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Two-step sintering of fine alumina–zirconia ceramics

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Abstract

This work investigates the feasibility to the fabrication of high density of fine alumina–5 wt.% zirconia ceramics by two-step sintering process. First step is carried out by constant-heating-rate (CHR) sintering in order to obtain an initial high density and a second step is held at a lower temperature by isothermal sintering aiming to increase the density without obvious grain growth. Experiments are conducted to determine the appropriate temperatures for each step. The temperature range between 1400 and 1450 °C is effective for the first step sintering (T_1) due to its highest densification rate. The isothermal sintering is then carried out at 1350–1400 °C (T_2) for various hours in order to avoid the surface diffusion and improve the density at the same time. The content of zirconia provides a pinning effect to the grain growth of alumina. A high ceramic density over 99% with small alumina size controlled in submicron level (0.62–0.88 μm) is achieved.

Keywords: A. Grain growth; A. Sintering; B. Inclusions; D. Alumina

1. Introduction

Since reducing the grain size in the alumina ceramics improves not only their mechanical properties, such as hardness [1–3], strength [4–7], wear resistance [8,9] and toughness [10], but also the transmittance of visible light [7,11–13]. Substantial research has been done on reducing grain size to below 1 μm aiming to pursue these favorable properties. However, most of the efforts are undergone by using a simultaneous pressure application during sintering, such as hot pressing sintering [2,14], hot isostatic pressing sintering [7,11,12] or spark plasma sintering [13,15]. In recent years, Chen and Wang [16,17] has developed an effective method for the sintering of Y_2O_3, called two-step sintering, designed to heat the sample to a high temperature T_1, and rapid cool down to a lower temperature T_2 for a long period. By this method, the grain boundary diffusion of the specimen is maintained but the grain boundary migration could be frozen under pressureless conditions. Therefore, the grain growth at the final sintering stage is suppressed successfully to yield Y_2O_3 ceramics with nano-sized grains. This method has been also applied in various materials, such as $BaTiO_3$ [18,19], Ni–Cu–Zn ferrite [18], ZnO [20], ZrO_2 [21,22], Al_2O_3 [23] and SiC [24]. According to the reported works, the attention has been focused on the choice of the sintering temperature T_1 and T_2, and the grain growth behavior during the second step of sintering [22,23].

This study presents a preparation of high-density alumina–5 wt.% zirconia ceramics with submicrometer grains via two-step sintering. Preliminary investigations on the sintered density, grain size, and pore size evolutions during constant-heating-rate (CHR) and isothermal sintering are carried out in order to determine the appropriate heating temperatures T_1 and T_2. Thereafter, the suggesting temperatures T_1 and T_2 are applied in the present work, and the effects of the applied two-step sintering process on the structural properties of alumina ceramics are discussed. On the other hand, the role of zirconia played on the choice of the heating temperature and the microstructure during the two-step sintering is also discussed.

2. Experimental procedures

2.1. Characterization of raw powder and forming

The as-received α-alumina powder is used as starting material (APD-100, Forever Chemical Co., Taiwan), which had an average particle size of 150 nm and a specific surface area of 20 m^2/g. About 5 wt.% of zirconia is contained in the as-

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received alumina powder which is due to the debris of zirconia ball milling from the manufacturer. Powder is uniaxially pressed at 150 MPa to prepare green compacts with diameter of 11 mm and thickness of 2 mm. The relative density of the green body is 50%.

2.2. Preliminary sintering and two-step sintering

Two preliminary sintering tests are undergone to determine the heating parameters of two-step sintering. One test consisted a constant-heating-rate (CHR) sintering which is used to determine the heating temperature (T_1) of the first step sintering. In this test, the sample is heated with 10 °C/min from room temperature to 1525 °C without any holding time and then cooled down to room temperature. The densification curve is simultaneously recorded by a dilatometer (DIL 402 C, Netzsch Instruments Inc., Germany). The densification rate is obtained by differentiating the measured linear shrinkage data. Another test is carried out by an isothermal sintering associated with the second sintering step in the range of 1250–1450 °C with heating rate of 10 °C/min for 0–8 h in a box furnace. Suitable temperatures are determined according to these preliminary tests and are employed in the following two-step sintering.

