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Fabrication of nano Y–TZP materials by superhigh pressure compaction

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Abstract

Y–TZP nanoceramics have been fabricated by superhigh pressure compacting and pressureless sintering. It was found that, by applying superhigh pressure of about 3GPa, the green compacts with a relative density of about 60% could be obtained, which was 12% higher than that by a normal cold isostatic pressure of 450 MPa. The obvious advantage of the higher relative density of the green compact is that the sintering temperature could be decreased to as low as 1050°C. The reason for the good sintering behavior is believed to be both the increase in contact points between the particles and the decrease in pore size. Nano Y–TZP ceramics with grain size of about 80 nm could be obtained when sintered at 1050°C for 5 h. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Compaction; Grain size; Nanostructures; Pressing; Sintering; ZrO_2

1. Introduction

Y–TZP nanoceramics, which are believed to have some special characteristics such as superplasticity at low temperature,[1] have got a worldwide interest in recent years. Lots of methods,[1] including hot-pressing, sinter-forging, hot-isostatic pressing and spark plasma sintering, have been used to fabricate Y–TZP nanoceramics. Among these methods, pressureless sintering is still a most promising one because of its low cost and easy technique. To produce bulk Y–TZP nanoceramics with grain size less than 100 nm by the pressureless sintering method, a relative low sintering temperature is indispensable. However, it is not easy for Y–TZP to reach a high density at low temperatures, many factors should be taken into account. Burggraaf and other researchers[2–5] have shown that ZrO_2 powders with small grain size, little agglomerate and green compacts with homogeneous microstructure, small pore size and narrow pore size distribution are necessary to ensure the low temperature sintering. By carefully controlling these factors, they obtained nano Y–TZP with high density (above 97%) and small grain size (<100 nm) successfully. High green density is also beneficial to densify samples at low temperatures. For example, earlier investigation by Rhodes[6] indicated that Y–TZP with 99.9% of theoretical density could be obtained in a 1 h 1100°C cycle by sintering green compact with a high density of 74% (although his main purpose was to show the good sintering ability of agglomerate-free powder). However, his method (centrifuge-cast) seems not to have gained enough attention, perhaps because of its low productivity and long preparation time. Some experiments show that a relative high green density could be attained easily by applying a high pressure on the green compact.[7,8] Unfortunately, under normal cold isostatic pressure conditions, it is very difficult to get a pressure higher than 600 MPa.[1] Although the high pressures could be obtained much more easily by using a cold uniaxial pressing, the density and residual stress gradients were often so serious that the specimen could not withstand the thermally induced stresses caused by sintering (except for very small samples).[1,7]

In this work, an isostatic pressure with a superhigh value of about 3 GPa was applied, while we obtained 99% dense Y–TZP nanoceramics having the average grain size of about 80 nm.

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2. Experimental

Three mol% Y_2O_3–ZrO_2 nanoscale powder was prepared by a co-precipitation method. $ZrOCl_2 \cdot 8H_2O$ and $Y(NO_3)_3 \cdot 6H_2O$ were used as starting materials and mixed together in a solution. 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 precipitates were 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 dried in the air at 120°C for 24 h, dried milled and then calcined at 600°C for 2 hours to get the final powder.

Compacting was carried out by using special superhigh pressure equipment (with the highest pressure of 50 000 barometric pressure) which had been used to synthesize diamond. Some modifications have already been made to fit our purpose. The powder was first dry compacted with a pressure of about 10 MPa, then the green compact was encapsulated in a cube die made of pyrophyllite. High mechanical pressure was then applied on all six faces of the die concurrently. Since pyrophyllite is soft, plastic deform would take place easily under high pressures, so the pressure could be transmitted to the sample homogeneously. In this way, an isostatic pressure of about 3 GPa could be obtained. All the green compacts were pellets of 2–5 g.

As comparison, a normal cold isostatic compacting (KIP100E) was also carried out by using the same nano powder and a commercial powder (TZ–3Y powder from the Tosoh Co., Tokyo, Japan). The CIP pressures were 450 MPa.

All the green compacts were pressureless sintered at predetermined temperatures with a heating rate of 5°C/min and a dwelling time of 2 h.

TEM (JEM-200CX) was employed to determine the morphology and the particle size of the calcined powders and the sintered samples; XRD (RAX-10) was used to deduce the crystalline phases of calcined powders. The BET specific surface area of the powders and BJH pore diameter distribution of the green compact were obtained by N_2 adsorption–desorption isotherms (ASAP-2010) at 77 K. Archimedes' principle was used to measure the bulk density.

3. Results and discussion

3.1. Characteristics of the powder and green compacts

Fig. 1 shows the TEM micrograph of the nano ZrO_2(3Y) powder. From Fig. 1, it could be seen that the particles were about 12 nm in diameter and well distributed. XRD result shows that the powders was composed of tetragonal phase.

