Abstract

In the present work, transparent submicrometer grains alumina formed by gel casting using agar as gelling additive was investigated. Green bodies were obtained by mixing well-dispersed alumina slurries (65-75 wt.%) with agar solution (0.1-0.3 wt%) at 45°C and changed to gel on cooling. The density of green bodies ranging from 51-57 % was obtained. The density of bodies sintered at 1300 and 1350°C in air was in the range of 91-97 % of TD. After HIPing, the specimen transparent with mean grain size of 0.56 μm. The transmittance measured at 645 nm was 17%.

1. Introduction

The production of transparent alumina with submicrometer size grains is still one of the most challenging in advanced ceramics technologies. Submicrometer grains size alumina for obtaining component with improved hardness[1], wear resistance[2], and optical properties[3].

To obtain dense alumina ceramic with submicrometer size grains, very fine and high purity alumina powder are required, but agglomeration present in the early stage of the forming process. Colloidal forming of ceramic green compacts from suspension shows advantages for shaping of complicated figure parts compared with die pressing. It also has ability to improve microstructure of final products due to the elimination of agglomerates by using well dispersed suspension.[4]

Gel casting is a new ceramic forming method that provides green body with complicated figure part and sufficient physical strength. Recently, transparent alumina with submicrometer size grains formed by gel casting method could be made[3, 5]. This method is based on the in situ polymerization of organic monomer (usually acrylamide), but acrylamide is harmful to health. Agar is one of gelling additives. It is soluble in hot water and gel on cooling. Many researchers used agar derivatives as gelling additive replaced acrylamide system, because it is environmental friendly. Nevertheless transparent alumina formed by gel casting using agar as gelling additive have not been developed so far. In this work, the formation of uniformly packed green body by gel casting using agar as gelling additive is investigated as an essential precondition to obtain full dense polycrystalline alumina with submicrometer grains that allows high transparency for visible light.

2. Experimental Procedures

2.1 Materials

High purity alumina powder (>99.99%, Taimicron TMMA, Taimei Chemical Co., Ltd., Japan) with mean particle size of 0.35 μm and specific surface area of 12.6 m2/g was used. Magnesium nitrate hexahydrate (Mg(NO3)2⋅6H2O) was used as a grain growth inhibitor. A gelling additive, agar powder (M7) was supplied by Ina-shokuhin Kogyo Co., Ltd., Japan. A commercial NH4 salt of poly- (methacrylic acid) (Aron A6114, MW 6000, Toagousei Co., Ltd., Tokyo, Japan) was used as deflocculant.

2.2 Preparation alumina slurry for gel casting

Alumina slurries were prepared to solid loading of 65, 70 and 75 wt.% by ball milling for 16 h. As grain growth inhibitor MgO in the form of Mg(NO3)2⋅6H2O was used at the fixed concentration of 0.03 wt.% on a dry solid basis.

Agar solution was prepared by dissolving agar powder in distilled water at 90°C, this solution was maintained at 45°C and added to the alumina slurries at this temperature.

For preparing the gel casting slurries, the well dispersed alumina slurries were heated at 45°C. The agar solution was added until the concentration of agar introduced into alumina slurries were 0.1, 0.2 and 0.3 wt.% on the basis of dry alumina powder. Table 1 shows the initial and final solid loading of the slurries, as well as the agar content for the different compositions. The rheological characteristic of the slurries were measured using viscometer.

Alumina green bodies were obtained by pouring the slurries in PVC molds and then cooled down to 10°C in a refrigerator. After the alumina slurred changed to gel, they were dried before demoulding in closed chamber (40 litre of volume) at room temperature. After that, they were dried in a convection oven at 105°C. The dried bodies were calcined at 800°C for 2 h in air to remove the deflocculant and organic binder. The calcined bodies were sintered at 1300 and 1350°C for 2 h in air furnace followed by hot isostatic pressing at 1300°C under Ar gas pressure of 150 Mpa.

2.3 Properties measurement

The rheological properties of agar solution and alumina slurry was measured by rotary rheometer (Brookfield RVDV-E) at 45°C and a constant shear rate of 100 S-1. The densities were determined by Archimedes'
method. The microstructures were observed by scanning electron microscopy (SEM, JOEL: JSM-6301F). The transmittance was measured by UV/Vis spectrophotometer (Perkin Elmer Lamda 35).

3. Experimental results and discussion

Fig. 1 shows the relationship between the viscosity values of alumina slurries containing different content of agar. In all solid contents, the viscosity increased with increasing agar contents from 0.1 to 0.2 wt.% but slightly decreased with agar content from 0.2 to 0.3 wt.% except in the case of 65 wt.% solid loading. This was in agreement with the strong reduction of solid loading in the final slurries, as can be seen in Table 1. However, all composition exhibited good fluidity and could be poured into the mould. After casting and cooling in a refrigerator at 10°C, they change to gel due to hydrogen bonding that leads to the development of double helix structure [4].