For two-step sintering, samples are sintered in a furnace with heating rate of 10 °C/min to the desired temperature (T_1), and then rapidly down to T_2 with cooling rate of 30 °C/min. In this work, the temperature T_1 and T_2 are varied at the range of 1400–1450 °C and 1300–1400 °C, respectively, according to the preliminary tests mentioned above. The isothermal holding time is set to be shorter than 24 h because the sintering is considered to be failed if the samples are not fully dense after this long period of sintering.

2.3. Characterization of sintered bulk

The pore size and distribution of some partial sintered bulks are measured using a mercury porosimeter (PoreMaster, Quantachrome Instruments, USA). The densities of the sintered bulks are determined using Archimedes' method with deionized water as the immersion medium. The microstructure is observed by SEM (S-4200, Hitachi Ltd., Japan) of the thermal etched surface, and at least 300 grains are examined to calculate the mean grain size of alumina using an image analyzer (LUCIA V4.81, Laboratory Imaging, Czech.).

3. Results and discussion

3.1. Isothermal sintering

The isothermal densification curves and grain growth evolutions for alumina compacts at various temperatures are shown in Figs. 1 and 2, respectively. The specimens begin to show an evident densification at temperatures higher than 1350 °C and exhibit a density of 98.5% after sintering at 1450 °C for 4 h as presented in Fig. 1. During the isothermal period, grain size varied linearly with sintering time (see Fig. 2), and the grain growth rates (given by the slope of the fitting line) are 0.06, 0.10, 0.19 μm/h for 1350, 1400 and 1450 °C, respectively. The rapid growth rate at the high temperature of 1450 °C produced grains of size larger than 1 μm after holding for 4 h. It is also shown Fig. 2 that the grain size has been grown to larger than 0.8 μm after heating over 1500 °C/0 h indicating a rapid grain growth may generate if holding at such high temperature for a longer time. Therefore, an isothermal sintering has to be done at lower than 1500 °C in order to keep the grain size under micrometer level.

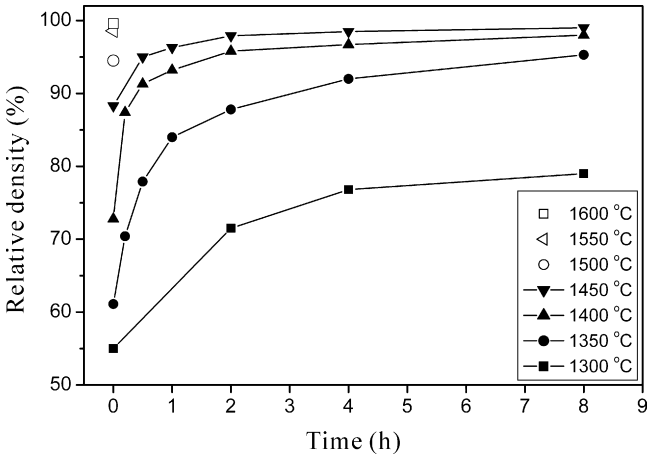

Fig. 1. Relative density for alumina specimens as function of sintering time at various temperatures.

