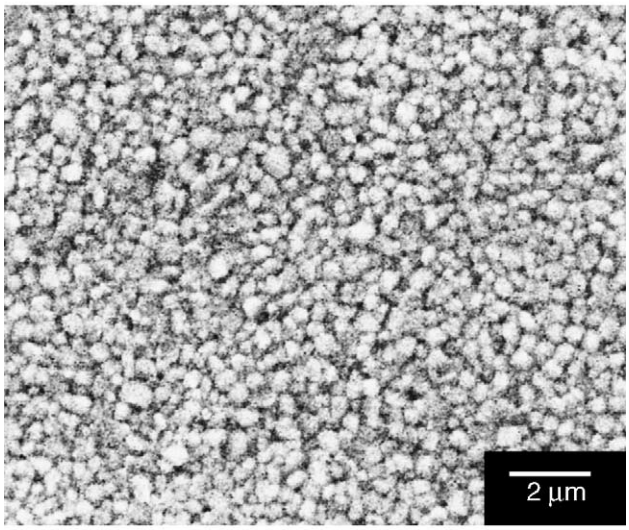
Fig. 7. Scanning electron micrographs of injection-molded Z3Y fired at 1500 °C for 30 min under normal sintering process: (a) 75 wt.% and (b) 82 wt.% solid content.

relative density) because it consists of tetragonal and monoclinic phases. Similar phenomenon is also reflected on the water absorption shown in Fig. 6 at which nearly zero absorption was observed for the molded Z3Y with solid content above 80 wt.%.

Fig. 7 illustrates the typical microstructure of molded Z3Y containing different solid loading and fired by normal sintering process. As shown in Fig. 7a, the microstructure of 75 wt.% solid content sample presents bimodal grain size distribution (1.45 and 0.67 μm). It means that some grains grow rapidly and other grains are frozen because the average size of the starting powder is about 0.27 μm measured by particle size analyzer. As increasing solid content, the microstructure does not only become dense but also the grain size becomes uniform (narrow grain size distribution was obtained) as shown in Fig. 7b. The average grain size of the sintered 82 wt.% Z3Y is about 1.05 μm. On the other hand, as the two-stage sintering was used, although bimodal grain



(a)



(b)

Fig. 8. Scanning electron micrographs of injection-molded Z3Y fired under two-stage sintering process (1500 °C for 5 min and rapidly cooled to 1300 °C for 10 h): (a) 75 wt.% and (b) 82 wt.% solid content.

size is also observed for molded Z3Y with a lower solid content of 75 wt.% as show in Fig. 8a, the average grain size in this sample is smaller than that fired with normal sintering process. Furthermore, it was found that with increasing solid content above 80 wt.% (i.e. 82 wt.%), a denser microstructure with much finer grains (average grain size of 0.59 μm) was obtained for the molded Z3Y sample sintered by a two-stage process as compared to normally continuous sintering process.

The bending strength of as-sintered-molded Z3Y samples was measured from bars fabricated from the powders with different solid content. As shown in Fig. 9, the room-temperature strength increases with solid content from 75 up to 80 wt.% for the samples with normal sintering process. The maximum attained average strength is about 295 MPa. However, it was noted that the bending

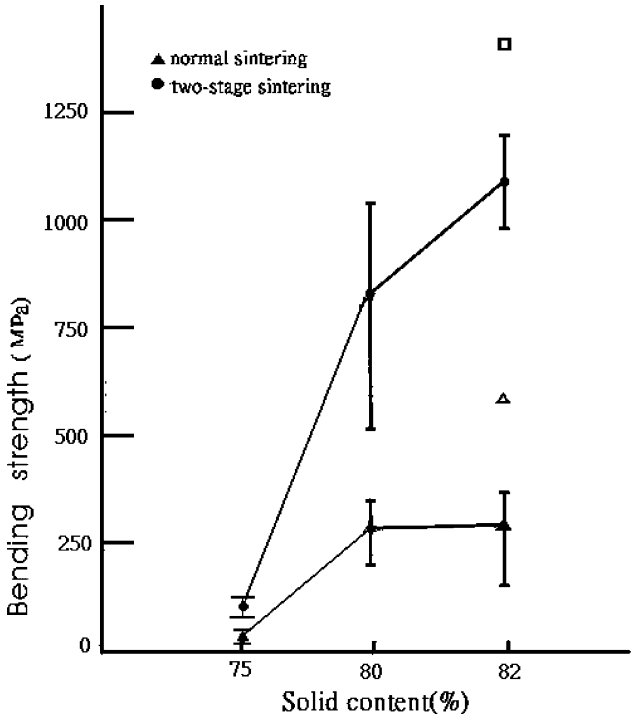


Fig. 9. Dependence of bending strength of injection-molded Z3Y on solid content under normal and two-stage sintering profiles. The bending strength of TZP with 82 wt.% solid content is also indicated as "△" and "□" for normal and two-stage sintering, respectively.

