Study on the anisotropic grain growth of alumina by gel-casting route

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Abstract

Anisotropic grain growth is not one of the intrinsic properties of alumina but rather is an extrinsic property that is controlled by certain additives that are introduced during powder synthesis, processing, or sintering. In this paper, 96\% of alumina ceramics with different additives were fabricated by gel-casting, the microstructures of the ceramics were investigated and the sintering mechanism was discussed. The results showed that only spherical grains were obtained when only liquid-forming additives of silica (SiO\textsubscript{2}) and calcium oxide (CaO) were introduced. Alternatively, only CaF\textsubscript{2} was introduced to the specimen, the grains grew abnormally. When three kinds of additives, i.e., SiO\textsubscript{2}, CaO and CaF\textsubscript{2}, with appropriate amount were introduced, elongated grains could be achieved which matched our target microstructure and density.

1. Introduction

Alumina ceramics is widely applied as engineering and functional materials due to its excellent mechanical properties, high temperature resistance and low cost, however, as all other kinds of ceramics, fragility is inhibiting its further service. Over the last decade significant improvements in enhancing fracture toughness have been gained by tailoring the additives employed.[1-4] Modification of the specific additives amount has been shown to enhance the fracture toughness. Among all the fracture toughening researches, the formation of a microstructure consisting of elongated grains in a fine grained matrix can significantly impact on improve mechanical properties of Al\textsubscript{2}O\textsubscript{3} ceramics where the elongated...
grains can function as reinforcements similar to whiskers or fibers in reinforced ceramics, such elongated reinforcing grains in Al₂O₃ ceramics can be introduced by seeding techniques[5] or enhanced by anisotropic grain growth during sintering [6]. A numerous of experimental results demonstrate that the anisotropy in the growth of alumina grains can be significantly altered by the choice of sintering additives, but most of them are among the glass-forming additives like Kaolin, SiO₂, CaO, CaO and MgO or changeable electrovalence oxide like TiO₂, Cr₂O₃, Fe₂O₃ and MnO₂. In the former research, CaF₂ was introduced as additive was mentioned once[7], the work was also carried out in my search team, it just happened to detect the phenomenon of elongated grains growth with fluoride additive but no quantitative research. In this paper, both fluoride and liquid-forming additives were researched about their effect on the grain growth and the appropriate amount of them for achieving the desired microstructure.

2. Experimental

2.1. Raw Materials.

Table 1 Compositions of different specimens with raw materials

| Specimen No. | No.0 | No.1 | No.2 | No.3 | No.4 | No.5 | No.6 | No.7 |
|--------------|------|------|------|------|------|------|------|------|
| Raw Materials | SiO₂/g | 0 | 24.00 | 0 | 24.00 | 21.82 | 25.71 | 27.10 | 31.11 |
| | CaCO₃/g | 0 | 28.57 | 0 | 12.70 | 16.60 | 9.64 | 7.17 | 0 |
| | CaF₂/g | 0 | 0 | 55.70 | 12.38 | 12.38 | 12.38 | 12.38 | 12.38 |
| | Al(OH)₃/g | 15.29 | | | | | | |
| | α- Al₂O₃/g | 950.00 | | | | | | |
| | Deionized water/mL | 150.00 | | | | | | |
| | Dispersant/mL | 15.00 | | | | | | |
| | Modifier/mL | 15.00 | | | | | | |
| | Monomer/g | 25.00 | | | | | | |
| | Crosslinker/g | 1.30 | | | | | | |

α- Al₂O₃ (Shangdong Aopeng Industry and Trade Co., Ltd) was the main starting material with average particles size of 2.5μm, Talc (Haicheng Talc Powder Factory), SiO₂ (Sinoma Kaolin Company), CaCO₃ (Zibo Rifen Factory) and CaF₂ were used as additives. All of the above materials were commercially pure. The composition of all the specimens are showed in table 1. The specimen of No.0 only contained α- Al₂O₃, no any additive. The additives of SiO₂ and CaCO₃ with a weight ratio of 1.5 were introduced into the specimen of No.1. CaF₂ was a unique additive for No. 2. For the specimens of No.3 – No.7, the amount of CaF₂ was constant, alternatively, the weight ratios of SiO₂ to CaO were 1.2, 1.8, 2.1 and 3.5, respectively.
2.2. Experimental Procedure

The experimental procedure of gel-casting is illustrated in Fig.1.

First, a ceramic suspension was needed to be prepared. Deionized water and glycol were used as solvents, AM (CH=CHCONH₂) as monomer, MBAM[(C₂H₃CONH)₂CH₃] as crosslinker, NH₄OH(27V%) as dispersant and organic alkali as regulator. After milling for 22h with alumina milling balls in mill jar, the suspension became homogeneous and castable ceramic slurry with moderate solid loading, then the castable ceramic slurry was de-gased with vacuum bubble trap until there were no any bubbles observed by naked eye. After that, appropriate amount of (NH₄)₂S₂O₈ as initiator and TEMED[(CH₃)₂NCH₂CH₂N(CH₃)₂] as catalyst were added slowly into the slurry. Subsequently, the slurry was injected into the mould which made from glass, the monomer and the cross linker were activated by initiator and catalyst. As a result, a three-dimensional network structure which made the in-

![Flow chart of gel-casting procedure](image-url)

![Sintering schedule of alumina ceramics](image-url)
situ solidification of the ceramic powders slurry was formed. After the gelation for 10 min and demoulding process, a homogeneous wet green ceramic body with uniform chemistry composition and density that contained only a few percent organic binder was prepared. Whereafter, drying process was carried out in an oven at 80 °C for 24 h, and meanwhile controlled its arc shape with plaster moulds. Binder removal and subsequent pressureless sintering in high temperature furnace are showed in Fig.2. After sintering, the densities of the specimens were measured by the Archimedes method using distilled water. Microstructural analysis was conducted by SEM (JSM 840A, JEOL, Tokyo, Japan).