3.2. Criterion for determining sintering temperature

According to Chen and Wang [16,17], the success of two-step sintering strongly depends on the choices of temperatures T_1 and T_2. In their experiment, a sample is sintered to the higher temperature T_1 to yield a density higher than 75%, corresponding to a state in which all pores in the sample are unstable and shrinkable. However, other authors have claimed that T_1 should be higher to yield a sintered density of around

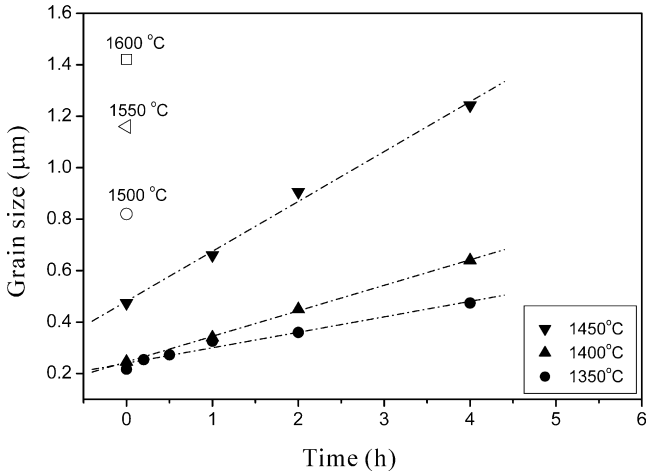

Fig. 2. Grain size of alumina specimens against sintering time at various temperatures.

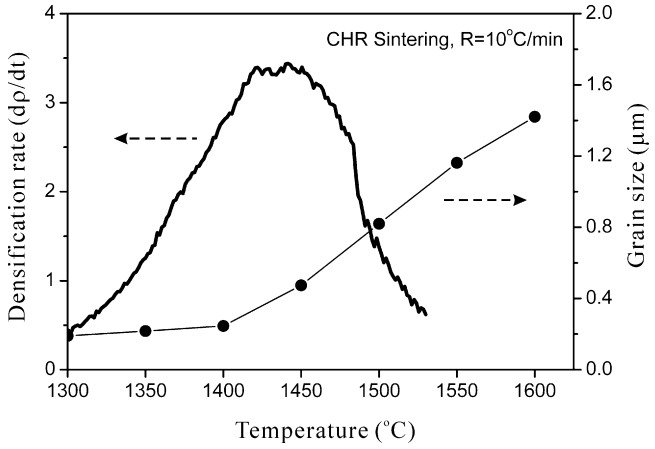

Fig. 3. Variation of densification rate and grain size for constant-heating-rate (CHR) sintering.

92%, at which the pores transition from open to closed status and the grain growth may be triggered [19,23].

In this study, T_1 is determined according to the evolution of densification rate ($d\rho/dt$) and grain growth during CHR sintering as shown in Fig. 3, in which the former is performed by a DIL experiment up to the highest temperature of the instrument limit, i.e. 1525 °C, and the later by a box furnace with a higher temperature up to 1600 °C. The result reveals that the densification rate increases with the sintering temperature to a plateau in the range 1400–1450 °C and then decreases rapidly from 1450 to 1525 °C. Based on Hansen et al.'s sintering model [25], the exhausting of densification rate is associated with the final sintering stage or the coarsening of the grain size. In this case, an obvious grain growth is observed when the sintering temperature is high than 1400 °C corresponding to the decrease of densification rate. It is known that the grain growth increases the diffusion distance and makes the sintering become difficult. Since the state of the specimen after the first step sintering critically affects the subsequent second step, the grain growth resulted from over-heating must be cautiously avoided. Accordingly, the appropriate temperature T_1 is set at the range of 1400–1450 °C where the densification rate shows a highest value throughout CHR sintering, and the corresponding relative density is from 72 to 88%.

Regarding to the determination of temperature T_2 for the second step sintering, previous research [16] has reported that it should be restricted within a range, called the ''kinetic window'', where the grain boundary or the volume diffusion operates while the grain boundary motion is frozen. It is worthy

