Densification and Grain Growth of Nanocrystalline 3Y-TZP Powder Compacts During Two-Step Sintering

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Abstract: Two-step sintering (TSS) was applied on nanocrystalline yttria stabilized tetragonal zirconia (3Y-TZP) to control the accelerated grain growth during the last stage of sintering. The process involves firing at a high temperature (T1) followed by rapidly cooling to a lower temperature (T2) and soaking for a prolonged time (t). It was shown that for nanocrystalline 3Y-TZP (27 nm) the optimum processing condition is T1=1300 °C, T2=1150 °C and t=30 h. In this case, the grain growth is significantly retarded. And grain size of 127 nm is obtained by TSS compared with 260 nm in single-step sintering. It was also found that the density of the compacts must reach to 83% of the theoretical density in first step (sintering at high temperature) to make pores unstable for the further densification at lower temperature.

Keywords: Tetragonal stabilized zirconia; Densification; Grain growth; Two-step sintering

Introduction

Yttria stabilized zirconia ceramics display extremely high values of fracture toughness that makes them suitable for a wide range of structural applications such as cutting tools, valve guides, extrusion dies, abrasive tools, etc [1,2]. Recently, it has been shown that superplastic deformation and higher hardness are gained when an ultrafine-grained toughened ceramics are utilized [2]. Superior properties of 3Y-TZP are also predicted to be enhance when the grain size reduce to the nano-scale [3]. In order to achieve ultrafine grain size, it is essential to control the grain growth during firing. The present work attempts to study the TSS process for elimination of residual porosity from nanocrystalline 3Y-TZP powder compacts. The temperature range in which the residual porosity can be eliminated without the final stage of grain growth is reported. The effect of firing temperature on the density and grain size of the nanopowder compacts are addressed. A comparison is made between TSS and conventional sintering procedure.

Experimental

ZrO2-3mol% Y2O3 powder was supplied from Tosoh Co. (Tokyo, Japan). The aggregate particle size is 75 nm and the particle shape is polygonal. The Powder was compacted in a cylindrical die at 150 MPa to produce green compacts with 12.7 mm diameter and 3 mm height. The green density was 43% of the pore free density. Single-step sintering (SSS) was carried out in air at temperature range of 1100-1500 °C with a dual time of 1 min. The heating rate of 5 °C min⁻¹ was applied. The cycles of TSS are reported in Table 1. The density of the sintered sample was measured by the water displacement method. Microstructure of the sintered compacts was observed by SEM (Philips XL30, Netherlands) after sequential mechanical polishing using diamond pastes and thermal etching. The average grain size of the sintered compacts was determined by the linear intercept method (ASTM Standard E112).

Results and Discussion

Fig. 1 shows the grain size of the sintered samples as a function of density for the applied sintering cycles. In SSS cycle, the grains grow with a low rate up to the intermediate densification range, i.e. 0.52-0.83 %theoretical density (TD). Here, the average grain size increased from 62 to 94 nm. It is known that dispersed open pores pin grain boundaries and hinder grain-boundary migration at intermediate stage of sintering [4]. At higher densities (density>0.94 %TD), the grains grow rapidly and ultrafine structure with an average grain size of 275 nm is obtained (Fig. 2a). Formation of closed pores at the final stage of sintering results in a substantial decrease in pore pinning, which triggers the accelerated grain growth [7,8]. From Fig. 1, one can notice that the effect of TSS on the grain growth significantly depends on the selected temperatures. Although TSS1 succeeds to inhibit grain growth at the final stage of sintering (density of 0.94-0.97 %TD), an accelerated grain growth is noticed during prolonged firing at the low temperature (1150 °C). Even though, finer grain structure is obtained as compared with SSS (Fig. 2b).

<table>
<thead>
<tr>
<th>Cycle</th>
<th>T1 (°C)</th>
<th>T2 (°C)</th>
<th>Holding time at T2 (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TSS1</td>
<td>1350</td>
<td>1150</td>
<td>2, 5, 8, 12, 15, 20</td>
</tr>
<tr>
<td>TSS2</td>
<td>1300</td>
<td>1150</td>
<td>2, 5, 8, 12, 15, 20, 25, 30</td>
</tr>
</tbody>
</table>

Table 1. Cycles of two-step sintering
Another TSS cycle (TSS2) was performed at T1=1300 °C, T2=1150 °C. As seen in Fig. 1, the densification proceeds with a rather constant grain size. Fig. 2c illustrates a SEM micrograph of the microstructure, showing grains with an average size of 127 nm. Chen and Wang [5] have explained that to achieve densification without grain growth, grain boundary diffusion needs to remain active, while the grain boundary migration is to be suppressed. A mechanism to inhibit grain boundary movement is a triple-point (junction) drag. In fact, the grain growth entails a competition between grain-boundary mobility and the junction mobility. Once the latter becomes less at low temperatures in which junctions are rather motionless, the mentioned drag would occur. Consequently, the grain growth is prohibited by the two-step sintering process. Achievement of a better density during the TSS2 can also be due to the reduced entrapped gas pressure within the micropores at a lower temperature [6,8]. A reduction in gas pressure may not be able to oppose the matter transport due to the diffusion mechanism and thus the sintering process may proceed in the forward direction. Fig. 1 determines that in contrary to TSS1 schedule, the incubation time is long enough to gain a fully dense structure in TSS2 cycle. This can be due to the grain size difference at the end of the first firing step at T1. Based on the experimental results, it can therefore be concluded that the critical density (ρ*) for available granulated nanocrystalline 3Y-TZP is 0.83 %TD to render pores unstable.

Conclusion

Two-step sintering process was applied on nanocrystalline 3Y-TZP ceramic. It was shown that up to the intermediate densification range, no remarkable grain growth occurs due to the pinning effect of open pores. When the pores become closed, an accelerated grain growth occurs. TSS can retard the initial grain growth during firing: thereby, finer grain structure is obtained. If proper temperature cycle is applied, the pores become unstable and limited grain growth is observed. It is shown that for nanocrystalline 3Y-TZP, heating to 1300 °C and then rapid cooling to 1150 °C and soaking for a prolonged time of 30 h yields ultrafine ceramic with an average grain size of 127 nm.

References