Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 37 (2011) 1973–1977
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Fabrication of ultrafine-grained alumina ceramics by two different fast sintering methods

Fancheng Meng [a], Fan Zhang [b], Weijiu Huang [a,*], Youli Yang [a], Minna Guo [a], Xiaojuan Jiang [a], Zhongqing Tian [a]

[a] Department of Materials, Chongqing University of Technology, Chongqing, 400050, China
[b] State Key Lab of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, China

Received 6 November 2010; received in revised form 16 November 2010; accepted 18 February 2011
Available online 29 March 2011

Abstract

The preparation of ultrafine-grained alumina ceramics by the fast sintering technique Self-propagating High-temperature Synthesis plus Quick Pressing (SHS-QP) method and spark plasma sintering (SPS) technique was reported. The effects of different heating rates (SHS-QP-1600 °C/min, SPS-200 °C/min) on the preparation of ultrafine structure were compared. The densification and grain growth as a function of sintering time and temperature were discussed. Within a short sintering time (<3 min), the full-dense alumina with ultrafine-grained structure was obtained by SHS-QP at 1550 °C under 100 MPa. By SPS, the sintering temperature was lower (1200 °C) than that of SHS-QP. The differences in densification parameters were explained by analyzing the thermodynamics of sintering process.

Keywords: Alumina; Fast sintering; Ultrafine-grained structure; Densification

1. Introduction

Dense ceramics with ultrafine-grained structure have attracted increasing attention, because of their unusual mechanical properties, high-temperature or optical properties [1–3]. However, to obtain full dense ceramics, while preserving their nanostructure character is still a challenging task. This is mainly due to the inevitable grain growth during the final stage of sintering. In addition, the relatively slow heating rate used in conventional sintering allow long heating durations up to the sintering temperature, during which the nanoparticles may also coarsen [4,5]. To overcome the problem of grain growth, unconventional sintering and densification methods have been proposed. Fast sintering technique is regarded as a promising method to limit grain growth because of short sintering duration [5]. The significant difference between the conventional sintering and fast sintering is the heating rate. Spark plasma sintering (SPS) and Self-propagating High-temperature Synthesis plus Quick Pressing (SHS-QP) method are among such rapid sintering techniques. The SPS process is similar to conventional hot pressing, in that the precursors are loaded in a die and a uniaxial pressure is applied, but the heating rate in the SPS process is high (up to 600 °C/min). SHS/QP is a new fast fabrication technique for preparing nano-grained materials [6,7]. The heat generated by a combustion reaction or self-propagating high-temperature synthesis (SHS) is applied to act as a high-temperature source, which is also called an ''SHS furnace''. A large mechanical pressure is applied when the sintering temperature reach the maximum. Compared with other fast fabrication techniques, this method has higher heating rate (up to 2300 °C/min) and shorter densification time [6–8].

In our previous study, we reported the feasibility of preparing dense nanostructured alumina ceramic with high heating rate (1600 °C/min) by SHS-QP method [6,7]. However, the relative density of sintered Al_2O_3 with ultrafine-grained structure was only 98% [6]. This work is aimed to determine the optimum processing parameters for making full-dense alumina ceramic with ultrafine-grained structure by SHS-QP method. The other purpose is to compare the effects of different heating

* Corresponding author. Tel.: +86 23 62408527.
E-mail address: huangweijiu@cqut.edu.cn (W. Huang).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.02.015

rates (between SHS-QP method and SPS technique) on densification and coarsening in the preparation of ultrafine-grained alumina.