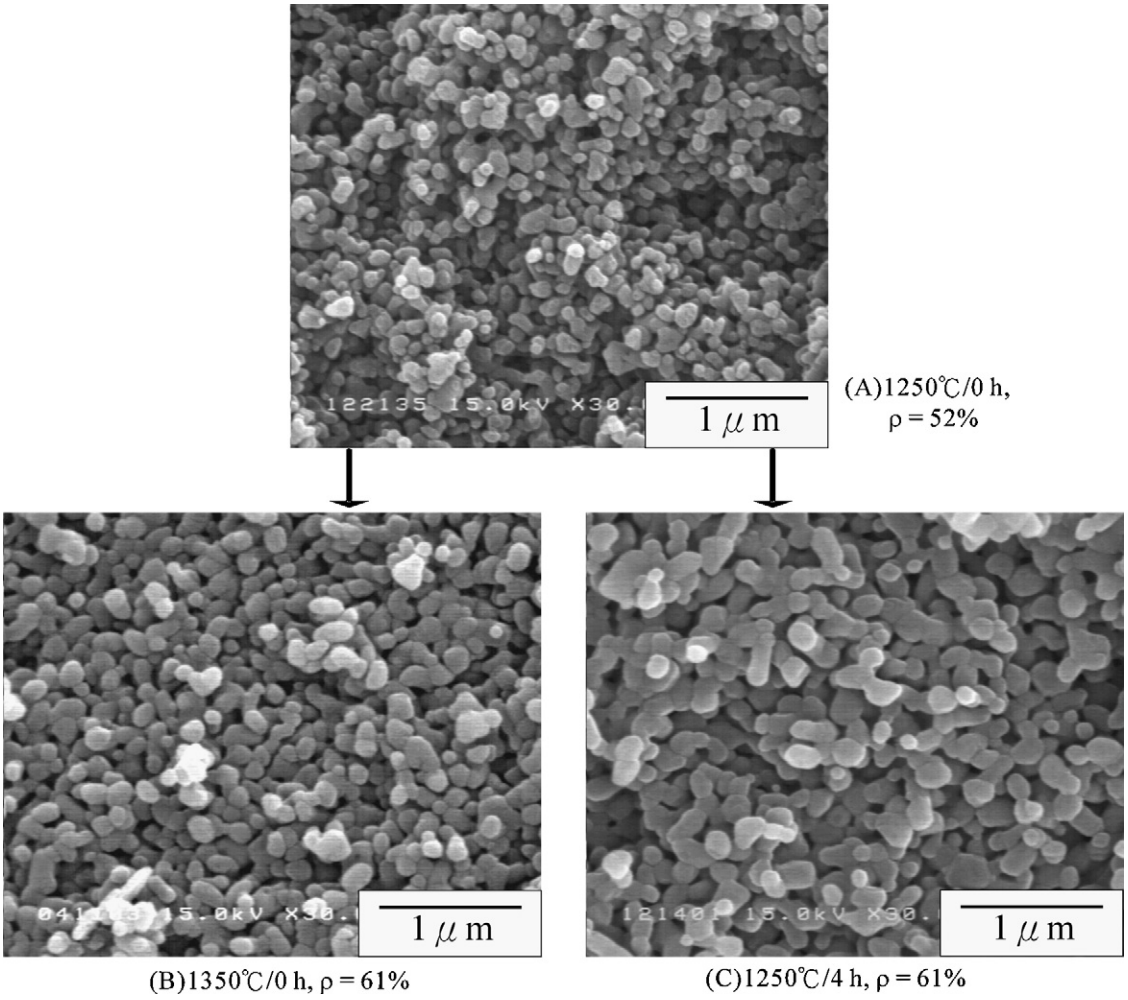

Fig. 4. SEM micrographs of specimens sintered at (A) 1250 °C/0 h, (B) 1350 °C/0 h and (C) 1250 °C/4 h. The sintered density is given at each micrographs.

