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Rapid sintering of nanocrystalline ZrO_2(3Y) by spark plasma sintering

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Abstract

SPS (spark plasma sintering) process was used to sinter nanocrystalline ZrO_2 (3Y). It was found to be different with the usual rapid sintering method, the density of the samples kept increasing with the rising of the sintering temperature. A higher density could be reached at a lower temperature and shorter dwelling time than that by hot-pressing under the similar pressures. In contrast to the samples with a differential densification from edge to center prepared by a rapid hot-pressing, no obvious densification gradient could be found in the samples sintered by SPS. The grain sizes of the Y-TZP obtained by SPS were smaller than those by the pressureless sintering method, while the grain growth speed was much higher under SPS conditions. All these unique sintering behaviors were explained by the special sintering process of SPS.

Keywords: Microstructure-final; Sintering; Spark plasma sintering; SPS; ZrO_2

1. Introduction

Rapid sintering methods have been widely used to sinter many kinds of materials in the past. The most obvious advantage of the rapid sintering is that the fast heating and cooling rate and the short dwelling time make it possible that the sample was skipped over the low-temperature regime and was sintered directly at higher temperatures to reach a high density with fine grains.[1–3] Recently, some investigations have been tried to sinter nanocrystalline ZrO_2-3 mol% Y_2O_3 with rapid sintering methods.[4–7] However, the usual rapid sintering was often carried out by heating outside of the sample. Because of the low thermal conductivity of Y-TZP materials, thermal gradient effect could only be ignored for very small samples (<0.1 g).[4] If the volume is larger, sample cracking would take place.

Spark plasma sintering (SPS) is a new rapid sintering method which was developed recently for the fabrication of ceramics and composites.[8–11] In this method, the powder in a carbon die is pressed uniaxially and direct current pulse voltage is applied. So besides keeping the advantages of hot-pressure sintering, the most important character of SPS is that the powder is heated by spark discharge between the particles. As a result, the sample can be sintered uniformly and rapidly from both inside and outside.[10,12] Thus, the SPS method is considered to be suitable for the fabrication of large samples of Y-TZP materials by using nanocrystalline ZrO_2 (3Y) powder. However, few reports on this aspect have been published which means some further investigation should be done.

2. Experimental

ZrO_2 (3Y) nanopowder was synthesized by a co-precipitation method. $ZrOCl_2{\cdot}8H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ solutions were mixed together according to the composition of 97 mol% $ZrO_2 + 3$ mol% Y_2O_3. This precursor solution was added slowly to an excess of a 25% ammonia solution. During this period the pH value remained at 9. After reaction, the precipitate was washed six times with water in order to remove Cl^- and washed three times with ethanol to remove the free water within the precipitates. The precipitates were then

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dried in the air at 120°C for 24 h, dried milled and then calcined at 450°C for 5 h to get the final powder.

The SPS process was carried out by using a apparatus Dr Sinter 1020 SPS (Sumitomo Coal Mining Co.). Details of this apparatus were introduced elsewhere.[8] The powder was put into a carbon die and heated to a predetermined temperature at a heating rate of 600°C/min, at the same time, a pressure of 40 MPa was applied. After dwelling for a certain period of time (1–10 min), the pressure was released and the sample was cooled to below 600°C in 2 min. The sintered samples were pellets (20 mm in diameter, 1–4 mm in thickness and 2–6 g in weight).

For the comparison, the usual hot-pressing, the rapid hot-pressing and the pressureless sintering methods were also used to sinter Y-TZP by using the same ZrO_2 (3Y) nanopowder. With the usual hot-pressing, a heating rate of 30°C/min and a pressure of 40 MPa and a dwelling time of 30 min were applied; with the rapid hot-pressing, a heating rate of 200°C/min and a pressure of 80 MPa and a dwelling time of 10 min were applied. With the pressureless sintering, the green compact was conducted at 450 MPa, then a heating rate of 5°C/min and a dwelling time of 2 h were applied. The sample sizes were similar as those sintered by SPS.

The morphology of the powder was observed by transmission electron microscopy (TEM). The specific surface area of the calcined powder was measured by the BET method. Sintered densities of the pellets were measured by the Archimedes method in distilled water. The crystal phase of the powder was determined by X-ray diffraction (XRD). The grain sizes of the sintering samples were determined by electron-microscope (SEM) observation.

