Micrometer-sized porosity, which cannot be recognized by typical density measurement method, was observed inside transparent polycrystalline alumina prepared by pulsed electric current sintering (PECS). The pores derive from hard agglomerates in starting powder and appear as black dots inside transparent bulk samples. In this study, porosity coming from the agglomeration was studied to degrade by chemical and mechanical treatments. Starting alumina powder was mixed with some surfactants as aqueous solutions. The slurries were ball-milled in 1 d, followed by drying and heat treatment to obtain treated alumina powders. Sintering of those alumina powders was carried out by two-step PECS technique. Transparent alumina specimens were evaluated by the density of black dots and the apparent transmittance. In summary, their treatments of alumina powder can break agglomerates and dramatically reduce the total density of black dots within transparent polycrystalline alumina. Consequently, the transmittance of polycrystalline alumina increased, from 68% for untreated sample to 72–74% for treated samples.

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Key-words: Transparent polycrystalline alumina, Pulsed electric current sintering, Agglomeration, Micrometer-size porosity, Surfactant, Transparency

1. Introduction

Alumina (Al₂O₃) is one of the most widely used ceramic materials in industrial applications because of its superior properties such as high hardness, high thermal conductivity, good abrasion resistance and excellent chemical inertia. With good transparency, single crystal alumina, or commonly called sapphire, has been used in many optical applications. However, the production of sapphire requires long process with high production cost. Polycrystalline alumina becomes a remarkable material because of comparatively excellent properties of sapphire with easier and cheaper manufacturing process. Density and grain size are two of the most important factors in the preparation of transparent polycrystalline ceramics. Because of the high efficiency of pores as light scattering regions, transparency in polycrystalline materials requires extremely low porosity (< 0.01 vol %). Samples with porosity of this level could only be made under sintering conditions involving high temperature, high pressure and long holding time. It is also believed that polycrystalline materials with grain size at nanometer level would provide better transparency than materials with a grain size in the micrometric range. Furthermore, the nanostructure of the matrix provides significant improvement in the mechanical strength and hardness. Polycrystalline alumina with low porosity (< 0.01 vol %) and small grain size (< 1 μm) may attain excellent mechanical and thermal properties and good optical transparency comparable with single crystal sapphire. It can substitute for sapphire to be used widely in optical applications.

Transparent polycrystalline alumina (TPA) has become the focus of recent investigations for its unique combination of optical, mechanical and thermal properties. Traditional types of TPA are prepared by sintering in hydrogen gas at temperature generally above 1700°C. The high sintering temperature provides low porosity but causes extensive grain growth and seriously affects the mechanical strength, hardness and optical transparency of the material. As a result, in-line transmission of traditional transparent polycrystalline Al₂O₃ is typically below 10%, which makes the material appear translucent rather than transparent.

Both low mechanical strength and low transmission limit the applications of TPA. In the recent years, fine-grained TPA has been prepared by using hot pressing (HP), hot isostatic pressing (HIP) or pulsed electric current sintering (PECS) at low temperature ranging from 1150 to 1400°C. Its fine-grained microstructure (< 1 μm) provides a significant improvement in both mechanical strength and optical transparency. It is reported that the fine-grained TPA has 400–600 MPa in bending strength with a high in-line transmission up to 60% for visible light.

Recently, PECS has become an alternative method to obtain TPA. Kim et al. demonstrated that a slow heating rate such as 2 K/min was the critical PECS parameter for densification with less grain growth and high transparency of Al₂O₃. Grasso et al. reported that a high pressure of 500 MPa promoted densified and transparent Al₂O₃ in PECS at low temperature of 1000°C. Langer et al. reported a comparison between HP and PECS processing for Al₂O₃ powder. By fixing the sample geometry, the heating program, the applied pressure and the atmosphere for both sintering processes, for given constant time, PECS samples achieved higher relative density than HP ones. Makino et al. successfully obtained TPA by PECS with fast
heating rate such as 200 K/min, although they showed the inhomogeneity in TPA samples. In the most recent years, Nanko et al. established a new technique in PECS with two-step heating profile (TS-PECS), to prepare polycrystalline alumina with high transparency. Instead of slowly heating up to the final sintering temperature, a holding stage with lower temperature was added for partial densification without serious grain growth. After that, the temperature was increased to the final sintering temperature and kept for a shorter duration to complete densification with remaining grain size. In both two steps to increase temperature, the heating rate was up to 100 K/min. Although TPA was successfully obtained with advanced sintering techniques such as TS-PECS, it is found that some small black dots with size of a few tens micrometers exist within TPA bodies. In this study, those black dots were studied to be reduced by treating the starting Al₂O₃ powder with surfactants in order to fabricate TPA by TS-PECS. Transparency of TPA prepared by TS-PECS was also discussed with the density of black dots.