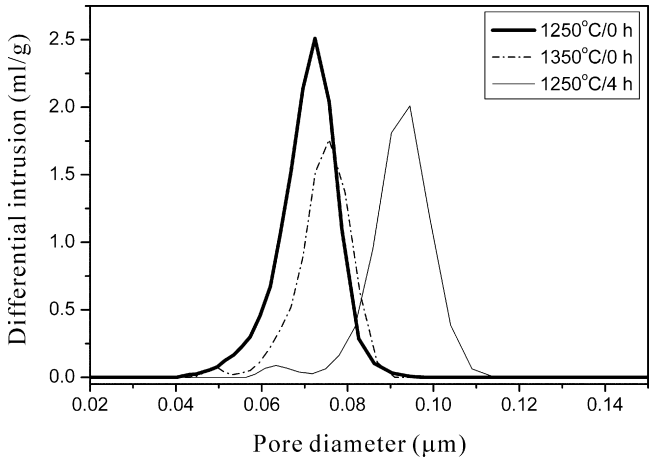

Fig. 5. Pore size distributions of specimens sintered under various conditions.

to remark that the choice of temperature T_2 is very important because the grain growth may be generated when the setting T_2 is too high; in contrary the densification is exhausted due to the suppression of atomic diffusion and results in an incomplete densification.

In this study, the upper bound of T_2 is set at 1400 °C, since this temperature is associated with a relatively slow rate of grain growth according to the previous experience of isothermal sintering. The lower bound of T_2 is determined according to the two microstructural evolutions observed at different sintering histories. At the initiation of CHR sintering from 1250 to 1350 °C, the bulk density increases rapidly from 52 to 61%, accompanies with a rounding of particles (see Figs. 4(A) and (B)). When isothermal sintering is performed at 1250 °C, the relative density remains 61% without improvement even though the holding time has increased to 4 h and a typical finger-like growth among alumina particles is taken place at the same time as shown in Fig. 4(C), meaning that the sintering mechanism via surface diffusion is carried out through the diffusion of atoms along the surface of adjacent particles without linear shrinkage. Furthermore, the pore size analysis presented in Fig. 5 reveals that the mean pore size coarsens from 73 to 95 nm upon heating at 1250 °C from 0 to 4 h due to the finger-like growth of alumina grains; nevertheless, the pore size increases only slightly to 76 nm (with a narrower distribution) after CHR sintering at 1350 °C. In fact, pore coarsening induced by surface diffusion or Ostwald ripening had been reported for alumina [26] and zirconia [27] when heated at low temperature around 800–900 °C for long period. The surface diffusion is still observed at temperature as high as 1250 °C for this study is due to the effect of zirconia that will be discussed later. Since surface diffusion is recognized to be unfavorable for the densification, the temperature T_2 for second sintering step is set in the range 1350–1400 °C in order to avoid the surface diffusion and the rapid grain growth.

3.3. Microstructural evolution in two-step sintering

Based on the preliminary sintering tests mentioned in the previous section, two-step sintering experiments are performed by CHR sintering to T_1 and isothermal sintering at T_2 for various holding time. The resulting density and grain size are summarized in Table 1. Various T_1 at 1400, 1425 and 1450 °C are conducted for T_2 at 1350 °C to examine the influence of T_1 on the sequent densification. The results shown in Table 1 indicate that the samples with lower T_1 always present a lower sintering density regardless the holding time in the second step. It is confirmed that setting T_1 at 1450 °C is the best choice that allows saving the holding time for the second step to achieve the full density.

Table 1
Sintered densities and grain sizes of alumina specimens under various heating parameters of two-step sintering

T_1 (°C)	T_2 (°C)	Holding time (h)	Relative density (%)	Grain size (μm)
1400	1350	4	92.1	0.38
		8	95.0	0.44
		12	96.6	0.49
1425	1350	4	93.2	0.42
		8	96.4	0.48
		12	98.0	0.53
1450	1350	4	94.0	0.49
		8	97.5	0.55
		12	99.2	0.62
1450	1400	4	97.3	0.69
		8	99.4	0.88
1450	1300	24	95.0	0.50