2. Experimental procedure

A fine powder with an average particle size of 200 nm (Sumitomo Chemical Co., Tokyo, Japan) was used in this experiment. Three grams of powder were uniaxially pressed in a steel die into disks with a diameter of 2 cm and a height of 0.5 cm. Then, the disks were subjected to cold isostatic pressing (CIP) at 200 MPa. An SHS reaction with high exothermic heat was chosen [7]. The reaction is shown as follows: $3Cr_2O_3 + 6Al + 4C \rightarrow 2Cr_3C_2 + 3Al_2O_3$. The Cr_2O_3, Al, and C powders were mixed in a molar ratio of 3:6:4 according to the above reaction. Series of sintered samples were prepared by using the different weight SHS powders. The weight of SHS powders was varied from 100 g to 400 g. With the variation of the SHS reactant mass, the sintering times were ranging from 1 min to 4 min. The different mass mixtures with CIP alumina body in the center were pressed into a cylindrical compact in different diameters and heights. The alumina body was covered by a thin sheet of graphite foil to separate the alumina and the reactants. XRD spectrum (not shown here) reveals that only alumina phase is found in the sintered specimen, suggesting that no impurity (or contamination) is introduced in the sintered alumina by use of chemical-furnace. Same experimental results were also found in our previous studies [6,7]. The combustion process was carried out in a homemade instrument and the details of the technique were given in Refs. [6,7]. The temperature of the alumina was measured using a WRe5/26-type thermocouple inserted in the center of the alumina. The measured maximum temperatures were maintained within 1660 ± 20 °C and had the same heating rate of 1600 °C/min. In the conventional sintering, the holding times were easily controlled at a certain temperature. However, this is more difficult for SHS because of the high reaction rates. For a concise illustration, holding times were selected to the duration of the temperature higher than 1550 °C [7]. The density range and microstructure variation were adjustable at 1550 °C using different sintering times. When the temperature reached the maximum (1550 °C), a quick hydraulic pressing (100 MPa) was applied on the sample and held constant until the ending of the sintering time. Then the pressure was released and the sample was allowed to cool naturally.

For comparison, SPS sintering of Al_2O_3 was also conducted in this work. The CIP compact was placed into a 2-cm diameter graphite die and sintered using a SPS system (SPS-1050, Sumitomo Coal Mining Co. Ltd.) by heating to the sintering temperature at a heating rate of 200 °C/min under a pressure of 100 MPa; the pressure also held constant until the ending of the sintering time. The density was measured by Archimedes method. The microstructure was investigated via field-emission scanning electron microscope (SEM, FEI-Sirion200, Amsterdam, and the Netherlands) after being polished, thermally etched, and carbon coated. Grain size analysis was performed from the digitized SEM photographs using image analysis software (Nikon Image, Nikon Corporation, Japan).

3. Results and discussions

3.1. SHS/QP results

The average grain size and relative density as a function of sintering time at 1550 °C by SHS/QP are displayed in Fig. 1. The relative density and grain size both increased with increasing time. For densification, when the sintering time increased from 1 to 3 min, that plot exhibited a faster densification. The relative density increased from 95% to 99%. With a further increase in sintering time, it showed a small increase in density. Compared with the variation of density, the grain growth was rather limited at <2.5 min and tended to follow a moderate trend. As the sintering time increased beyond 3 min, the grain growth increased dramatically. At a holding time of 4 min, the size was increased to about 2 μm.

The microstructural evolutions of SHS-QP samples are illustrated in Fig. 2. The SEM image (Fig. 2(a) and (b)) shows that the specimens (holding time 1 and 2.5 min) consists of grains of approximately the same size as the corresponding initial powders. The grain-grown rate was very low at the time < 2.5 min and the ultrafine microstructure were clearly observed. As shown in Fig. 2(c), whereas the time >3 min, the grain grown became more rapid. Some closed pores were formed and entrapped in Al_2O_3 grains. Long sintering times resulted in a larger grain size in the sample.

3.2. SPS results

Fig. 3 shows the effect of sintering temperature on density and grain size of SPS samples. Sintering temperatures were increased from 1100 to 1300 °C with an interval of 50 °C and a holding time of 2 min. As shown in this figure, the densification rate increased dramatically when the temperatures went up to 1200 °C. When the sintering temperature was 1100 °C, the