2. Experimental procedure

The starting powder is α-Al₂O₃ powder (TM-DAR, Taiimei Chemicals Co., Ltd.) with average particle size of 140 nm. Two-step PECS was conducted by using the PECS equipment (Sinterland Inc., LABOX™-1550i755) for α-Al₂O₃ powder to obtain transparent specimens. Table 1 shows the parameters of the PECS process. Within each TPA specimen, some large black dots with size of a few tens micrometers could be observed and located by naked eyes because of the good transparency of alumina. The cross sections of some large black dots were attained by precise polishing with diamond slurry. In order to study the origin of the black dots, the cross sections of black dots were observed under optical microscope (KEYENCE VW-9000) and scanning electron microscope (KEYENCE VE-7800S). EDX mapping of cross sections of black dots was analyzed by integrated device (Genesys APEX, AMETEK Co., Ltd.) in SEM.

With the purpose of decreasing the black dots within TPA, both mechanical and chemical processes were used for treating the starting α-Al₂O₃ powder. Three chemical compounds were chosen as surfactants for chemical treatments: acetic acid C₂H₄O₂ (Wako Pure Chemical Industries Ltd., liquid 99.7%), stearic acid C₁₇H₃₅O₂ (Sigma-Aldrich, powder 95%) and aluminon C₂₂H₂₃N₃O₉ (or aurintricarboxylic acid ammonium salt, Sigma-Aldrich). The starting alumina powder was mixed with surfactants by different ratios in distilled water. In the cases of stearic acid and aluminon, the ratio in mass of surfactants to alumina powder was 1%. In the case of acetic acid, the original state of acetic acid is a solution that makes some difficulties to control the concentration in mass ratio. Hence, the mixture of alumina powder with acetic acid was controlled at pH value of 5.0. All of the aqueous solutions were ultrasonically shaken for 15 min, followed by ball milling for 1 d. Used milling media was high purity alumina ball with diameter of 5 mm. The mass ratio of powder to balls was 1:5.

The milled slurries, as divided into two parts, were dried by two different methods. The first part was dried by heating in air up to 120°C for 12 h. The second part was dried with freeze-drying system (FDU-1200, EYELA). The powders after drying in both two methods were milled manually by using an alumina mortar and a pestle for approximately 15 min. After drying by both methods, all powders were annealed in air at 400°C for 4 h. Purpose of this annealing process is to eliminate all the carbon contaminant which came from the surfactant compounds.

Ball milling in dry condition was also carried out with annealed powders. For this experiment, starting α-Al₂O₃ powder was only treated with alumina and dried by heating up in air as described above. After annealing step, the powder was milled by high purity alumina ball. Mass ratio of powder to ball was equal to 1:5. Ball milling lasted for different interval of time from 30 min to 24 h. Untreated and treated powders were observed via scanning electron microscope for confirmation of the agglomeration within the powders before sintering. Table 2 lists the notations for all treatments in this study.

Two-step PECS was conducted by using the PECS equipment for all alumina powder with the same set of parameters shown in Table 1. After sintering, disk-shaped bulk samples had 15 mm in diameter and approximately 2 mm in thickness. All disk shaped samples were ground both two surfaces to remove residual carbon sheet. After that, their density was evaluated by Archimedes method within toluene. The samples were cut into 4 × 4 mm² pieces by diamond cutter in consideration of fixing the observation area. All square specimens were polished two faces to a final thickness of approximately 1.5 mm by diamond slurries. The evaluations were carried out with square specimens with 4 × 4 mm² in area and approximately 1.5 mm in thickness.

In this study, the optical microscope was used to observe and count the black dots inside TPA specimens. At a low magnification (×100), only black dots with size of a few tens of microns were counted. On the other hand, at a high magnification (×1000), many small dots with size of only a few microns appeared. However, at this high magnification, only a small area approximately 300 × 230 μm² was observed and counted while the full area of the specimen (approximately 4 × 4 mm²) could be observed at low magnification. From the counted amount of black dots, the density of black dots was obtained.

