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Effect of characteristics of submicrometer powder on the sintering behaviors of Al_2O_3 ceramic

Qingbo Tian[a], Jinshan Dai[a], Zhijie Lv[a] and Tongguang Zhai[a,b,*]

[a]*School of Material Science and Engineering, Shandong Jianzhu University, Jinan 250101, P. R. China;*
[b]*Department of Chemical and Materials Engineering, University of Kentucky, Lexington KY,40508 USA*

The sintering behaviors of high purity Al_2O_3 ceramics prepared from a submicron-scale powder were investigated. The effects of ball milling on the evolution of alumina powders' compressibility, sinterability, grain growth and microstructure during sintering process were studied. It was observed that the relative density of the Al_2O_3 ceramics increased with increasing compaction pressure on the green compacts and the sintering temperature. However, the applied pressure had less influence on the relative density of ceramics sintered from green compact with narrower size distribution and finer powder. The fast grain growth of the Al_2O_3 ceramics occurred in different temperature ranges and was influenced by milling time and forming methods. The effect of milling on the microstructural evolution of alumina during sintering was also discussed.

Key words: Sintering, High purity alumina, Submicrometer powder, Microstructure.

Introduction

The alumina ceramics with a high density have been used in engineering applications in chemistry, biology, electronics, medical and material industries, etc., because of their unique combination of properties such as high hardness, corrosion resistance, wear resistance, good electrical resistivity and catalytic abilities, high strength, or optical performance [1-2]. Among these ceramics, the high purity α-Al_2O_3 ceramics possess the ability to present unique features/functions, which attract more attentions from the researchers and engineers in the ceramic field over the last decades [3-6].

However, it is difficult to sinter the pure Al_2O_3 ceramic with a high relative density and fine grains. A high sintering temperature is often adopted in its fabrication to enhance the density of the pure Al_2O_3 ceramics. In general, a sintering temperature over 1600 °C, even as high as 1800 °C, is needed to obtain the highly densified Al_2O_3 ceramics [7-9]. However, the use of such a high temperature can induce rapid grain growth, which in turn undermines the strength of the Al_2O_3 ceramic [3, 9, 10].

It was recognized that Al_2O_3 ceramic with fine powders could be readily fabricated by lower temperature sintering. It was also confirmed that the relative density of the sintered Al_2O_3 nanoceramics increased rapidly with decreasing the mean particle size below 15 nm [3]. According to Herring's scaling law [11], Al_2O_3 ceramic with fine grains could be formed at the sintering temperature of below 1000 °C if the size of powder particles was less than 20 nm in size on average. However, to our knowledge, the predicted low temperature sintering of alumina has not been achieved so far. The possible reason is likely to be that the Al_2O_3 with a fine powder is inclined to agglomerate, which deteriorates the compressibility and sinterability of the powder. Also, Krell et al proposed [12] that it was not the finest powder that yielded the ceramic with the smallest grains, because the interaction between nano-size particles could lead to agglomeration, thereby undermining the ceramic density more than could be offset by increased diffusion [13].

Despite of the argument, as discussed above, about the optimum power particle size for fabrication of fine grained Al_2O_3 ceramic, it is undoubtedly unanimous that high green density is one of the key factors to obtain the ceramics with a high density at a relatively low sintering temperature [3, 14-16]. It has been recognized that the variation of the relative density of the Al_2O_3 ceramics is in good agreement with the relative density of the green compacts [3].

In this paper, ball milling was employed to modify the submicron-sized Al_2O_3 powders. The effects of milling on dispersion of the powder and on sintering behaviors were studied. Meanwhile, the comparison in microstructure and relative density of the ceramics sintered in different processes were made.

Experimental

A high-purity α-Al_2O_3 powder (supplied by the Advanced Ceramic Center, Dalian Jiaotong University,

*Corresponding author:
Tel : +859-257 4958
Fax: +859-323 1929
E-mail: tzhai@engr.uky.edu