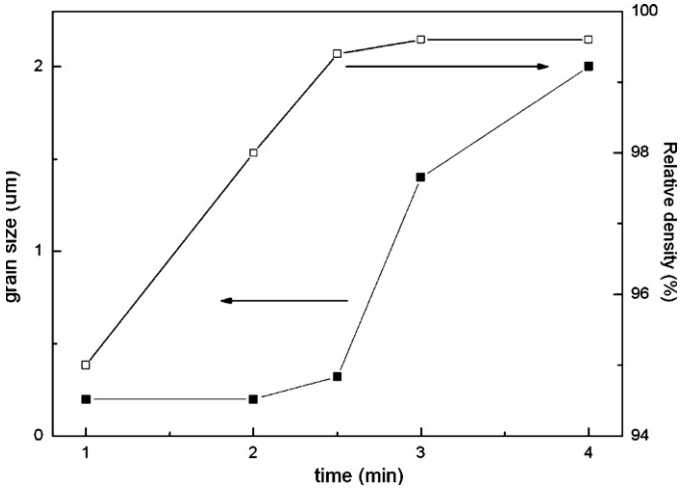

Fig. 1. Grain size and bulk density vs. sintering time of SHS-QP samples at 1550 °C under 100 MPa.

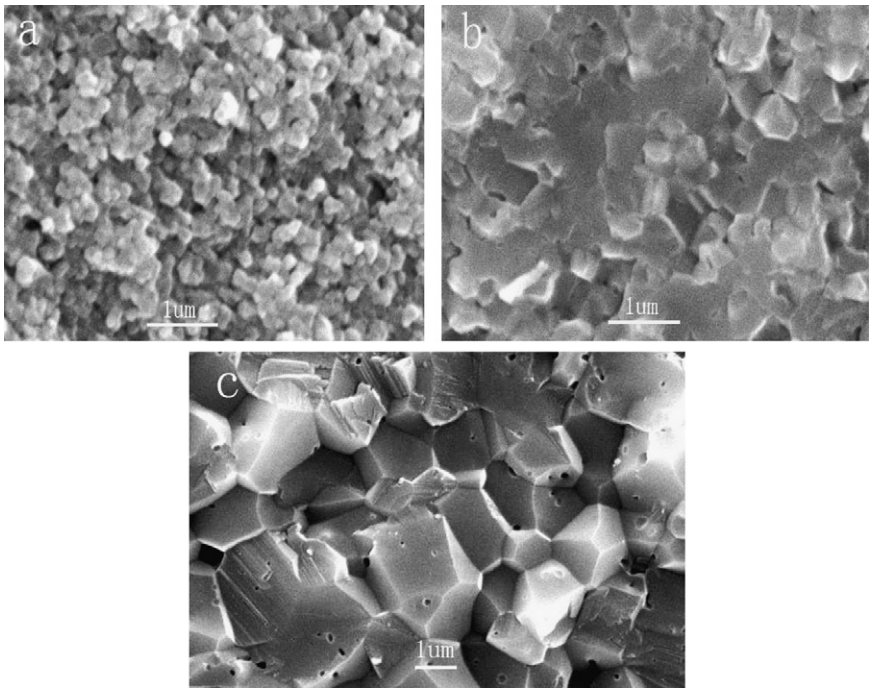

Fig. 2. SEM micrographs of the SHS-QP specimens at different sintering time (applied pressure: 100 MPa, heating rate: 1600 °C/min, sintering temperature: 1550 °C) (a) 1 min; (b) 2.5 min; (c) 4 min.

relative density was about 90%. When the sintering temperature increased from 1150 °C to 1300 °C, the relative density increased from 95% to 99.8%. Above 1200 °C, the change of the relative density was not obvious. For grain growth, as the sintering temperature increased from 1100 °C to 1200 °C, no obvious increase in size was seen. With subsequent increase in sintering temperature, the grain size increased in an apparent linear fashion. At a sintering temperature of 1300 °C, the grain size was increased to about 1.5 μm.

The microstructure developments of SPS samples are illustrated in Fig. 4. The SEM image (Fig. 4(a)) shows that no obvious increase in size was seen. The microstructure was not dense and some isolated pores were found. The dense ultrafine-grained microstructure was clearly observed in Fig. 4(b). With the further increase of sintering temperature, the grain size increased greatly to 1.5 μm (Fig. 4(c)).