Fig. 2 shows the compacting behavior of the nano powder. The relative density of the green compact increased with the applied pressure and it could reach 60% when a pressure of about 3 GPa was applied, which was about 12% higher than that by a normal cold isostatic pressure was applied. All the green compacts obtained by superhigh pressure were translucent. Since all pores are scattering centers for light, this result suggests that large pores and cracks are basically avoided in the compact[9] (it can also be confirmed by the pore size distribution in Fig. 5), and the packing homogeneity is very good.

3.2. Sintering behavior of the Y–TZP ceramics

Fig. 3 shows the relationship between the relative density of the Y–TZP ceramics with the sintering temperature for Y–TZP ceramics by compactions of the same nano ZrO_2 powder at 450 MPa and 3 GPa, respectively. From Fig. 3, it could be seen that the necessary sintering temperature to fully densify the sample had been decreased obviously when superhigh pressure was applied. A relative density of 98% could be reached at 1050°C and full density could be reached

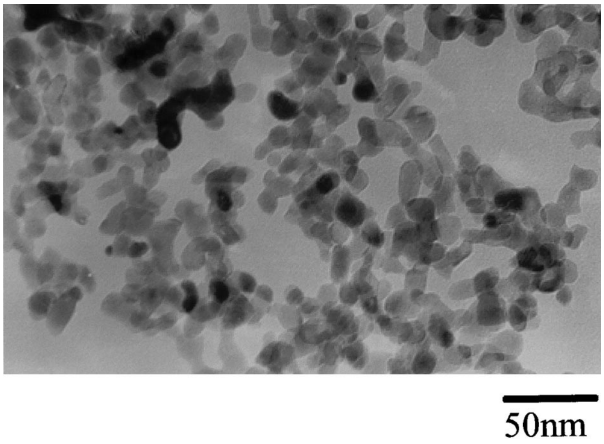

Fig. 1. TEM micrograph of nano ZrO_2(3Y) powder.

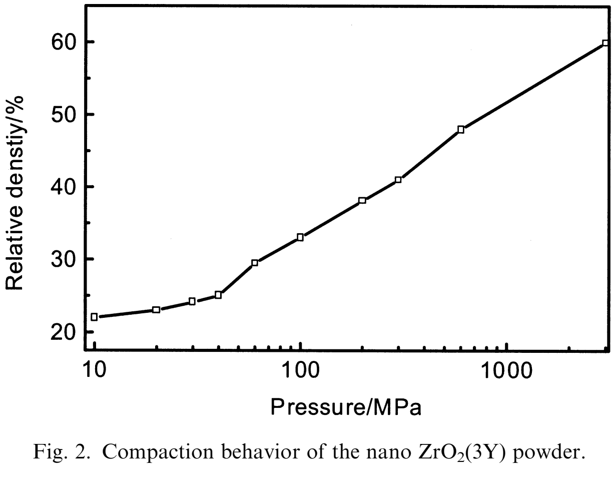

Fig. 2. Compaction behavior of the nano ZrO_2(3Y) powder.

at 1100°C. While only a relative density of 96% could be reached at 1150°C for the green compact by the normal CIP process where a cold isostatic pressure of 450 MPa was applied.

Fig. 4 shows the isothermal sintering behavior at 1050 and 1100°C, respectively, of Y–TZP nanosized compacts obtained by a superhigh pressure. Even at a sintering temperature as low as 1000°C, which is only 2/3°C of the sintering temperature (about 1450°C for full densification) for 3 mol% Y_2O_3–ZrO_2 commercial powder (compacted with the CIP of 450 MPa), a high relative density of 96% could be reached.

All the results above show that the sintering temperature of Y–TZP green compact formed by applying a superhigh pressure can be largely decreased. This phenomenon can be explained by two reasons. First, the number of contact points between particles (per unit volume) increased as the relative density of green compact increased. This increase of contact points would translate to a greater number of matter transport paths and thus the densification will be faster. For example, the green density of the powders after a cold isostatic compacting at 450 MPa was about 48%. If the size difference of the particles is ignored, the green compact could be approximately considered as a kind of simple cubic structure, in which each particle has six nearest neighbors. Similarly, the green compact with the relative density of about 60% obtained by a superhigh pressure compaction could be a kind of structure of half simple cubic and half close-packed cubic. With the number of matter transport paths of (6+12)/2=9, 50% more paths could be obtained than that by the cold isostatic pressure.[10] Second, many experiments of the cold isostatic press show that the pore radius will decrease as the applied pressure increase. It is generally accepted that the densification of ceramics during pressureless sintering occurs by diffusion,[1] and the instantaneous driving force for diffusion is assumed to be inversely proportional to the pore's radius of curvature. The driving force σ for sintering is often written as

$$\sigma = \frac{A\gamma}{r} \tag{1}$$

where A is a constant, γ is the surface tension associated with the pore/solid interface and r is the pore radius (inverse of pore curvature). The densification then occurs more quickly for pores with tighter curvatures: such pores have a higher vacancy concentration near the pore surface. Fig. 5 shows the pore size distribution curves determined from gas adsorption measurements. The average pore diameter decreased from 5.3 to 3.7 nm when the applied pressure increased form 450 MPa to 3 GPa. From Eq. (1), it could be calculated that the σ value increased about 43% accordingly when other factors kept unchanging. Based on this discussion, it could be concluded reasonably that the decreasing of sintering temperature of the Y–TZP ceramics compacted by a superhigh pressure was due to the increasing of the green density and the decreasing of the pore size.