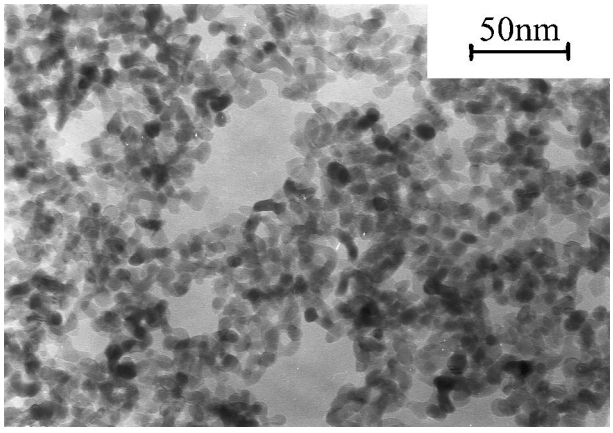

Fig.1. TEM micrograph of the prepared powder.

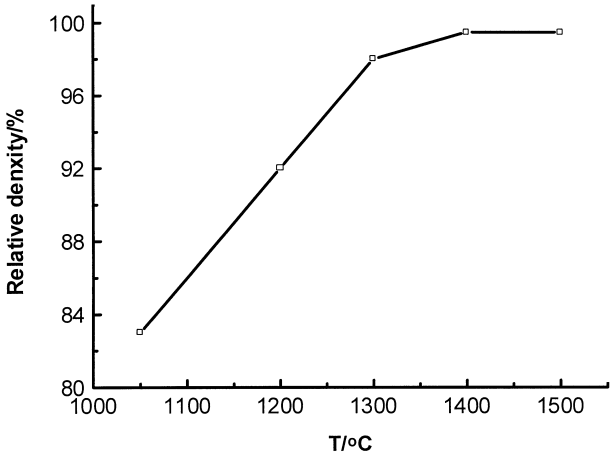

Fig. 2. Relationship between the relative density and the sintering temperature of Y-TZP densified by SPS (dwelling time of 3 min).

3. Results and discussions

3.1. Powder characteristics

Fig. 1 shows the TEM micrograph of the calcined powder. From Fig. 1 it could be seen that the particle size was about 6–8 nm and with a narrow-distribution. The specific surface area of the same powder measured by BET was 110 m^2/g which was equivalent to a 9 nm crystallite. Crystallite size of the powder — determined by means of the X-ray line broadening (XPCB) method — was about 8 nm. All the results were in good agreement with each other, which means that the formation of hard agglomerates was basically avoided. XRD result showed that the powder was mainly composed of the tetragonal zirconia phase.

3.2. Relative densities of the samples

Fig. 2 shows the relationship between the relative density of the sample and sintering temperature under SPS conditions. In spite of the short dwelling time of 3 min, the relative density exceeded 98% when the sintering temperatures were above 1300°C and it nearly reached the theoretical density when the sintering temperature was 1400°C. An obvious difference could be seen when comparing the SPS sintering curve in Fig. 2 with many other sintering curves of rapid sintering.[4–7] Many experiments showed that the relative density would reach top value when the Y-TZP was rapidly sintered at a certain temperature and the relative density would decrease if the sintering temperature was too high. However, no such behavior was observed in Fig. 2. This difference could be explained by different sintering mechanisms from the ordinary rapid sintering and SPS. Under the usual rapid sintering conditions, samples are always heated from outside. Because of the low thermal conductivity of Y-TZP, it is likely that the outside of the sample will experience heat much sooner. At a too high sintering temperature, the completely densified outside of the sample will constrain the inside of the sample from shrinking as it normally would, as a result, the

final density would be poor.[4] But when the SPS sintering method was used, spark discharge would be happening between the particles, so the sample could be heated uniformly because no heating conduction needed. Thus, the abnormal phenomena in usual rapid sintering will not be happened.

Table 1 shows the comparison of relative densities of Y-TZP between SPS and hot-pressing. In the case when the applied pressure was similar, a high density of 99% could be attained at 1180°C in 9 min by SPS, while a low density of about 96% was obtained at 1250°C in 30 min by the hot-pressing.