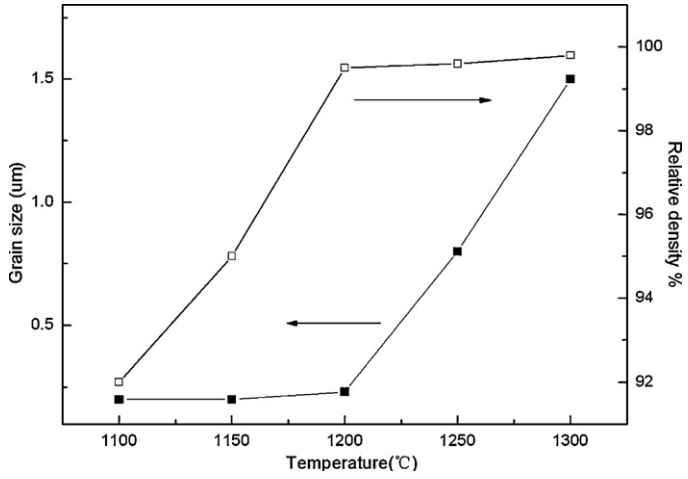

Fig. 3. Grain size and bulk density vs. sintering temperature of SPS samples with a holding time 2 min under 100 MPa.

The average grain size and relative density as a function of sintering time at 1200 °C by SPS are displayed in Fig. 5. The samples were sintered with different holding times from 1 min to 10 min. The densification plot showed that, after sintering at 1200 °C for 1 min, a low relative density of 97% was obtained. Fully densified samples were obtained with holding times of 2 min or longer. From this figure, it was also shown no significant grain growth occurred at whole sintering period, and the grain size of all sintered samples maintained at sub-micro scale. At a holding time of 10 min, the grain size was the largest and of about 0.6 μm.

Fig. 6 compares the microstructures of sintered specimens by two different fast processes (SHS-QP and SPS). SEM images showed that both the samples were dense and had ultrafine-grained structure. Image 6(a) revealed that the sample had an average grain size of about 300 nm and the distribution in grain sizes ranged from 150 to 600 nm. Image 6(b) shows that the average grain size of the sintered specimen was about 250 nm and the distribution in grain sizes ranged from 100 to 600 nm.

3.3. Discussions

From above experiment results, it can be concluded that both SHS-QP and SPS method could be used to prepare the full-dense alumina ceramics with ultrafine-grained microstructure, and the difference and similarity in densification parameters can be observed obviously. One similar is that the variation trends of density and grain size with holding time are same. At given temperatures, density and grain size increased with

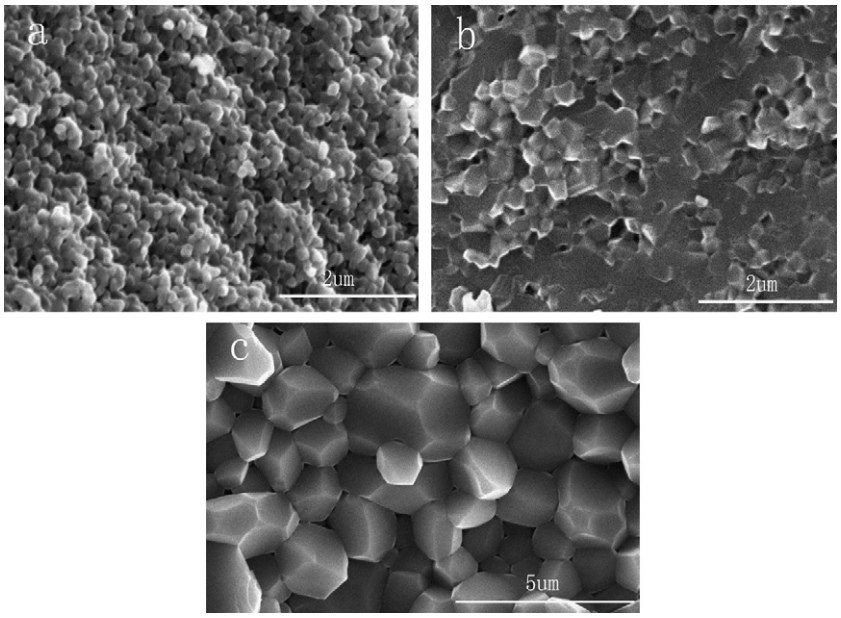

Fig. 4. SEM micrographs of the SPS specimens at different sintering temperature (applied pressure: 100 MPa, sintering time: 2 min, heating rate: 200 °C/min) (a) 1100 °C; (b) 1200 °C; (c) 1300 °C.

holding time in both processes. The other similar is that a shorter sintering time is the necessary condition for a limited grain growth. The main differences between SHS-QP and SPS are the sintering temperature (1550 °C and 1200 °C) and heating rate (1600 °C/min and 200 °C/min); temperature and heating rate have different impact on densification and grain growth.