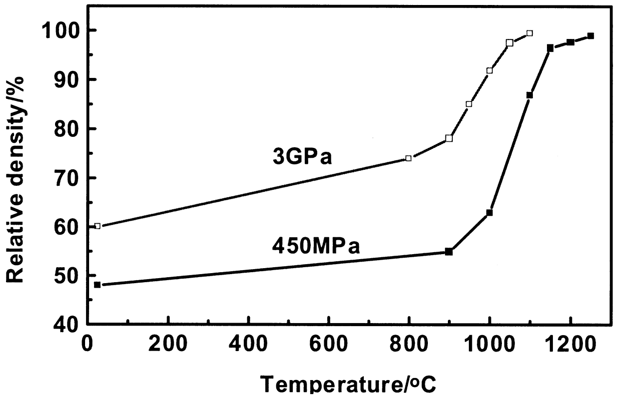

Fig. 3. Relative density vs sintering temperature for Y–TZP ceramics by compactions at 450 MPa and 3 GPa, respectively.

The grain growth was restrained effectively because of the low sintering temperature. Fig. 6 shows the TEM

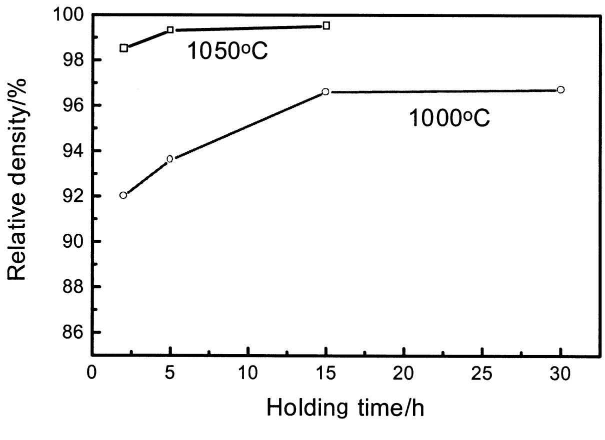

Fig. 4. Isothermal sintering behavior of Y–TZP nanosized compacts obtained under a superhigh pressure.

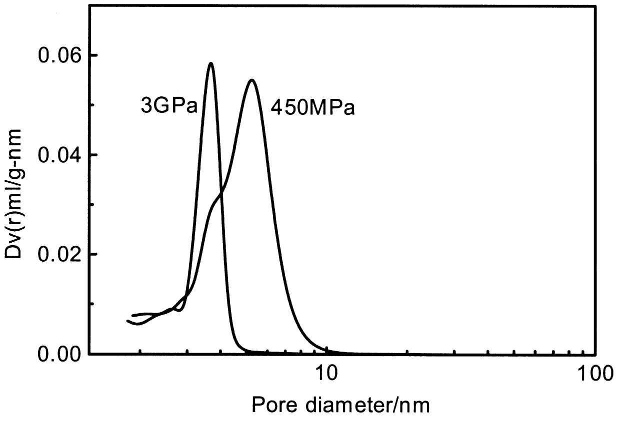

Fig. 5. Pore size distribution curves determined from gas adsorption measurements.

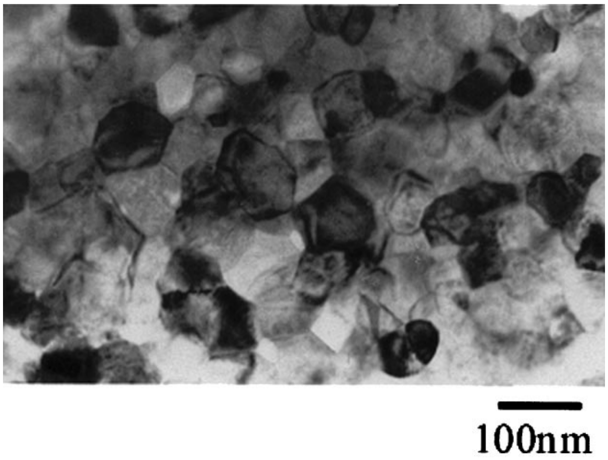

Fig. 6. TEM micrograph of nano Y–TZP ceramics sintered at 1050°C for 5 h.

micrograph of nano Y–TZP ceramics sintered at 1050°C for 5 h. Analyzed by the lineal intercept technique using $D=1.56L$ (L is the average lineal intercept), the grain size was only about 80 nm.

4. Conclusion

Green compacts with a relative density of about 60% could be obtained by applying a superhigh pressure of about 3 GPa, which was 12% higher than that by a normal cold isostatic pressure of 450 MPa. The obvious advantage of the relative density increasing of the green compact is that the sintering temperature decreased to as low as 1050°C. The reason of the good sintering behavior is believed to be both the increases in contact points between the particles and the decreases in pore size. Nano Y–TZP ceramics with grain size of about 80 nm could be obtained when sintered at 1050°C for 5 h.

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