China) with Al_2O_3 > 99.995%; Si < 30 ppm, Mg < 10 ppm, Cu < 10 ppm, and Fe < 20 ppm, was used throughout the course of this investigation. The as-received powder had an average particle size of 0.35 mm. In order to reduce the tendency for agglomeration, alumina powders were dispersed in the deionized water after milling for various times at a speed of 150 rpm in a planetary ball mill (Nanda, QM-1SP, China) in a sealed air atmosphere. The weight ratio of ball-to-powder was 30 : 1. Then the milled powders were dried at 80 °C for 24 hrs and were uniaxially pressed up to 700 MPa into discs of 15 mm in diameter and ~ 5 mm in height. To compare the difference in densification and grain growth of the specimen between the different fabrication methods, several disk samples were made by cold isostatic pressing (CIP) in a DJY-HIP (Keqi, China) at 160 MPa for 5 min. All the green plates were covered with high purity alumina powders and sintered at temperatures between 1400-1650 °C for 2 hrs. Green density was calculated by geometric method and the sintered density was measured by the Archimedes method with distilled water as the fluid medium. The value of 3.98 $g \cdot cm^{-3}$ was used as the theoretical density. The microstructure was examined on the fractured surfaces by scanning electron microscopy (SEM: Quanta FEG 250, USA). The average grain size was estimated in the SEM images.

Results and Discussion

Fig. 1 shows the particle size distribution of the as-received powder and the powders milled for various times. The as-received powder had a broader particle size distribution (0.26 μm-4.03 μm) containing two types of particle size ranges, in which there was about 15.1 vol% powders with a diameter larger than 1.0 μm. Milling time showed a profound effect on the particle size distribution of powders. The particle size distribution became narrower and finer with increase in milling time. As milling time attained 20 hrs, the particle size distribution was between 0.05 μm and 1.24 μm, in which only 1.0 vol% powders with a diameter larger than 1.0 μm left. The agglomeration was partially removed by the ball milling method.

Fig. 2 shows the densification curves of the samples for non-milled and milled powders as the function of the sintering temperature (applied 600 MPa on the green powder and sintered for 2 hrs at various sintering temperatures). As observed, curves for each powder presented a similar trend, in which the relative density of the sintered Al_2O_3 ceramic monotonously rose with increasing of the sintering temperatures. In the case of the milled powders, sintering at 1400-1650 °C led to bulks having a density of between 88.7% and 93.7%. A relative density of 92.1% was already attained in the sample with upon reaching the temperature of 1550 °C.

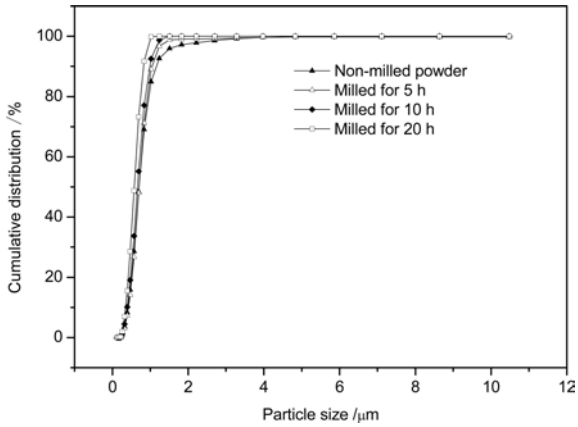

Fig. 1. Particle size cumulative distribution of powders as the function of milling times.

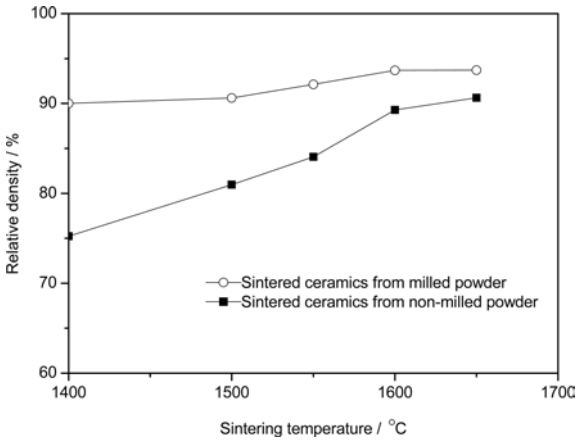

Fig. 2. Influences of sintering temperature on the relative density of Al_2O_3 ceramics.

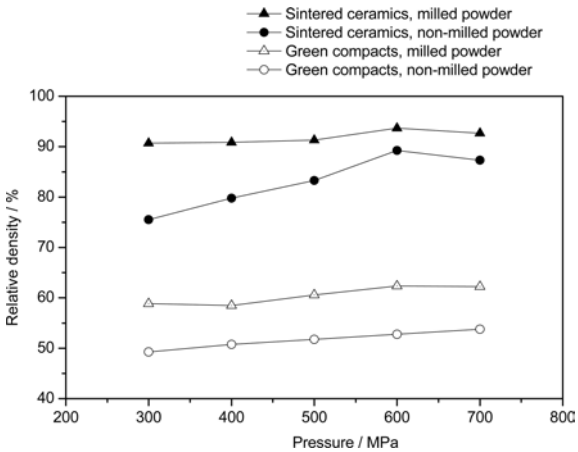

Fig. 3. Influences of applied pressure on the relative density of Al_2O_3 ceramics sintered for 2 h at 1600 °C.

