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Highly transparent α-alumina obtained by low cost high pressure SPS

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Abstract

Highly transparent pure alumina (65.4%) with an average grain size of 200 nm was fabricated using high-pressure (> 400 MPa) spark plasma sintering. For the first time, highly transparent alumina ceramics were produced using low cost carbon fiber composite for the pressing punches. The high pressure device was also used to fabricate fully dense nanostructured alpha alumina with average grain size of 107 nm. The developed low cost high pressure sintering apparatus might be applied to produce a wide range of pore free nanostructured materials.
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1. Introduction

Hot isostatic pressing (HIP) at temperatures of 1150–1300 °C and pressure as high as 200 MPa have been traditionally used [1,2] to attain highly transparent MgO doped alumina. The tri-axial pressure application in HIP together with optimized powder processing route can easily lower the porosity below 0.05% resulting in line transmittance of up to 71% [1].

Recently, spark plasma sintering (SPS), especially under high pressure conditions, has been demonstrated effective to produce highly transparent ceramics with grain size of the order 140–200 nm. Grasso et al. [3] obtained transparent alumina ceramics with in line transmittance of 64% for a wavelength of 645 nm. More recently Kim et al., by employing high pressure SPS sintering in the temperature range 1000–1200 °C achieved an in line transmittance of 69% for α-alumina doped with 0.03 wt% MgO [4]. A similar high pressure SPS technique was applied by Zhang et al. to achieve transparent tetragonal zirconia and yttria [5,6]. Similar to the case of hot isostatic, the application of SPS pressure exceeding 200 MPa has been demonstrated to be effective in producing pore free highly transparent ceramics.

There is great interest in manufacturing polycrystalline transparent alumina ceramics because of its superior mechanical properties compared to sapphire [1], spinel [7] or AlON. Transparent polycrystalline alumina might be applied in a wide range of applications including armor protection, security windows, infrared detectors, etc. The manufacture of alumina ceramics is strongly hindered by the complexity of the HIP processing route. It has been demonstrated that high pressure SPS results in highly transparent ceramics without any powder preparation in a very short time (i.e. holding time of about 10 min) [3].

Anselmi-Tamburini et al. [8] developed the SPS sintering method based on short thermal cycles (< 10 min) coupled with pressure up to 1 GPa. Aiming to develop industrially scalable high pressure SPS molds, Kamikawa and Kano [9] patented a new-concept die design (see figure 23(b) of Ref. [10]) based on two coaxial hollow cylinders, the inner made of inexpensive (sacrificial) graphite and the outer made of high strength ceramic. However, the exploitation of high pressure SPS technique has been strongly limited by the cost of high pressure molds and their reliability. The present research work is focused on the development of low cost high pressure sintering dies to manufacture nanostructured materials.

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2. Experimental procedure

Commercial α-Al_2O_3 powder (Super TM-DAR, Taimei Chemicals Co. Ltd., Japan), with a purity of 99.99% and an average particle size of 0.13 μm was used. Most of the previous investigations to produce transparent alumina used TM-DAR [3]. TM DAR and Super-TM DAR are compared in Fig. 1. The Super TM-DR has an average particle size of about 0.13 μm (17.5 g/m^2 BET), which is slightly smaller than the 0.17 μm [14] of TM-DAR (14.5 g/m^2 BET). Scanning electron microscope (SEM) images of the Super TM-DAR powder showed that the spherical particles are finer, less agglomerated and more rounded as compared to TM-DAR. As reported by the manufacturer, the super grade is more pure, the level of impurity (ppm) of Si, Fe, Na, K, Ca, and Mg were 10, 8, 8, 3, 2, 2 and 4, 2, 2, 1, 1, and 1 respectively. By comparing the two grades, both the finer particle size and the higher purity of the super grade might favorably contribute to producing ceramics with improved transparency.