Table 1
Comparison of relative densities of Y-TZP between SPS (dwelling time of 9 min) and HP (dwelling time of 30 min)

Sintering temperature/°C	1100	1180	1200	1250
Relative density/% (SPS)	95	99	–	–
Relative density/% (hot-pressing)	–	–	95	96

3.3. Microstructures of the sintered samples

Both the samples sintered by SPS and the rapid hot-pressing were observed by eyes and SEM. It was found that all the samples sintered by SPS were intact with no cracks, however, all the samples sintered by rapid hot-pressing had some defects. Fig. 3 shows the microstructures on the polished surfaces of the two kinds of sintered samples. Although both samples were sintered at 1100°C, the microstructures were obviously different. In sample A, a differential densification from edge to center could be observed clearly. The outside of the sample is nearly dense, while there is increasing porosity as one approaches the sample center. On the other hand, in sample B, no demonstrable differential densification could be observed. From edge to center, the

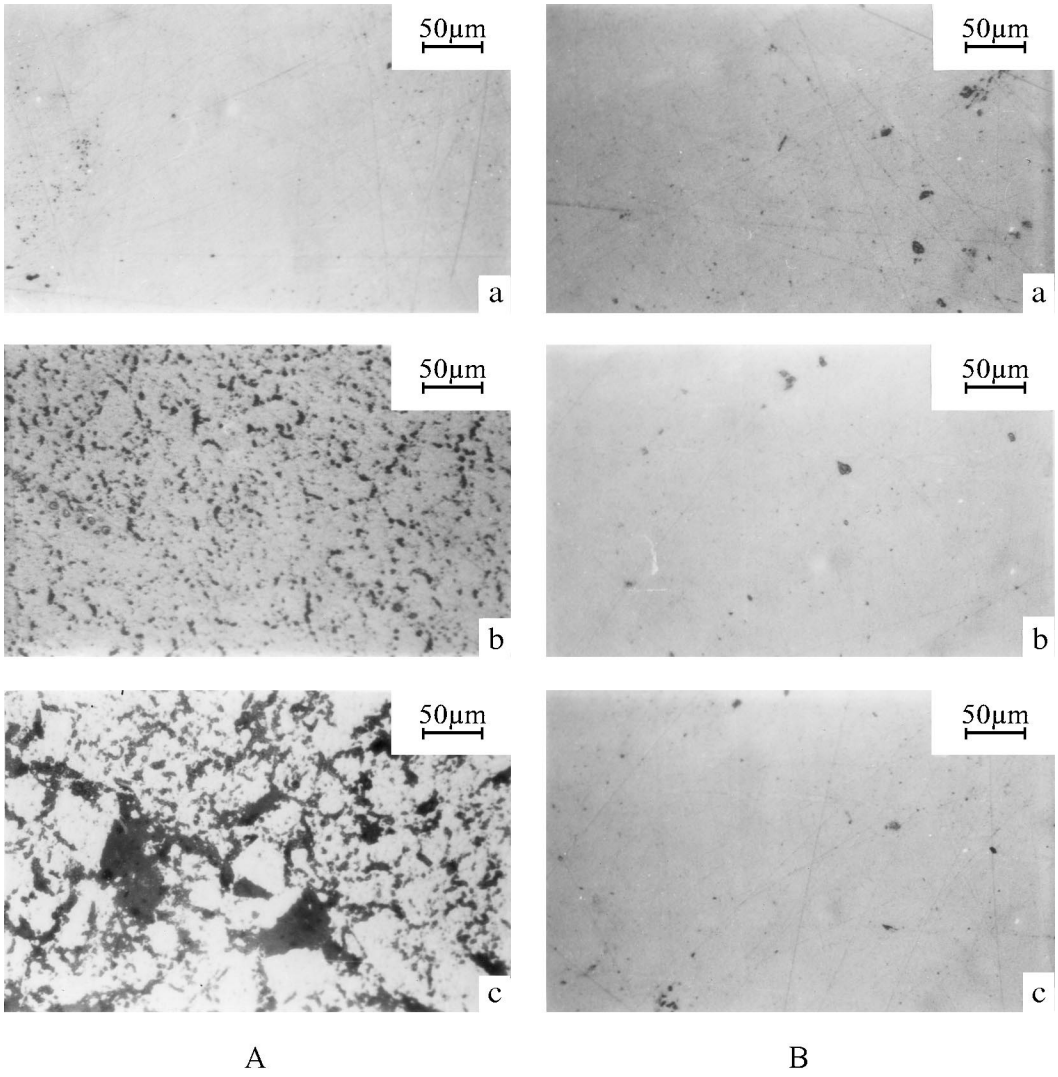

Fig. 3. Micrographs of the polished surfaces of Y-TZP densified by rapid hot-pressing (A) and SPS (B), respectively (a: edge; b: middle; c: center).

micrographs were similar and the pores were distributed uniformly.