While the bulks from the non-milled powders exhibited densities of about 73.2-90.6%, in which only limited densification of 84.1% had taken place at 1600 °C.

Fig. 3 shows the relative density of the green compacts and Al_2O_3 ceramics sintered at 1600 °C for 2 hrs as the function of the compaction pressures on the green compacts. It was observed that the obvious

effects of the milling on the compressibility of Al_2O_3 powder, owning to the breakage of agglomerates of Al_2O_3 powder[4]. Before milling, the relative green density of the powder compacted at 600 MPa reached ~ 52.8% while after milling the green density increased to 62.3%. Increase of the applied pressure from 300 MPa to 700 MPa led to 9.3% and 5.8% increase in the non-milled and milled density respectively.

The milling was also effective to the sintered ceramics. In the non-milled powder, the relative density of the Al_2O_3 ceramics increased rapidly with increasing compaction pressure. As the pressure increased to 700 MPa, the relative density reached 87.3%, which was 10.6% increase compare with that compacted at 300MPa. However, the final relative density of the sample sintered at 1600 °C was at best 89.2%. Whilst, in the milled powder, the relative density of the Al_2O_3 ceramics increased slowly from 90.6% to 92.7% with increasing compaction pressure at the same pressure range, in which the highest relative density of 93.7% was achieved in the ceramic also sintered at 1600 °C, indicating that the milling had a positive effect on the sintering of Al_2O_3 ceramics. It seemed that the pressure had less influence on the relative density in the milled powder. Upon increasing pressure gave rise to an only 3.3% increase in relative density. In fact, the homogeneity of the alumina particle distribution made easier the rearrangement of the particles as well as reducing the interspacing of the particles and increasing the number and area of particles contacts. In the milled powder, alumina particle distribution tended to come more homogeneous and finer with the milling time from the curve of the particle analysis (as seen in Fig.1). So, the particles were brought closer in distance, it caused a positive effect on the sintering, and accordingly brought the increase of relative density [17]. This was accordance to the Eskandari's results [4].

It was also seen that from Fig. 3, the relative densities showed a slight decrease after applying 700 MPa in either unmilled or milled powders, because of the release of residual stress caused by a directional force applied on the grain during the compaction process. Eskandari et al [4] reported that the critical applying pressure causing relative densities to decrease was 500 MPa. Here, we achieved a continuous increase with rise of applied pressure until 700 MPa by merely lengthening the dwell time of loading, and the relative density of 62.3% was obtained in the green compact at the pressure of 600 MPa. It was claimed that the holding time could relieve the lamination phenomenon brought about by elastic springback in the uniaxial dry pressing[18]. Therefore, the green densities of compacts were increased, so were those of the sintered ceramics.

Microstructure

The microstructure developments of the sintered alumina at different sintering temperatures are illustrated in Fig. 4 and Fig. 5, respectively. In the sample prepared from the non-milled alumina powder, the regular, polyhedral shape of the bulk ceramic was found in the SEM micrographs (Fig. 4(a)). The average grain size was about 0.3-0.5 μm in the sample sintered at 1400 °C, which had approximately the same size as the corresponding initial powders. It was also found that some larger grains were observed. The temperature had much effect on the grain size and grain shape. The grains had an obvious growth at the temperature of above 1500 °C (Fig. 4(b-f)). The average grain size in the sample sintered at 1650 °C was 1.5-2.0 μm, which was 4-5 times larger than the grain size at 1400 °C (Figs. 4(a) and 4(f)).