Table 1 Contents of agar and solid loading of alumina in the slurries.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Initial solid Loading (wt.%)</th>
<th>Amount of agar (wt.%)</th>
<th>Final solid loading (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G1</td>
<td>65.0</td>
<td>0.10</td>
<td>63.0</td>
</tr>
<tr>
<td>G2</td>
<td>65.0</td>
<td>0.20</td>
<td>61.1</td>
</tr>
<tr>
<td>G3</td>
<td>65.0</td>
<td>0.30</td>
<td>59.3</td>
</tr>
<tr>
<td>G4</td>
<td>70.0</td>
<td>0.10</td>
<td>67.7</td>
</tr>
<tr>
<td>G5</td>
<td>70.0</td>
<td>0.20</td>
<td>65.5</td>
</tr>
<tr>
<td>G6</td>
<td>70.0</td>
<td>0.30</td>
<td>63.4</td>
</tr>
<tr>
<td>G7</td>
<td>75.0</td>
<td>0.10</td>
<td>72.3</td>
</tr>
<tr>
<td>G8</td>
<td>75.0</td>
<td>0.20</td>
<td>69.8</td>
</tr>
<tr>
<td>G9</td>
<td>75.0</td>
<td>0.30</td>
<td>67.5</td>
</tr>
</tbody>
</table>

Fig. 1 Viscosity of alumina slurries as a function of total content of agar.

The shrinkage and density of dried bodies were characterized, as shown in Table 2. The shrinkage of dried bodies ranging from 1 to 12 % depended on solids content. Shrinkage is lower when the solid content is higher. The density of dried bodies ranging from 51-57% of TD depended on the final solid loading. From these results, G7 had highest density due to highest solid loading. Homogeneity of green bodies are observed as shown in Fig. 2, which compares the SEM microstructure of sample G7, G8 and G9. All sample exhibited good particle packing. Furthermore, agglomeration was not found in these bodies.

Table 2 Linear shrinkage (%) and density of dried bodies.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Linear Shrinkage (%)</th>
<th>Green density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>G2</td>
<td>10.1±0.74</td>
<td>52.0±0.10</td>
</tr>
<tr>
<td>G3</td>
<td>11.1±0.76</td>
<td>51.2±0.04</td>
</tr>
<tr>
<td>G5</td>
<td>8.17±0.87</td>
<td>54.8±0.04</td>
</tr>
<tr>
<td>G6</td>
<td>9.52±0.31</td>
<td>54.6±0.36</td>
</tr>
<tr>
<td>G7</td>
<td>4.35±0.70</td>
<td>57.2±0.55</td>
</tr>
<tr>
<td>G8</td>
<td>5.63±0.46</td>
<td>55.8±0.49</td>
</tr>
<tr>
<td>G9</td>
<td>8.66±0.73</td>
<td>55.9±0.30</td>
</tr>
</tbody>
</table>

Fig. 2 SEM micrographs of fractured surface of green bodies prepared from composition (a) G7, (b) G8 and (c) G9.

Green casts bodies were sintered at 1300 and 1350°C for 2 h in air. Only G7 could be sintered to the condition of closed porosity (>95% of TD.) at 1300°C. When the temperature was increased to 1350°C, the densities of all compositions reached to >95 % TD. However, lower sintering temperature was desirable to suppress the grain growth, so G7 sintered at 1300°C was selected for HIPing. The density of sinter specimens is shown in Fig. 3.

Sintered specimens were put in a graphite crucible, and then hot isostatic pressed under Ar gas pressure at 1300°C for 2 h. After HIPing, density reached to 100% of TD, grain size was 0.56 μm, as shown in Fig. 4.

Fig. 5 shows the transparency of HIPed specimen. The transmittance increased with increasing wavelength, as shown in Fig. 6. The transmittance measured at wavelength 645 nm was 17 %. Table 3 compares the transmittance of our specimen (G7) to that of sapphire and fine grained transparent alumina in the literatures [3, 5, 6]
Table 3 Percent transmittance for our (G7) specimen vs. sapphire and other submicrometer alumina.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (mm)</th>
<th>%T at 645 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sapphire[3]</td>
<td>3.17</td>
<td>85.8</td>
</tr>
<tr>
<td>Ref.3</td>
<td>0.80</td>
<td>71.0</td>
</tr>
<tr>
<td>Ref.5</td>
<td>0.80</td>
<td>60.0</td>
</tr>
<tr>
<td>Ref.6</td>
<td>0.80</td>
<td>61.3</td>
</tr>
<tr>
<td>G7</td>
<td>0.80</td>
<td>16.9</td>
</tr>
</tbody>
</table>

Fig. 3 Densities of sintered specimens formed by gel casting method.

Fig. 4 SEM micrograph of G7 pre-sintered in air at 1300°C for 2 h followed by hot isostatic press at 1300°C for 2 h.

Fig. 5 Transparency of sintered specimen formed by gel casting using agar as gelling additive.

4. Conclusions

Alumina green bodies were obtained by mixing well dispersed 65-75 wt.% alumina slurries with agar solution until content of agar introduced into alumina were 0.1, 0.2 and 0.3 wt% based on dry solid. The density distributed in the range from 51-57% of TD. It depended on final solid loading and increased with increasing solid loading. Only 75 wt.% alumina and 0.1 wt.% agar composition could be sintered and exceed 95% of TD at 1300°C, so it was selected for HIPing. After HIPing, specimen showed transparency with mean grain size was 0.56 μm. The transmittance measured at 645 nm was 17%. However, the transmittance of our specimen was relative low compared to specimens from literature. Decreasing alumina grain to nanometer level can be achieved by decreasing sintering temperature. The alumina will show better optical transparency.

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References