The as-received Super TM-DAR powder was sintered at 950 and 1000 °C, without any treatment or additives, under a uniaxial pressure of 200, 400 and 500 MPa using a spark plasma sintering machine (SPS-FCT 1020, Germany). The sample size was 10 mm in diameter and about 2.5 mm thickness. In a typical sintering experiment, 0.6 g of alumina powder was poured into the die. The high pressure device is composed of an outer and inner graphite die, and the powders are pressed between two punches made of carbon fiber composite (CFC) or binderless tungsten carbide (WC) between two intermediated discs (CFC or WC) [3]. Different experiments were carried out by employing either WC or CFC, hereinafter defined as WC and CFC configurations. The temperature was accurately measured using a pyrometer focused on the surface of the inner die (i.e., 1 cm far from the sample). Graphite felt was used to reduce the heat loss by radiation. The powders were heated from room temperature up to 800 °C in 10 min, subsequently, up to the sintering temperature (i.e. 1000 °C) in 20 min. The dwell time was 20 min and pressure was raised stepwise during the heating from 800 °C. Heating was conducted using a sequence consisting of DC pulses (15 ms) followed by zero current for 5 ms.

The sintered samples were machined to a disc of 10 mm diameter with a thickness of 0.8 mm and mirror polished carefully on both sides using diamond slurry. The final thickness of the samples was 0.8 mm. The in-line transmission was measured in the wavelength range 0.24–1.6 μm using a double-beam spectrophotometer (SolidSpec-3700DUV, Shimadzu) by inserting an aperture (3 mm diameter) in front of the detector in order to allow the detection of only the specularly transmitted portion of the incident light beam. The distance between the sample and the detector was about 55 cm.

The microstructure of the samples was observed on thermal etched surfaces, using a scanning electron microscope (SEM) (SU-8000, Hitachi). The porosity was measured on SEM images taken at a magnification of 10,000. We did not measure the absolute density because conventional techniques such as the Archimedes method are insensitive to extremely low porosity. The grain size was measured by obtaining the average cross section area per grain and by assuming spherical grains. The measured grain size is an apparent one, so it was multiplied by 1.225 [3] to determine the true grain size.

3. Results and discussion

Contrary to the work of Anselmi-Tamburini et al. [8], which employed electrically insulating SiC punches

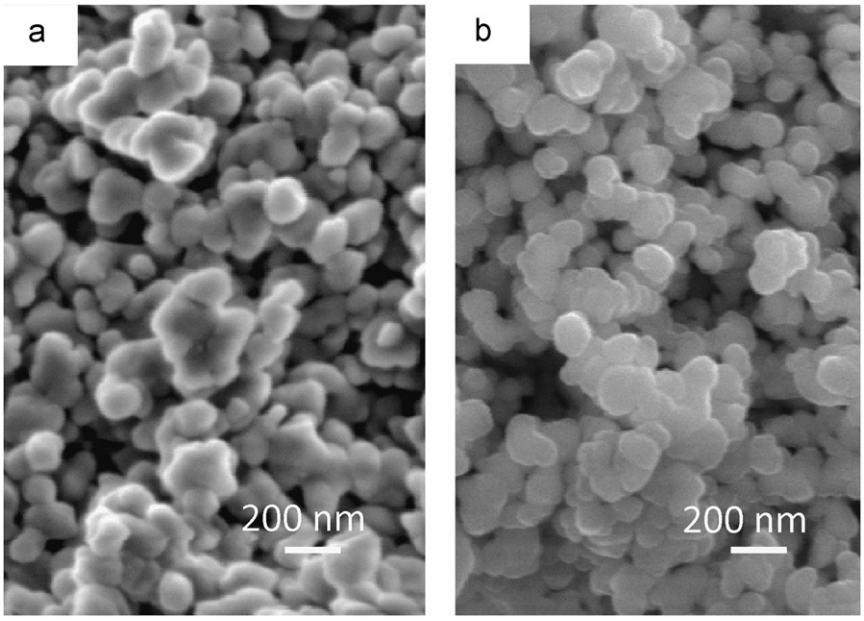

Fig. 1. FESEM images of as received TM-DAR (a) and Super TM DAR (b) α-alumina. The Super TM-DAR was employed.