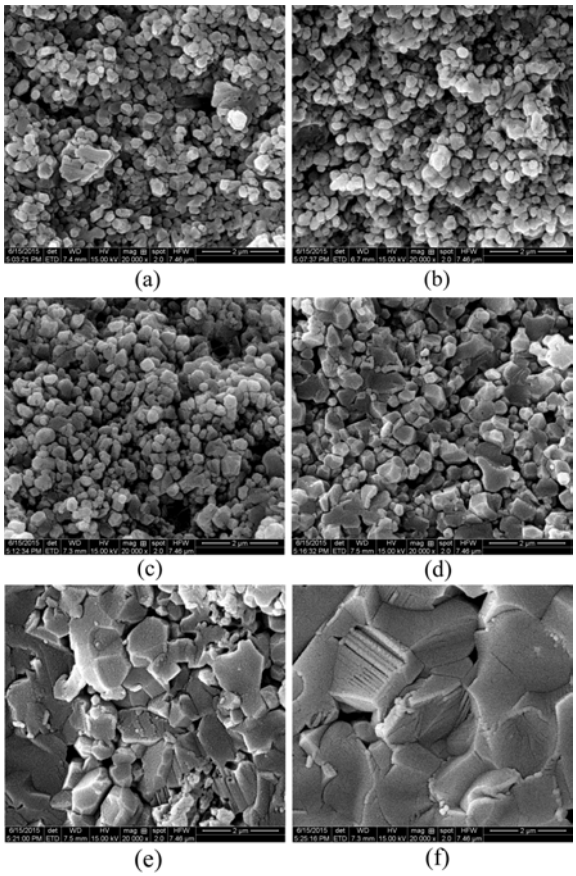

Fig. 4. SEM images of sintered ceramics prepared from non-milled powder at different temperatures: (a) 1400 °C, (b) 1450 °C, (c) 1500 °C, (d) 1550 °C, (e) 1600 °C and (f) 1650 °C.

In the sample compacted from the milled alumina powder, the grains with more homogeneous distribution and polyhedral morphology were observed, as was seen in Fig. 5. The particles were in the range of 0.2 μm-1.2 μm in the samples sintered at between 1400-1650 °C. A steep increase, as highlighted in Fig. 5, started at the temperature of above 1550 °C, which was about 50 °C lower than that of non-milled powder, revealing that the previously milling delayed the fast grain growth of the sintering activity. This might be attributed to the longer milling time, which made the powder particle

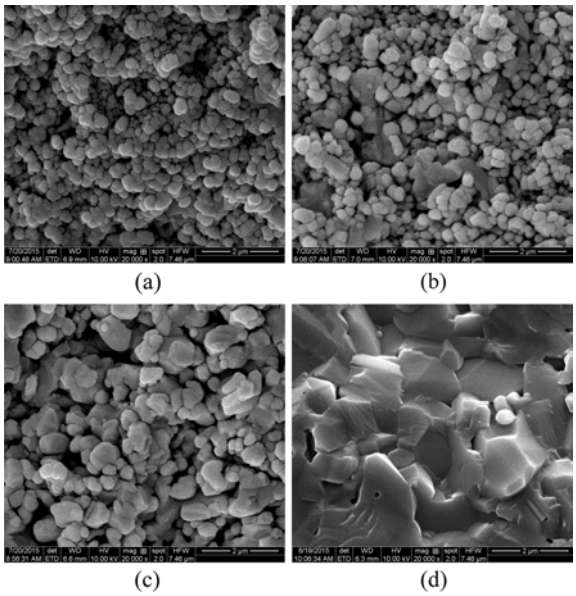

Fig. 5. SEM images of sintered ceramics prepared from milled powder at different temperatures: (a) 1400 °C, (b) 1500 °C, (c) 1600 °C and (d) 1650 °C.

more regular and finer, and made the particle distribution more appropriate and narrower. However, the further increase of the sintering temperature to 1650 °C, the average grain size increased to 1.2 mm, which had similar size with that in the non-milled bulks for the same consolidation conditions (Figs. 4(f) and 5(d)). This suggested that the final grain sizes of samples sintered at 1650 °C had not apparent difference, indicating that acceleration of the grain growth induced by the high temperature sintering offset the inhibiting effects of grain growth caused by the initial finer powders.

From the results, it was suggested that a fine-grained microstructure could be obtained in the milled powder at below 1650 °C. Asaga et al. [19] proposed that the particle-size distribution had a significant influence on the pore radius in the intermediate stage of sintering. The pores of the powder with boarder particle-size distribution became isolated earlier than those of the narrower powder. Therefore, for the powder compacts with a fine particle and uniform size distribution, the pore channels pinched off at higher critical density, which in turn prolonged the intermediate stage of sintering and effectively inhibited grain growth [20].