Along with counting the amount of black dots within bulk alumina specimens, the apparent transmittance of each type of specimens was checked by a custom design with a mobile laser power meter (Sanwa, Mobiken series, LP1). A green laser with 1 mW power and wavelength of 532 nm was used for this measurement. The laser head was fixed with a vertical stand with 50 mm in distance from the sensor surface of laser power meter. At the beginning of each measurement, reference value was recorded by emitting laser beam directly to the laser sensor. After that, each transparent specimen was placed on the surface of laser sensor and absolute value of light transmittance for that specimen was measured. Relative transmittance of a specimen was determined by the ratio of the absolute value to the reference value. During all measurements, the system was put in a black

<table>
<thead>
<tr>
<th>Parameters of TS-PECS process</th>
<th>1st step temperature/holding time</th>
<th>2nd step temperature/holding time</th>
<th>Heating rate</th>
<th>Uniaxial pressure</th>
<th>Vacuum condition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1000°C/60 min</td>
<td>1200°C/20 min</td>
<td>100 K/min</td>
<td>100 MPa</td>
<td>&lt;5 × 10⁻⁷ Pa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>List of notations of specimens</th>
<th>Used surfactant</th>
</tr>
</thead>
<tbody>
<tr>
<td>Normal drying method</td>
<td>Al-n.d.</td>
</tr>
<tr>
<td>Freeze-drying method</td>
<td>Al-f.d.</td>
</tr>
<tr>
<td>Untreated</td>
<td>AA-n.d.</td>
</tr>
<tr>
<td>Treated</td>
<td>AA-f.d.</td>
</tr>
<tr>
<td>Aluminon</td>
<td>SA-n.d.</td>
</tr>
<tr>
<td>Acetic Acid</td>
<td>SA-f.d.</td>
</tr>
</tbody>
</table>
box to eliminate noises from external light.

3. Results

Figures 1(a) and 1(b) show the SEM images of as-received TM-DAR powder and SA-f.d. powder. In those images, both powders similarly contained a large amount of agglomerates.

Figure 2 shows black dots within TPA samples. There are some black dots which can be detected by naked eyes.

Figure 3 shows the cross sections of black dots observed by optical microscope (a) and scanning electron microscopy (b). From images in Figs. 3(a) and 3(b), the black dots were revealed as some porous parts within TPA specimens. Obviously, these porous parts are not individual pores which may exist among grains in polycrystalline structure. Because of the round shape of all black dots, they are not cracks inside specimens which should have strip shapes. Those porous parts were formed from less-packed parts in the powder compaction before sintering.

Figure 4 shows the appearances of large black dots at low magnification (×100) and of small black dots at high magnification (×1000). Many black dots were observed in TPA specimens. Although some porous parts still appeared within untreated and treated samples as black dots, relative density of all samples attained higher than 99.9%.

Density of black dots (amount of black dots per unit volume) was shown in Fig. 5. With normal drying method, the density of black dots dramatically reduced with AA-n.d. sample (from 570
in untreated sample reduced to 107 dots/mm$^3$) and AL-n.d. sample (to 116 dots/mm$^3$) but increased in SA-n.d. sample (to 1054 dots/mm$^3$). By treatment with aluminon and usage of freeze-drying device, the density of black dots increased from 116 dots/mm$^3$ in AL-n.d. sample to 435 dots/mm$^3$ in AL-f.d. sample. Similarly, the density of black dots within AA-f.d. and SA-f.d. was higher than that within AA-n.d. and SA-n.d. correspondingly. From above results, it is shown that freeze-drying process using with current treatments gave poorer effects than normal drying method.

The apparent transmittance of TPA specimens which were treated with three kinds of surfactants along with two drying methods is also showed in Fig. 5. The apparent transmittance of untreated specimen was 67.4%. AL-n.d. and AA-n.d. specimens have higher apparent transmittance than the untreated one, relatively at 73.1 and 71.6%. On the other hand, the SA-n.d. specimen reached only 70.7% of light transmittance. The influence of freeze-drying method on transparency of polycrystalline alumina was also seen there. Suitably with the increment of density of black dots inside TPA samples using freeze-drying method, the apparent transmittance of those TPA samples is lower than the samples using normal drying method. With aluminon treated samples, the apparent transmittance decreased from 73.1% in AL-n.d. specimen to 68.1% in AL-f.d. specimen. The relative decrement of acetic acid treated samples is from 71.6 to 67.3% and that of stearic acid treated samples is from 70.7 to 68.5% if using freeze-drying method instead of normal drying method. Obviously, the increments of black dots due to usage of freeze-drying technique have clear influence on the transparency of TPA.

Figure 6 plotted the density of black dots within AL-n.d. specimens with different duration of dry ball milling. At the beginning of dry ball milling process, the density of black dots increased from 116 to 309 dots/mm$^3$. However, after dry ball milling for 1 h, density of black dots decreased to 155 dots/mm$^3$, still slightly higher than density of black dots within AL-n.d. specimen without dry ball milling. The results of dry ball milling for 1 to 24 h show that density of black dots slowly increased with longer ball milling process.