(i.e. Good Fellow SiC electric resistivity of 10^2–10^3 Ω cm), the configuration used electrically conductive CFC with good electrical conductivity which permitted the flow of current through the sintering powder, promoting densification through the electroplastic effect [11,12]. Although the sintering mechanisms of other oxide powders under SPS conditions are not completely elucidated [10], electric current may play some effect that is not simply limited to Joule heating during sintering. With this in mind, Langer et al. [13] compared the hot pressing (HP) and SPS technique for the alumina powder (TM-DAR). The results showed that at given constant time, SPSed samples reached a higher density compared with HPed ones. Thus to use electrically conductive punches might enhance the densification.

Fig. 2 shows the ram displacement profile of SPSed samples under pressures of 400 and 500 MPa by employing CFC and WC configuration respectively. As detailed in the experimental conditions, the pressure was slowly increased in the temperature range 800–1000 °C (heating rate 10 °C/min), resulting in a significant shrinkage. The curves in Fig. 2 are compared, with 0.6 g of powder employed in both experiments. However, in the case of the CFC the shrinkage was significantly higher than the WC configuration. At 1000 °C, when the maximum load was reached, the displacements were 2.7 mm and 5.7 mm for the WC and CFC configurations respectively. Such a significant difference in displacement was attributed to the strain induced by the applied pressure on CFC punches. As shown in Fig. 2, when the pressure was released the strain of CFC configurations was partially recovered. The compression behavior of CFC is described in detail in Ref. [14].

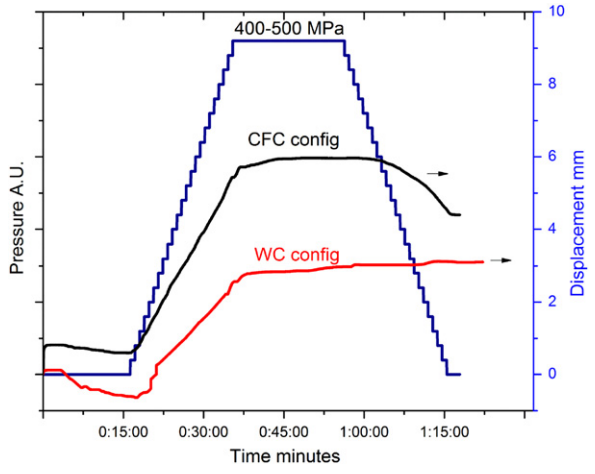

Fig. 2. Plot of the displacement profile as function of time for the WC and CFC configurations. The pressure application is also shown.

The material used in this study was a two-dimensional CFC composite plate supplied by Toyo Tanso, Co. Ltd. with the commercial name of CX-31. The macroscopic appearance of the CX-31 is showed in Fig. 1 of Ref [15]. The C/C composite was made, starting from phenol resin, into carbon fiber cloth and then pressed under a high temperature. The fiber bundle (yarn), approximately 1 mm in width, consists of warp-yarn in longitudinal direction and fill-yarn perpendicular to the warp-yarn.

As summarized in Table 1, the CFC material has great potential to be applied in high pressure SPS dies. The CFC material is about 50 times less expensive and easier to be machined compared to WC ceramic. Typically the high cost of WC [3] or SiC [8] punches is because of their fine machining and polishing. The degree of parallelism between flat surfaces must be within 10 μm in order to avoid preferential stress distribution resulting in immediate failure.