Fig. 6 plots the grain size–density curves of CHR sintering to 1600 °C and the cases of two two-step sintering. A relative density of >99% is achieved and the grain size increases rapidly to 1.42 μm as the sample is CHR sintered to 1600 °C. However, two-step sintering, with T_1 = 1450 °C and T_2 = 1400 °C for 8 h, reveals that grain growth is suppressed and the grains size can be controlled below 0.88 μm. As T_2 is down to 1350 °C (T_1 = 1450 °C), the grain size–density curve exhibits a much flatter slope and the sample is fully dense

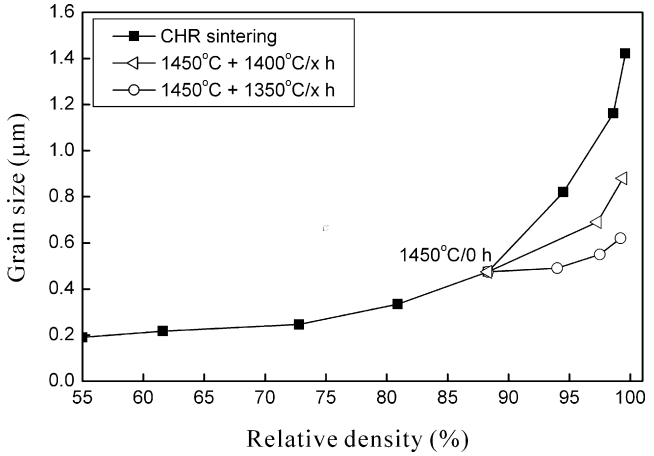

Fig. 6. Grain size vs. relative density of alumina specimens sintered with CHR and two-step sintering.

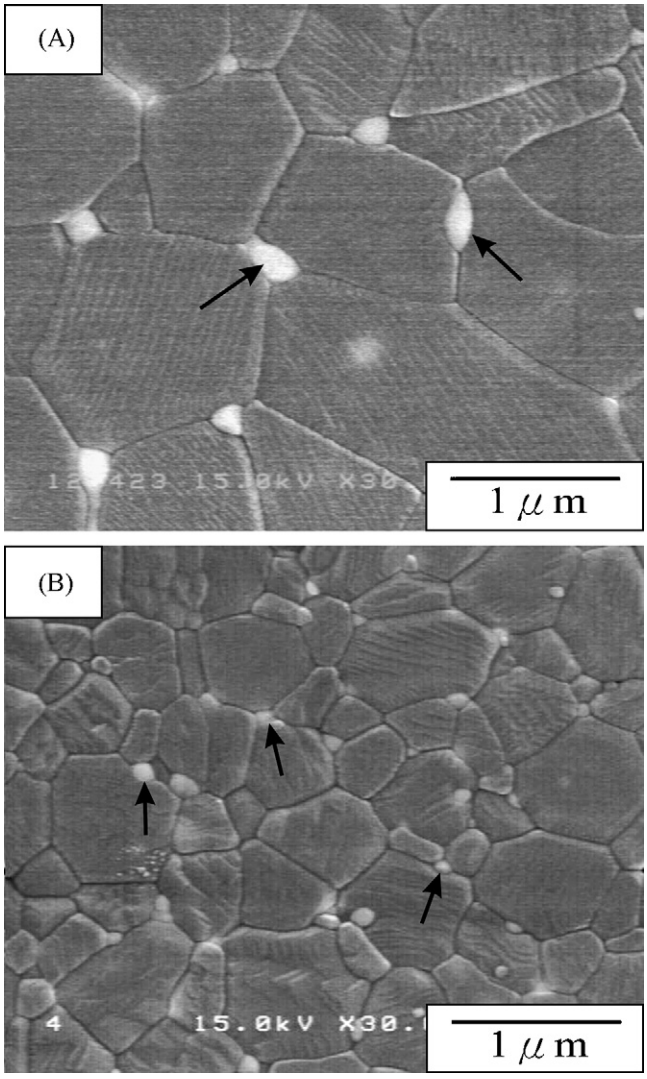

Fig. 7. Microstructures of full dense alumina prepared by (A) CHR sintering (1600 °C/0 h) and (B) two-step sintering (T_1 = 1450 °C, T_2 = 1350 °C/12 h). The bright grains indicated by arrows are the second phase zirconia.