The difference of the samples sintered by SPS and the rapid hot-pressing could also be seen from the difference of the hardness shown in Table 2. The hardness of the sample sintered by rapid hot-pressing decreased from edge to center rapidly, while no obvious change could be seen in the sample sintered by SPS. All these results were coincident with the results observed by SEM very well.

This difference could also be explained by the different sintering mechanisms of the usual rapid sintering and SPS. As mentioned above, Y-TZP materials have a very low thermal conductivity,[4] when the sintering rate was too high in the case of the rapid hot-pressing, the outside of the sample heated much more quickly than the inside which means that differential densification happened. As a result, the density and hardness of the final Y-TZP materials both decrease from outside to inside. However, under SPS sintering conditions, the spark discharge happened between all particles, so that the sample could be heated uniformly because there was no thermal conduction needed. So, the differential densification did not happened.

3.4. Grain growth of the samples

Fig. 4 shows the grain sizes of the Y-TZP obtained under SPS and pressureless sintering conditions, respectively. The grain size of the Y-TZP sintered by SPS is smaller than that by the pressureless sintering. The higher the sintering temperature, the more obvious the difference. This result could certainly be attributed to the very high sintering speed and very short dwelling time of SPS. However, considering the sintering time as short as only 3 min, the grain growth speed under SPS conditions was much higher than that under pressureless sintering conditions. The reason for this phenomenon was not yet clear, but it could be explained from two aspects. First, the applied pressure would accelerate the dynamic grain growth,[13] second, the spark discharge happened between the particles and would largely increase the surface activity of the particles which would then accelerate the surface diffusion and make the grains grow quickly. So, despite the rapid heating rate and short dwelling time in the SPS process, it was still very difficult to control the grain growth to prepare real nano ceramics.

Table 2
The comparison of the hardness of different location in the sample (Hv/GPa)

Part	Edge	Middle	Center
SPS	9.5±0.3	9.4±0.1	9.9±0.3
Rapid hot-pressuring	10.8±0.2	9.0±0.4	5.9±0.7

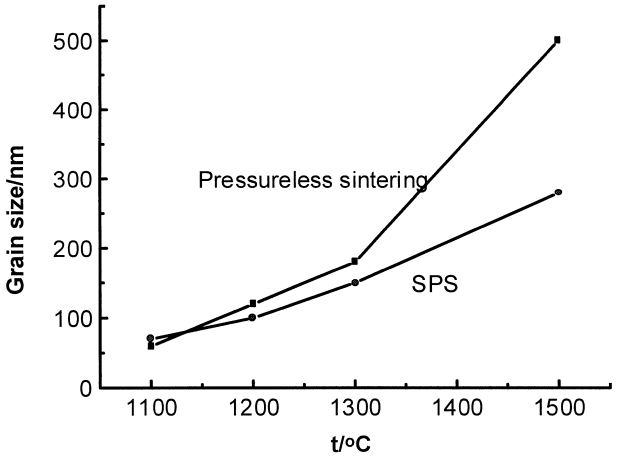

Fig. 4. The relationship between the grain size and the sintering temperature of Y-TZP densified by pressureless sintering (dwell time of 2 h) and SPS (dwelling time of 3 min), respectively.

4. Conclusions

1. Nanocrystalline ZrO_2(3Y) powder could be sintered by the SPS method and dense Y-TZP materials could be obtained. In contrast to the differential densification from the edge to the center in the rapid hot-pressing samples, no densification gradient could be found in the samples sintered by the SPS method in spite of its high heating rate of 600°C/min.
2. Relative densities of Y-TZP materials sintered by SPS increase with the rise of the sintering temperature. Under experiment conditions, the abnormal phenomenon that the final density decreases when the sintering temperature is too high, which often happens under usual sintering conditions, was avoided. A higher density could be attained at a lower temperature and shorter dwelling time than that by hot-pressing under similar pressure.
3. Grain sizes of the Y-TZP materials sintered by SPS were smaller than that by pressureless sintering, but the grain growth speed was much higher under SPS conditions. So, it is very difficult to prepare nano Y-TZP materials with the grain size smaller than 100 nm, by SPS.
4. All these unique sintering behaviors of SPS could be explained mainly by the special sintering process of spark discharge which was happening between the particles in the sample.

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