Similarly, for short duration of ball milling—after 0.5 h, as the density of black dots increased, the apparent transmittance dropped from 73% for no ball milling step to 69% for 0.5 h dry ball milling. After 1 to 3 h of ball milling, the density of black dots decreased again and the specimens had good transparency with about 74% of apparent transmittance. For longer dry ball milling, the density of black dots increased slowly, while the apparent transmittance seems to be slowly decreased.

4. Discussion

As shown in Fig. 3, black dots within TPA are actually porous parts which came from less-packed parts in the powder compaction before sintering. The less-packed parts may derive from agglomerates in starting powder. Depending on strength of bonding between powder particles in agglomerates, some of less-packed parts which come from hard agglomerates cannot be crashed and densified by the uniaxial pressing during PECS process. Consequently, those less-pack parts remained in sintered specimens as porous parts, which appears as black dots inside transparent alumina specimens. From the cross-sectional observation of black dots, it can be concluded that the black dots within TPA derive from hard agglomerates in starting powder which cannot be broken during the sintering process.

There is also a possibility that the black dots within TPA derive from some contaminants but not porous parts. In order to consider this possibility, EDX mapping analysis of the cross section of a black dot was conducted. Figure 7 shows the EDX mapping of a surface with a cross section of a black dot and Fig. 8 specifies the carbon mapping inside and outside the cross section area of a black dot. In the energy spectrum, there is no strange peak other than the peaks of O, Al and Au (a layer of Au was coated on the surface of Al$_2$O$_3$ in order to observing by SEM). EDX mappings shows no obvious boundary of the porous part and the equivalent level of carbon contaminant inside and outside of the porous parts. It proved that carbon contaminant larger than detective level of EDX did not exist in porous parts.
As showed in Fig. 1, the SEM image of untreated powder and SA-f.d. powder is similar to that of SA-f.d. powder with a large amount of agglomerates in both powders. On the other hand, Fig. 5 shows the much higher density of black dots within SA-f.d. sample than within untreated sample. Most of the agglomerates in raw powders were weak enough to be broken and densified during PECS process. Only a small amount of agglomerates, which had strong bonding between particles, remained as porous parts within sintered samples. By the above reason, although the SEM images of raw powders were quite similar, the results of density of black dots within samples sintered from untreated powder and from SA-f.d. powder were totally different. The observation of agglomerates within raw powders cannot represent the hard agglomerates which remain after sintering and appear in bulk TPA samples as black dots.

With all untreated or treated samples, there were the existence of porous parts as black dots within TPA samples. However, the relative density of all samples attained more than 99.9%. At this high relative density, the Archimedes method is not accurate enough to detect the differences in density between TPA samples from various treatments. Hence, the relative density of various TPA samples was not compared in this manuscript.

The influence of the surfactants on the amount of agglomerates within bulk TPA samples is shown more detailed in Table 3. With AL-n.d. treatment and AA-n.d. treatment, the amount of small agglomerates decreased dramatically. It means that aluminum and acetic acid can act as surfactants and break the hard agglomerates. However, the amount of large black dots increased because of the formation of some large agglomerates during drying stage. It was possibly caused by the capillary force in drying stage, the partial sintering effect during annealing process at 400°C or the humidity absorbance during cooling time after annealing process. Although the amount of large agglomerates increased, the density of large agglomerates increased insignificantly because they were counted on a wide area. On the other hand, counting over a much narrower area, the density of small agglomerates strongly decreased by AA-n.d. and AL-n.d. treatments and led to the decrement of total density of agglomerates. Consequently, the apparent transmittance of polycrystalline alumina increased 4-5% in the cases of AA-n.d. and AL-n.d. samples.

For stearic-acid treatments, the amount of both large and small agglomerates increased, especially the small agglomerates. The low solubility of stearic acid in water prevented its molecule to well disperse in the aqueous slurry with alumina particles, so that stearic acid molecules could not create the stabilization for alumina particles. While the total density of agglomerates strongly increased, the apparent transmittance also increased. The reasons for this inappropriate relationship are assumed as the error value of PECS process or the differences in average size of the agglomerates. Even with untreated samples, the error of apparent transmittance values was more than 1%. Moreover, the average size of hundreds of microscopic agglomerates for each case was still impossible to evaluate in this study.