strength could be increased by four times with a two-stage sintering process as compared to that with normal sintering process. The obtained strength of the molded Z3Y sample sintered by two-stage process is 1078 MPa. In order to investigate the effect of tetragonal/monoclinic phase ratio on the mechanical properties, high-purity TZP powder (Toyo Soda powder) composed of only tetragonal phase with solid loading of 82 wt.% was also prepared. The average bending strength of the TZP samples under normal process and two-stage sintering processes is measured about 615 and 1394 MPa, respectively. Because the present industrial Z3Y powder contains tetragonal and monoclinic phases, the obtained optimal or maximum mechanical strength should be influenced and reduced compared to that prepared with high-purity all tetragonal phase TZP powder. This result again demonstrates the importance of sintering process on the physical and mechanical properties of ceramic materials. Since both samples are primarily composed of tetragonal and monoclinic phases after fired with different sintering process and the relative intensity ratio of tetragonal to monoclinic in both samples is very close, the enhanced strength should not be due to the tetragonal/monoclinic phase ratio. In view of improving strength, both higher density and smaller grain size play important roles in the overall strength. As shown in Figs. 7 and 8 for the microstructure of these samples, with normal sintering process, the grain size of molded Z3Y samples increases continuously with the density and the sample has to be

sintered above 1500 °C to reach a maximum density. In this case, at 1500 °C for 0.5 h, the available maximum bulk density is 5.93 g/cm^3 for 82 wt.% solid content Z3Y. On the other hand, as the two-stage sintering process was used for the Z3Y samples with the same solid content (82 wt.%), a sufficiently high starting density above 70% should be obtained without grain growth during the first stage and all the pores in the Z3Y sample become subcritical and unstable against shrinkage. Subsequently, the sample was rapidly cooled down to 1300 °C for 10 h from 1500 °C during the second-stage sintering at which the sintering precedes in a "frozen" microstructure and it presents slower kinetics. Yet, the slower kinetics is sufficient for reaching full density, while providing the benefit of suppressing grain growth. As shown in Figs. 5 and 8, the measured bulk density and average grain size of the Z3Y samples are 6.04 g/cm^3 and 0.59 μm. In comparison with those ($\rho = 5.93$ g/cm^3 and $d = 1.05$ μm) of samples fired by normal sintering process, the two-stage sintered Z3Y samples exhibit higher dense and fine-grained microstructure. Therefore, the remarkably enhanced mechanical strength can be primarily attributed to high density and fine-grained microstructure due to the two-stage sintering. We believe that the simplicity of this approach should also make it useful for detailed exploration of other dense microstructure even nanostructured materials, in order to take advantage of their grain-size-dependent physical properties to achieve high-mechanical strength.

4. Conclusions

The injection molding Z3Y components were prepared from mixture of Z3Y powder and organic polymers of PVB and DBP in the ethanol solvent. It was found that both bulk density and mechanical strength increase with solid content from 75 to 80 wt.%, above that the bulk density remain unchanged with further increasing solid content to 82 wt.% independent of sintering process. Meanwhile, the water absorption was obviously reduced. Compared to normal continuous sintering at 1500 °C for 30 min, a novel two-stage sintering by firing the sample at 1500 °C for 5 min and then rapidly cooling down to 1300 °C for 10 h has demonstrated that the bending strength can be enhanced by four times (1078 MPa versus 295 MPa). Experimental results further reveal that a denser microstructure with finer grains can be obtained with the two-stage sintering. However, both XRD patterns show no apparent differences and are primarily composed of tetragonal and monoclinic phases. It might suggest that the enhanced strength is attributed to the high-dense and fine-grained microstructure but not to crystal tetragonal phase effect.

Acknowledgements

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