The relationship of the average grain size and relative density of the sintered alumina are shown in Fig. 6. Considerable grain growth during densification was evident in the case of sintering for both non-milled and milled powder. It was found that in the region where the relative density was lower than 85.0%, grain growth was negligible. The grain size increased considerably at densities higher than 88.0%, and 92.5%, in the case of sintering for the non-milled and milled powder, respectively, which was lower than the results achieved

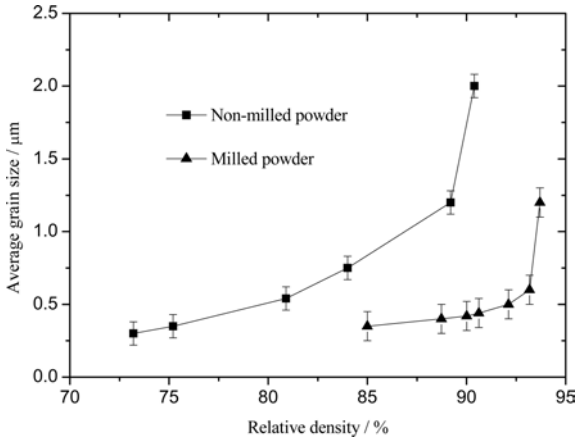

Fig. 6. Relationship of the average grain size and relative density of the sintered alumina.

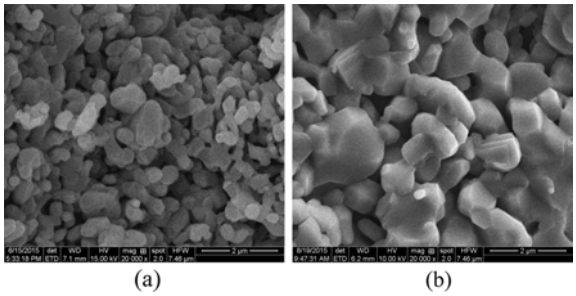

Fig. 7. SEM images of CIP-ed sintered ceramics prepared from milled powder at different temperatures: (a) 1600 °C and (b) 1650 °C.

by some authors [12, 21]. The reason might lie in the fact that the sub-micrometer particles were used, in which pores started to pinch off at lower relative density and the grain growth was enhanced [7].

In comparison, the CIP method was also employed to prepare samples of alumina. In our study, CIP-ed samples of alumina ceramics had a density higher than that of uniaxial-pressed counterparts, showing better compressibility (more than 50.8% green density at pressure of 160 MPa) and sinterability (92.6% and 93.8% fired density at 1550 °C and 1650 °C for 2 hrs) properties. The reason lay in the fact that CIP method could lead to both narrower pore size distribution and smaller pore size. Therefore, the uniform structure of green compacts prepared by CIP method provided higher sintered density in comparison with uniaxially pressed ones [22]. In addition, CIP presses had obvious effects on the microstructure. As observed in the sample sintered at 1600 °C for 2 hrs in Fig. 7, the grains size was about 400-500 nm, which was smaller by 15% than that of samples prepared by uniaxial press approach, indicating that CIP was more preferable than uniaxial press approach in controlling grain size. It was also found that CIP method led to grains much more homogeneous distribution and no local abnormal grain growth was observed. Almost equiaxed particles kept a constant grain size, which showed no significant grain

growth until sintered at 1650 °C, as was seen in Fig. 7. Krell et al. [12, 23] had reported that alumina ceramics formed by CIP process reached their approximate theoretical density at the temperature of 150 °C lower than those shaped by uniaxial press. In our investigation, the temperature of the fast grain growth was about 1600 °C in the CIP-ed samples, which was ~ 100 °C lower than that in samples formed by uniaxial press. The lower densification temperature was attributed to the smaller and narrower pore size distribution in the CIP-ed samples of alumina powder [13], which in turn inhibited the growth of grains [24].

Conclusions

Sintering the submicron high purity alumina by a uniaxial compression method showed that densification was enhanced by ball milling processing. It was demonstrated that ball milling led to the powder being finer and more uniform, and higher green and sintered density. In addition, the microstructure and average grain size were also influenced by the ball milling, in which more homogeneous and finer grains in the sintered ceramic were achieved with the milled powder. CIP was proved to be an effective forming method to improve the densification behavior of alumina powders. It could be concluded that cold isostatic pressing was more preferable than uniaxial press approach in controlling the grain size. There was about 15% small in grain size in the CIP-ed sample after same sintering process at 1600 °C. Furthermore, the temperature at which fast grain growth occurred during sintering of the compact prepared from the milled powder was lower than that prepared from the as-received powder, and the lowest temperature for fast grain growth was obtained in the compact sample formed by the CIP method.

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