There is an extensive literature on the compressive response of carbon fiber composites [16]. The compressive strength suggested by the CX-31 manufacturer at room temperature is 249 MPa [15]. Preliminary testing revealed that the upper limit of uniaxial stress for the CFC CX-31 punches at 1000 °C is about 450 MPa. Thus in order to reliably carry out the SPS processing with CFC punches, the upper pressure limit for the sintering experiments was set to 400 MPa. Much higher values have been reported by Park and Lee [14], who reached a room temperature

Table 1
Comparison between properties of CFC and WC punches employed for producing transparent alumina samples. Most significant features including cost, machining, maximum operating pressure/temperature are also listed.

	CFC configuration	WC configuration
Manufacturer and commercial name	Toyo Tanso, CX-31	Manufactured by Fuji Electronic Industrial Co., Ltd, M78 Binderless WC
Cost finished parts (full set 1 cm diameter sample, 2 punches + 2 pressing punches)	≈ 35 €	≈ 1500 €
Machining preparation	CNC controlled machining	Electric discharge machining followed by grinding/polishing
Critical tolerances	Non critical	Parallelism between compressing surfaces must be below 10 μm
Maximum operating compressive strength room temperature [a]	249 MPa [17]	4.8 GPa [19]
Maximum SPS operating pressure at 1000 °C	400 MPa	≈ 0.5,1 GPa[a]
Potentials maximum operating temperature in SPS	2000 °C [17]	1200 °C [18]

At higher pressure the sample extraction is critical.
[a]Load applied perpendicular to the 2-D fibers.

compressive stress as high as 900 MPa with strain of 0.2 (see Fig. 5b of Ref. [14]). In the case of WC punches the pressure can easily exceed 500 MPa, however for larger pressures it is difficult to extract the samples without damaging the high pressure die.

Another interesting property of the CFC material is its stability at high temperature. As reported by Hatta et al. [17], the compressive strength of the 3D-C/C increased up to a temperature of 2000 °C, thus, CFC material might be an ideal candidate for high pressure sintering punches at high temperature application (i.e. >1200 °C). On the contrary, the strength of WC rapidly decreases for temperatures exceeding 1200 °C, as reported by Reeber and Wang [18].

Fig. 3 shows a photograph of 10 mm diameter alumina sintered at 1000 °C under 200, 400 and 500 MPa. The text and the images can be clearly seen through the sample. After annealing the brownish color was reduced. The in-line transmission of the 0.8 mm samples sintered at 1000 °C is shown in Fig. 4(a) before, and (b) after annealing for 30 min at 900 °C. The in line transmittance measurement for a wavelength of 645 nm are summarized in Table 2. The sample sintered at 950 °C under 400 MPa was opaque and consequently its transparency was not measured. The sintering by CFC (400 MPa) and WC (500 MPa) resulted in nearly identical transparency. The lower pressure of 200 MPa resulted in significantly lower transparency evidencing the significant contribution of pressure to eliminate residual porosity. The transmission at a wavelength of 645 nm, for the sample sintered at 400 MPa (CFC) and 500 MPa (WC) were 61.3% and 63.0 for 0.8 mm thick sample. Thus CFC is as effective as the WC in producing transparent alumina ceramics. After annealing at 900 °C for 30 min in air, the in line transmittances were increased to 63.5 and 65.4 respectively. An in-line transmission of 65.4% is the highest value for pure alumina reported in literature. Slightly higher value (71%) was attained by HIP for MgO doped alumina [1]. In comparison with our previous work which employed TM-DAR powder, the Super-TM DAR grade resulted in a limited improvement of the in line transmittance [3].