within 12 h with grain size of 0.62 μm. Fig. 7 shows the microstructure of the bulks with CHR and two-step sintering, respectively. It is obvious that the grain size after CHR sintering is much larger than that heated by two-step sintering. Small zirconia grains are found at the grain boundaries or triple junctions of alumina grains. It shows that the growth ratio, i.e. final grain size/initial particle size (150 nm), can be reduced effectively from 9.5 to 4.1 after applying two-step sintering with the appropriate temperatures. On the other hand, under another experiment used T_2 of 1300 °C (T_1 = 1450 °C), revealing that even when the holding time is extended to 24 h, the sintered density reaches only 95% (the last row in Table 1). It has been discussed in the previous section that a surface diffusion occurs at 1250 °C which is disadvantageous for the densification. The low density by two-step sintering with T_1 = 1450 °C and T_2 = 1300 °C is possibly due to such surface diffusion which may also occur at 1300 °C and as consequence hinders the densification.

3.4. Effect of zirconia

Noteworthily, the existence of zirconia plays a critical role on the determination of T_1 and T_2 as well as the microstructure evolution. For pure alumina powder with a similar particle size of 0.15–0.20 μm, Bodišová et al. [23] has proposed that the optimal temperature T_1 is ranged within 1400–1450 °C and T_2 is around 1150 °C. The relatively high temperature T_2 used in this study is due to the effect of the zirconia, which has been demonstrated to increase the activation energy of densification of alumina [28,29]. It consists with the present observation that the surface diffusion is occurred at a temperature as high as 1250 °C. Besides, the influence of zirconia on microstructure evolution is noted through observing the grain growth behavior during the second step sintering. For pure alumina, grain growth could not be fully suppressed but still exhibits a little increase from 0.38 to 0.90 μm under a low T_2 of 1150 °C [23]. The cause is related to the inhomogeneous microstructure induced by uniaxial pressing [23] and provokes a differential sintering. For the alumina–5 wt.% zirconia powder compacted by the same forming technique, a smaller grain growth from 0.47 to 0.62 μm is presented, even though under a higher T_2 (1350 °C). The inhibitive trend is due to the pinning effect which is associated with the locations of small zirconia (∼100 nm) at grain boundaries or triple junctions of alumina (see Fig. 7(B)). Accordingly to the size and quantitative contents of zirconia, the coordination number for each alumina grain can be evaluated to be about 8, meaning that there is a strong pinning force act on the grain boundaries during the long isothermal period at the second step sintering. Conclusively, the function of zirconia induces a shift of the ''kinetic window'' to higher temperature and modifies the relation between grain size and density in comparison with the pure alumina ceramics.

4. Conclusions

Based on the experimental results, the following conclusions are drawn regarding the feasibility of the two-step sintering for fine alumina–5 wt.% zirconia powder.

(1) Temperature T_1 for the first step of sintering should be set at 1450 °C, corresponding to an optimal densification rate during constant-heating-rate sintering.
(2) For the choice of T_2, the effect of surface diffusion has to be taken into account. In the present study, the finger-like growth of particles induced by surface diffusion is observed after isothermal sintering at 1250 °C. A suitable range of T_2 is suggested to be around 1350–1400 °C, in which a densification is undergone without evident effect of surface diffusion.
(3) Fine zirconia grains in the two-step sintering sample induce a pinning effect on grain boundary migration of alumina. Thus, the degree of the grain growth during the second step sintering is effectively reduced as comparing with ultra-pure alumina powder.
(4) A high ceramic density over 99% with small alumina size controlled in submicron level (0.62–0.88 μm) is achieved after applying the two-step sintering. A comparison with

constant-heating-rate sintering shows that the growth ratio (final grain size/initial particle size) can be reduced from 9.5 to 4.1.

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