Table 3. Details of counted amount of black dots within TPA specimens with various powder treatments

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Counted amount of black dots</th>
<th>Total density of black dots /mm³</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>At high magn. (4 x 4 x 1.5 mm³)</td>
<td>At low magn. (0.23 x 0.30 x 1.5 mm³)</td>
</tr>
<tr>
<td>Untreated</td>
<td>159</td>
<td>570</td>
</tr>
<tr>
<td>AL-n.d.</td>
<td>12</td>
<td>116</td>
</tr>
<tr>
<td>AL-f.d.</td>
<td>4</td>
<td>435</td>
</tr>
<tr>
<td>AA-n.d.</td>
<td>8</td>
<td>107</td>
</tr>
<tr>
<td>AA-f.d.</td>
<td>15</td>
<td>899</td>
</tr>
<tr>
<td>SA-n.d.</td>
<td>15</td>
<td>1054</td>
</tr>
<tr>
<td>SA-f.d.</td>
<td>12</td>
<td>1450</td>
</tr>
</tbody>
</table>

Figure 9 shows the apparent transmittance as a function of density of large black dots (a) and small black dots (b). As shown in Fig. 9(a), no clear dependence of apparent transmittance values on the density of large agglomerates. In contrast, it is obvious that the apparent transmittance values increase while the density of small agglomerates decreases, as shown in Fig. 9(b). This result is compatible with the above results that the apparent transmittance still increased when the amount of small black dots decreased but the amount of large black dots increased. Therefore, the transparency of TPA is affected by the density of small
agglomerates more than that of large agglomerates.

Dry ball milling is one of the common mechanical routes for deagglomeration. However, along with reducing particle size and breaking agglomerates during a dry milling process, reagglomeration can also occur which will expand the particle size distribution of the powder. In the present study, a low-energy ball milling system was used with rotation speed lower than 100 rpm. Because of the low-energy milling, alumina powder with initial particle size of 140 nm would not be crushed. Both deagglomeration and reagglomeration occurred without particle size reduction. After half an hour of ball milling, it was seen that the total density of black dots increased. At this point of ball milling, there should be the fracture of the large agglomerates forming a more amount of smaller agglomerates. The fracture of agglomerates might overwhelm the opposite direction of reagglomeration until 1 h of ball milling process when the density of black dots still decreased. After 1 to 24 h of dry ball milling stage, the density of black dots slowly increased, showing that in this duration, reagglomeration occurred more and made stronger influence than deagglomeration. In all cases of dry ball milling, there was a strong relationship between the density of black dots and the apparent transmittance of TPA specimens. After half an hour, because of the fragments of large agglomerates, the density of agglomerates increased, causing the drop of the apparent transmittance to 69 from 73% without ball milling. After that, the apparent transmittance rose again to 74% at the point of 1 h ball milling. In ball milling process from 1 to 24 h, although the density of agglomerates slowly increased, the apparent transmittance of TPA slowly decreased but still comparative.

In all cases of surfactants, the freeze-drying method gave worse results than the normal drying method. For all cases of three surfactants, applying the freeze-drying method caused the total density of agglomerates increasing in comparison with applying the normal drying method. The apparent transmittance of the freeze-dried specimens was lower than that of the normal-dried specimens. It is quite clear that these three surfactants have the similar behavior when being used accompanied with freeze-drying method. Even aluminon or acetic acid acted well as a surfactant for alumina powder with normal drying step, they are not good when used with freeze-drying method. Obviously, freeze-drying method did not work properly in current treatments of alumina powder with aluminon, acetic acid or stearic acid.

5. Conclusions

The density of black dots within TPA prepared by pulsed electric current sintering was reduced by treatments of starting α-Al2O3 powder with surfactants. By using aluminon at 1 mass % or using acetic acid with pH of aqueous solution equal 5.0 with normal drying method, the treatments of alumina powder can break many microscopic agglomerates and dramatically reduce the total density of black dots inside transparent bulk bodies. Therefore, the apparent transmittance increased from 67.4 to 71.6% with acetic-acid treatment and 73.1% with aluminon treatment. Aluminon or acetic acid can work as good surfactants for treatments of alumina powder. On the other hand, stearic acid did not work properly as a surfactant for alumina powder due to its low solubility in water. Freeze-drying method was used instead of normal drying method in order to avoid large agglomeration occurred during drying process. However, freeze-drying method did not work well with the current treatments of alumina powder. It possibly works better with different concentration of surfactants or with different surfactants. With the same purpose of reducing large agglomerates after drying, a process of dry ball milling was conducted for 0.5 to 24 h. It showed the best results after 1 or 3 h of ball milling when the apparent transmittance attained the highest value at 74%, 1% higher than no-ball-milling sample.

In general, it was successful to reduce the total density of black dots inside transparent polycrystalline alumina. Consequently, the transmittance of polycrystalline alumina was significantly increased. However, the occurrence of large agglomeration has still not been completely solved.

References