Compared with SHS-QP, the densification temperature for SPS is lower (about 350 °C). In the densification process, the high temperature and pressure are all contributed to the densification. In the SPS technique, temperature is linked to DC current pulse intensity and die size. It is assumed that diffusion mechanisms are enhanced by current intensity. So the degree of densification at lower temperature is enhanced [4,5]. Temperature also plays a greater role in limiting grain growth. In SPS process, the grain size would growth beyond micro level at

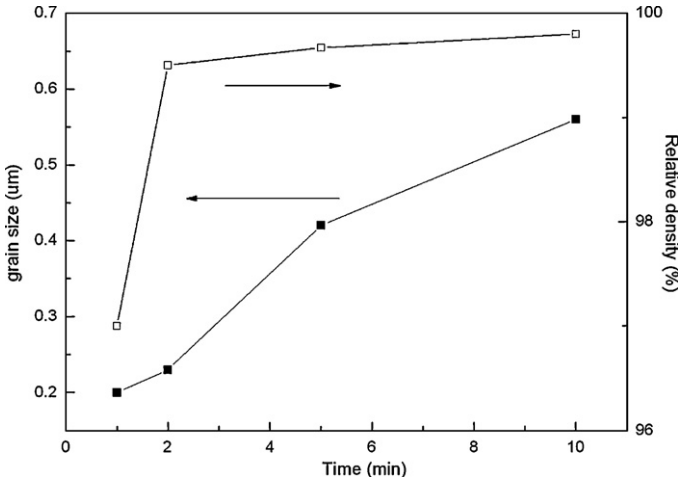

Fig. 5. Grain size and bulk density vs. sintering time of SPS samples sintering at 1200 °C under 100 MPa.

temperature above 1200 °C. It appeared that low temperature (1200 °C) and short time was the key to prepare ultra-grained structure. However, grain growth was found to be evitable when sintered at a high temperature (1550 °C) in SHS-QP process. The reason can be explained as follows. By considering the thermodynamics of the sintering process, traditionally, the isothermal rate of grain growth can be expressed by the phenomenological kinetic grain growth equation [9,10]:

$$G^n - G_0^n = k(T)t \tag{1}$$

where G and G_0 are the grain sizes at holding time t and $t = 0$, n and $k(T)$ are constants for a particular grain growth mechanism. Integrating grain grown law and the heating rate, Xu [9,10] gives the following Eq. (2):

$$G^n - G_0^n = \frac{k_0}{\alpha}\int_{T_0}^{T} \exp\left(\frac{-Q}{kT}\right)\mathrm{d}T \tag{2}$$

assuming that $k(T) = k_0 \exp(-Q/kT)$ and $T = T_0 + \alpha t$, where k_0 is a constant, Q is the activation energy for grain growth, and k is Bolzman's constant. G^n should be inversely proportional to the heating rate, α. When α is large enough, G will be nearly equal to G_0. This means that almost no grain growth will occur. Xu et al. had provided a conformation of this conclusion [10]; experiment results on sintering ZnO were reported by Xu that ultrahigh heating rates (500–4900 °C/min) could produce more uniform microstructures than slow heating rates. At the same time, high density can be achieved with almost complete suppression of grain growth. Our previous results [7] have also proved that the grain growth caused principally by surface diffusion could almost be avoided at fast heating rate. The sample quickly skips over a low-temperature regime (nondensifying mechanisms such as surface diffusion active) and proceeds directly to higher temperatures. Therefore, the grain