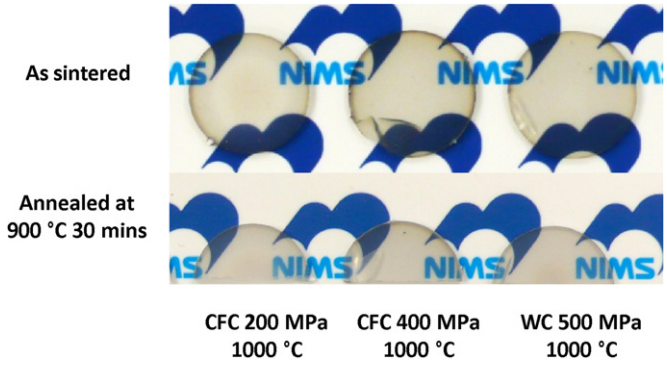

Fig. 3. Photograph of the transparent alumina sample on top of the text before and after annealing at 900 °C. Samples are 0.8 mm thick and polished on both side. The text was not retro illuminated.

Fig. 5 compares the microstructures of Super TM-DAR sintered by CFC configuration at 950 (Fig. 5a) and 1000 °C (Fig. 5b) under 400 MPa. Both samples showed high densification, and we did not observe any obvious porosity on the thermally etched surfaces. The average grain size of the sample sintered at 950 °C is 107 nm, while it is 203 nm for the sample sintered at 1000 °C. The morphology of the grains sintered at 950 °C resembles the particles of the initial powder as shown in Fig. 1(b). It is possible to distinguish a wide number of grains with average particle size below 50 nm existing together with larger grains up to 150 nm. As shown in Fig. 5(b), the average grain size of sample sintered at 1000 °C is distributed between 150 and 250 nm.

Alpha alumina is very prone to grain growth when sintered under high pressure conditions. Kim et al. [4] observed that the sintering pressure promoted grain growth for MgO doped alumina sintered at 1200 °C. They reported that an applied pressure of 50 and 400 MPa

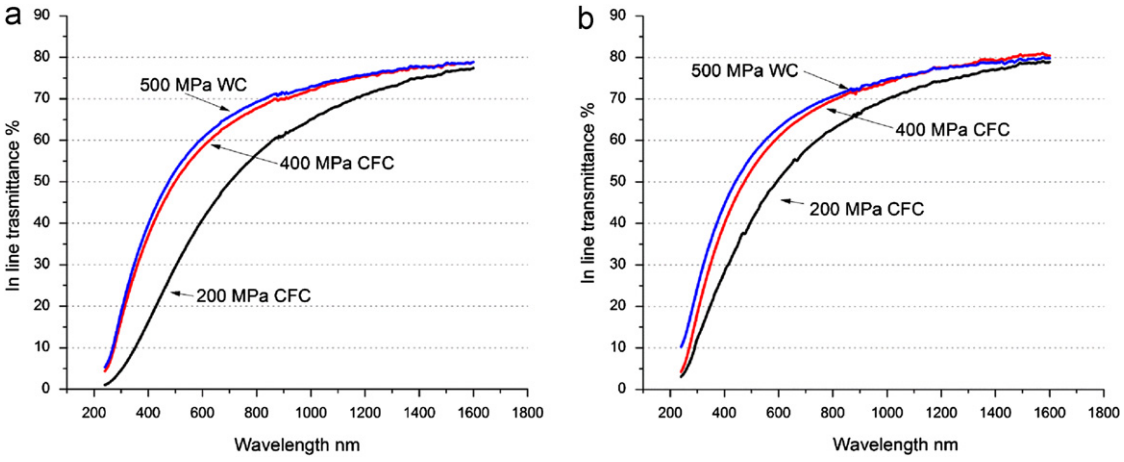

Fig. 4. In-line transmission of the alumina sintered at 1000 °C for 20 min under applied pressure of 200, 400 MPa (CFC configuration) and 500 MPa (WC configuration). The in line transmittance refers to the alumina sample (a) before and (b) after annealing.