3. Results and Discussion

3.1. Effects of different additives on the microstructure of alumina ceramics

Fig.3 The SEM photographs of sintering surface for the specimens No.0, No.1, No.2 and No. 3 sintered at 1560 ºC for 120 min.

The microstructures of sintering surface for the specimens No.0, No.1, No.2 and No. 3 sintered at 1560 ºC for 120 min are showed in Figs .3 and 4. It can be seen that only spherical grains were obtained with very low density when no additives were introduced (Fig3a and Fig4); when only liquid-forming additives silica (SiO₂) and calcium oxide (CaO) were introduced, grains morphology didn’t change but
density increased dramatically (Fig.3b and Fig.4). Only CaF$_2$ was introduced, the grains grew abnormally. Coarse platelet grains were observed (Fig.3c), and relative density was 93% (Fig.4). whereas, additives of SiO$_2$, CaO and CaF$_2$ coexisted, the microstructure changed significantly. Elongated corundum grains were gained (Fig.3d), furthermore, the density increased tremendously (Fig.4).

The dramatic effects of CaF$_2$ on the sinterability and microstructure of alumina were demonstrated. Why CaF$_2$ is so effective on the grains growth? There were no reports about it before. We suppose it may be the decomposition of CaF$_2$ to form gas phase, the evaporation of the gas accelerate the oriented grains growth. While both liquid-forming and the gas-forming additives coexisted, a synergistic effect resulted in a formation of columnar grains. Intergranular glass phase and gas phase are the prerequisite that leads to abnormal grain growth in alumina ceramics.

3.2. Effects of ratios of SiO$_2$ to CaO on the ceramics microstructures

Our intention to use different amounts of the additives was to seek the optimal ratios of SiO$_2$ to CaO for the highest density and corundum grains growth microstructure, which play a role like reinforced fiber or whiskers. Abnormal grain growth with the ratios of 1.2 and 1.8 for SiO$_2$ to CaO (Figs.5a and 5b) was observed. but the density of the specimens with a ratio of 1.2 was much higher than that of 1.8 (Fig.6).

However, as the ratio of SiO$_2$ to CaO increased, the abnormal grains growth phenomenon disappeared, instead, all grains were spherical (Figs.5c and 5d). The densities were out of expectation. When the ratio of SiO$_2$ to CaO was 2.1, only 95% relative density was reached. Whereas, relative density was 96.9% for the ratio of 3.5 (Fig.6). Therefore, not only the ceramics densities, but also the microstructures were influenced by the additive composition. So we may conclude that the best prescription is No.5 in the present study.

![Fig.4 The contrast chart of the specimen densities](image)

As for the liquid phase sintering, it is often divided into three stages [8]. First, particle rearrangement: motion of solid particles due to capillary forces is responsible for the initial densification of the compact; secondly, solution–reprecipitation: different solubilities of the solid in the liquid are responsible for the transport of the material from the points of solid–solid contacts to the free surfaces of the particles; thirdly, coalescence: permanent solid–solid contacts between particles form liquid phase sintering ends. S. Pejovnik [9] has concluded that particle rearrangement is the primary mechanism of densification in the
liquid phase sintered alumina. There are two types of rearrangement, they are the rearrangement of initial alumina particles and the rearrangement of alumina grains after a liquid has dissolved the solid necks between these grains. The second type of rearrangement can take place in different stages of the liquid phase sintering process and affects densification. Viscosity of the liquid phase sintering is a very important characteristic, which can influence the densification and also microstructure in these stages. Viscosity depends on the temperature and also on the chemical composition of the liquid phase. In this study, the sinter temperature was fixed, so the viscosity was only affected by the chemical composition of the liquid phase here. Theoretically, the higher the ratio of SiO₂ to CaO is, the higher viscosity is. It was at the eutectic temperature. Thus, the particles sizes were supposed smaller and smaller as the high viscosity inhibited the grains grow and linear densification was achieved as the ratio of SiO₂ to CaO increased.

For explaining our results, the viscosity and also the evaporation of CaF₂ could be regarded as two forces to the ceramic grains, when the force from the viscosity was smaller than the force from the evaporation, or rather, no force from the viscosity at all, very coarse grains were detected. Contrarily, the grain growth was limited when viscosity was high. Only when the moderate amount of the liquid-forming additives and fluoride were introduced, the elongated corundum grains could be obtained which was the desired columnar microstructure.

Fig.5 The SEM photographs of sintering surface for the specimens with different ratios of SiO₂ to CaO sintered at 1560 °C for 120min.
4. Conclusions

1. In contrast to the alumina ceramics without additives, the specimen with glass-forming additives SiO₂ and CaO, still showed equiaxed grains morphology accompanying with an increase of density.
2. While CaF₂ was introduced as a unique additive, the grains grew abnormally, i.e., a specimen with coarse platelet grains and low density was obtained.
3. A synergistic effect of CaF₂, SiO₂ and CaO, the grains morphology changed dramatically. Elongated corundum grains evolved.
4. The ratio of SiO₂ to CaO affected not only the density, but also grain morphology of specimen, the optimal ratio of SiO₂ to CaO in the present study was 1.8.

Acknowledgments

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