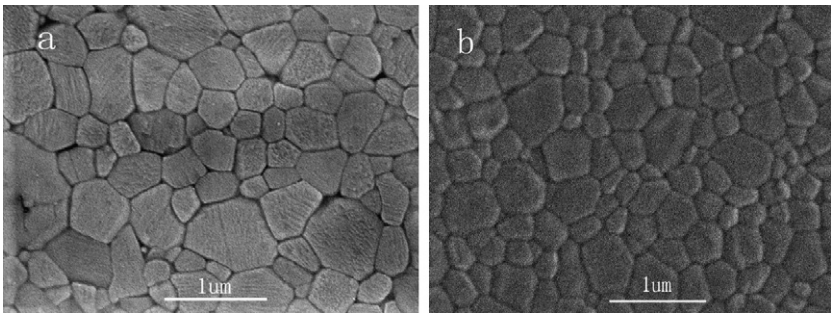

Fig. 6. The surface micrographs with different heating rates under the same pressure of 100 MPa (a) SHS-QP sintered at 1550 °C, 2.5 min and 1600 °C/min; (b) SPS sintered at 1200 °C, 2 min and 200 °C/min.

growths beginning at the initial and intermediate stages of sintering can be controllable. By using fast heating rate, significant control can be exerted over the mass transport mechanisms, and ultrafine microstructure could be obtained.

4. Conclusion

The Al_2O_3 powders with particle size 200 nm were sintered with the heating rate of 1600 °C/min and 200 °C/min by SHS-QP method and SPS technique, respectively. The densification and grain growth as a function of sintering time and temperature were discussed. The relative density and grain size of both specimens increased with increasing sintering time. Within a certain short sintering time and same applied pressure (100 MPa), full-dense alumina with ultrafine-grained structure could be obtained by SHS-QP at 1550 °C and SPS at 1200 °C. For SPS, low temperature and short time was the key to prepare ultrafine-grained structure. However, for SHS-QP, grain growth was found to be evitable when sintered at a high temperature (1550 °C) at higher heating rate.

Acknowledgements

This work was financially supported by National Natural Science Foundation of China (50975302), the Natural Science Foundation Project of CQ (CSTC2009BB4385) and Chongqing key Science Foundation of Chongqing Science and Technology Commission (CSTC, 2008BA4037).

References

[1] A. Krell, P. Blank, Grain size dependence of hardness in dense submicrometer alumina, J. Am. Ceram. Soc. 78 (4) (1995) 1118–1120.
[2] R. Riedel, H.J. Kleebe, H. Schnfelder, F. Aldinger, A covalent micro/nano-composite resistant to high-temperature oxidation, Nature 374 (1995) 526–528.
[3] R. Apetz, M.P.B. van Bruggen, Transparent alumina: a light-scattering model, J. Am. Ceram. Soc. 86 (3) (2003) 480–486.
[4] Z.A. Munir, U. Anselmi-Tamburini, M. Ohyanagi, The effect of electric field and pressure on the synthesis and consolidation of materials: a review of the spark plasma sintering method, J. Mater. Sci. 41 (2006) 763–777.
[5] U. Anselmi-Tamburini, J.E. Garay, Z.A. Munir, A. Tacca, F. Maglia, G. Spinolo, spark plasma sintering and characterization of bulk nanostructured fully stabilized zirconia. Part 1. Densification studies, J. Mater. Res. 19 (11) (2004) 3255–3262.
[6] F.C. Meng, Z.Y. Fu, J.Y. Zhang, H. Wang, W.M. Wang, Y.C. Wang, Q.J. Zhang, Rapid densification of nano-grained alumina by high temperature and pressure with a very high heating rate, J. Am. Ceram. Soc. 90 (4) (2007) 1262–1264.
[7] F.C. Meng, Z.Y. Fu, W.M. Wang, Q.J. Zhang, Microstructural evolution of nanocrystalline Al_2O_3 sintered at a high heating rate, Ceram. Int. 36 (2010) 555–559.
[8] F. Zhang, Z.Y. Fu, J.Y. Zhang, H. Wang, W.M. Wang, Ultra-fast densification of boron carbide ceramics under high heating rate and high pressure, Ceram. Int. 36 (2010) 1491–1494.
[9] F.F. Lange, B.J. Kellett, Thermodynamics of densification. II. Grain growth in porous compacts and relation to densification, J. Am. Ceram. Soc. 72 (5) (1989) 735–741.
[10] G.F. Xu, I.K. Lloyd, O.C. Wilson, Microwave sintering of ZnO at ultra high heating rates, J. Mater. Res. 16 (10) (2001) 2850–2858.