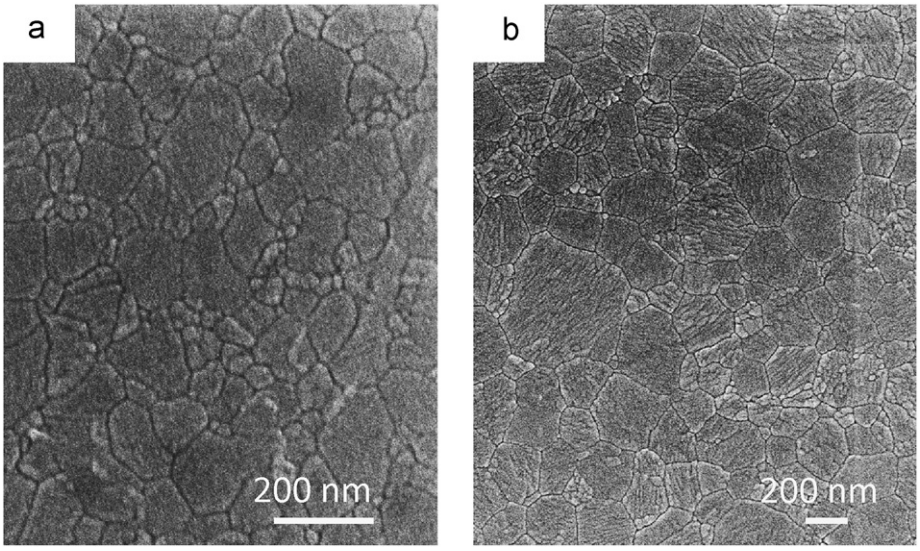

Fig. 5. FESEM of thermal etched surface. The samples were sintered at (a) 950 and (b) 1000 °C under 400 MPa for 20 min.

Table 2
In line transmittance measured at 645 nm for sample sintered at 1000 °C for 20 min under pressure of 200 and 400 MPa by employing CFC configuration, and 500 MPa with WC configuration.

In-line transmittance at 645 nm	200 MPa CFC	400 MPa CFC	500 MPa WC
Before annealing	45.2	61.3	63.0
After annealing	54.2	63.5	65.4

resulted in grain size of 230 and 670 nm respectively. The marked grain growth between the samples sintered at 950 and 1000 °C (Fig. 5), might be similarly attributed to grain coalescence effect induced by the high pressure compaction [4].

Using conventional sintering techniques such as hot isostatic pressing [1], hot pressing, pressureless sintering [20] and SPS [13] it is not possible to produce fully dense material while maintaining the grain size below 100 nm. Conventional sintering techniques result in grain sizes largely above 300 nm [2,13,20]. However, Mishra et al. [21,22] reported processing of nanocrystalline alumina and alumina composites at high pressures using the piston-cylinder apparatus, at 1 GPa and temperatures between 700 and 1000 °C. They obtained fully dense alumina with an average grain size of 142 nm and hardness of 25.3 GPa [21]. The reported hardness and toughness is considerably higher than the value for coarse-grained alumina (20.1 GPa).

As demonstrated in the present research, the use of CFC dies permitted the use of pressures up to 400 MPa to achieve fully dense material with grain size as fine as 107 nm. CFC high pressure SPS sintering, because of its low cost has great potentials to be up-scaled to larger size samples. In general, if compared to the HIP methods of Apetz and Bruggen [1] and Krell et al. [2], the SPS method proposed in the present work is extremely rapid and simple. It does not require any powder deagglomeration/preparation, the as received powder can simply be poured into the die with holding time just 15–20 min against the 4–17 h in HIP [1,2].

4. Conclusions

In comparison with conventional HIP [1,2], high pressure SPS based on low cost CFC dies lead to significant scientific and technological achievements. First, full dense alumina with average grain size of 107 nm with no considerable grain growth was produced. The samples sintered starting from Super TM-DAR pure alumina powder without any pre-paration possessed a real in line transmittance of 65.4%, which is the highest value reported for pure alumina. We demonstrated the feasibility of high pressure SPS based on low cost carbon fiber dies which might have great potential to be applied for sintering nanostructured materials under high pressure conditions up to 2000 °C.

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