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Effect of a small amount of liquid-forming additives on the microstructure of Al_2O_3 ceramics

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Sintering behaviour and microstructure of Al_2O_3 ceramics without additives and with 0.02–0.25 mol % $CaO + SiO_2$ ($CaO/SiO_2 = 1$) were investigated. When Al_2O_3 bodies were sintered at 1400 °C, the sinterability and the grain size decreased as the content of $CaO + SiO_2$ increased. When Al_2O_3 ceramics with 0.05–0.25 mol % $CaO + SiO_2$ were sintered at higher sintering temperature, both CaO and SiO_2 reacted with Al_2O_3 to produce the liquid phase along grain boundaries, and exaggerated platelet Al_2O_3 grains, with an aspect ratio of about 4.5, were formed. Because the size of platelet grains decreased as the content of $CaO + SiO_2$ increased, the distribution of either SiO_2 particles or this intergranular phase of $CaO–Al_2O_3–SiO_2$ might control the microstructure.

1. Introduction

Since the development of high-purity Al_2O_3 powders, the effect of impurities on the microstructure of Al_2O_3 ceramics has been recognized. In particular, impurities, such as calcium, magnesium and silicon, can affect the sintering behaviour and the grain shape of Al_2O_3 ceramics. The addition of silicon prevented the growth of Al_2O_3 grains, but the existence of both silicon and calcium caused the production of liquid phase along the grain boundaries by the reaction with Al_2O_3 [1]. This liquid phase made the distribution of grain boundary–grain boundary dihedral angles wide and the grains grew discontinuously. The addition of MgO could reduce the effects of impurities on grain growth by increasing the bulk solubility and decreasing interfacial segregation of impurities (i.e. silicon and calcium) and by narrowing the distribution of the dihedral angle [2].

It was reported that elongated grains were observed with plate-like and platelet shape, when $Na_2O + SiO_2$, $CaO + SiO_2$, $SrO + SiO_2$ or $BaO + SiO_2$ were added. It was considered that the flat boundaries along the long axis were wetted by the liquid phase during sintering [3, 4]. This microstructure was obtained by the addition of other liquid-forming additives such as anorthite [5], and $CuO + TiO_2 + B_2O_3 + MgO$ [6]. These flat boundaries were basal plane and they changed to curved boundaries after impingement of plate-like grains.

The objective of this study was to investigate the effect of the amount of liquid-forming additives on the sintering behaviour and the microstructure of Al_2O_3 ceramics. We chose both CaO and SiO_2 as additives and their molar ratio was 1.

2. Experimental procedure

High-purity (99.99%) Al_2O_3 powder was used as the starting powder in order to prevent contamination. Both CaO and SiO_2 were chosen as additives and their molar ratio was 1. CaO and SiO_2 were added in the form of $CaCO_3$ and SiO_2 powder.

0.02, 0.05, 0.15 and 0.25 mol % $CaO + SiO_2$ were added to Al_2O_3 powder and ball-milled in ethanol for 24 h with high-purity (99.5%) Al_2O_3 balls. These powder mixes were calcined at 800 °C for 1 h after being dried.

The powder mixes were uniaxially pressed at 8 MPa and cold isostatically pressed at 250 MPa. The green density was about 60% theoretical density. These green compacts were sintered at 1300–1600 °C for 4 h in air. The sintered samples were cut off, polished with a series of diamond pastes down to a final polish of 0.5 μm, and thermally etched at 1300–1400 °C for 30 min. The etched surfaces were examined by scanning electron microscopy (SEM) to investigate the Al_2O_3 grain size. The distribution of calcium and silicon was analysed by electron probe microanalysis (EPMA).

The grain size of Al_2O_3 ceramics with equi-axed grains was obtained by a linear-intercept method. The size of platelet grains was calculated from the equation derived by Fullman [7]. We assumed that the shape of the platelet grains was circular, and measured the size

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of about 100 grains for each sample to obtain the diameter, the thickness, the aspect ratio and the volume.

3. Results and discussion

Sintering behaviour of undoped and CaO + SiO_2-doped Al_2O_3 ceramics is shown in Fig. 1. The undoped sample could be densified at 1300 °C, but the sinterability of doped samples decreased as the content of additives increased.

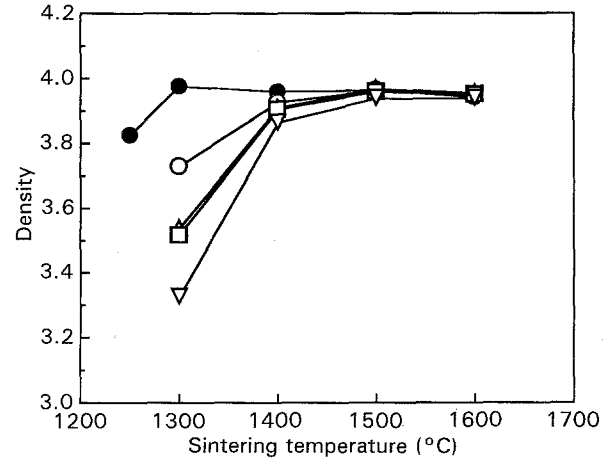

Figure 1 Influence of CaO + SiO_2 content on the sintering behaviour of Al_2O_3 ceramics. (●) 0, (○) 0.02, (△) 0.05, (□) 0.15, (▽) 0.25 mol %.

The microstructure of Al_2O_3 ceramics is shown in Fig. 2. The grain shape of the undoped samples was equi-axed and the grain growth occurred when sintered at higher sintering temperature. CaO + SiO_2-doped samples had equi-axed grains at 1400 °C, which decreased in size as the content of additives increased. When sintered at 1500 °C, 0.02 mol %-doped sample did not show discontinuous grain growth, but a part of grains with 0.05 mol % additives grew discontinuously to platelet grains among the fine grains, and all grains grew exaggeratedly in the samples with 0.15–0.25 mol % additives. When sintered at 1600 °C, all samples with the content of more than 0.05 mol % had platelet grains.

The grain size and the aspect ratio of Al_2O_3 ceramics are shown in Fig. 3. The grain size decreased at 1400 °C as the content of additives increased. When sintered at 1500 and 1600 °C, the samples with a content of more than 0.05 mol % grew discontinuously to produce platelet grains, the diameter and thickness of which decreased as the content increased and their aspect ratio was about 4.5. The size of the platelet grains in the samples with 0.15 and 0.25 mol% CaO + SiO_2 slightly increased when the sintering temperature was raised from 1500 °C to 1600 °C.

During sintering, CaO and SiO_2 reacted with Al_2O_3 to produce liquid phase. The phase diagram of the Al_2O_3–CaO–SiO_2 system indicates that the liquid is formed at 1170 °C, but it was considered that it was

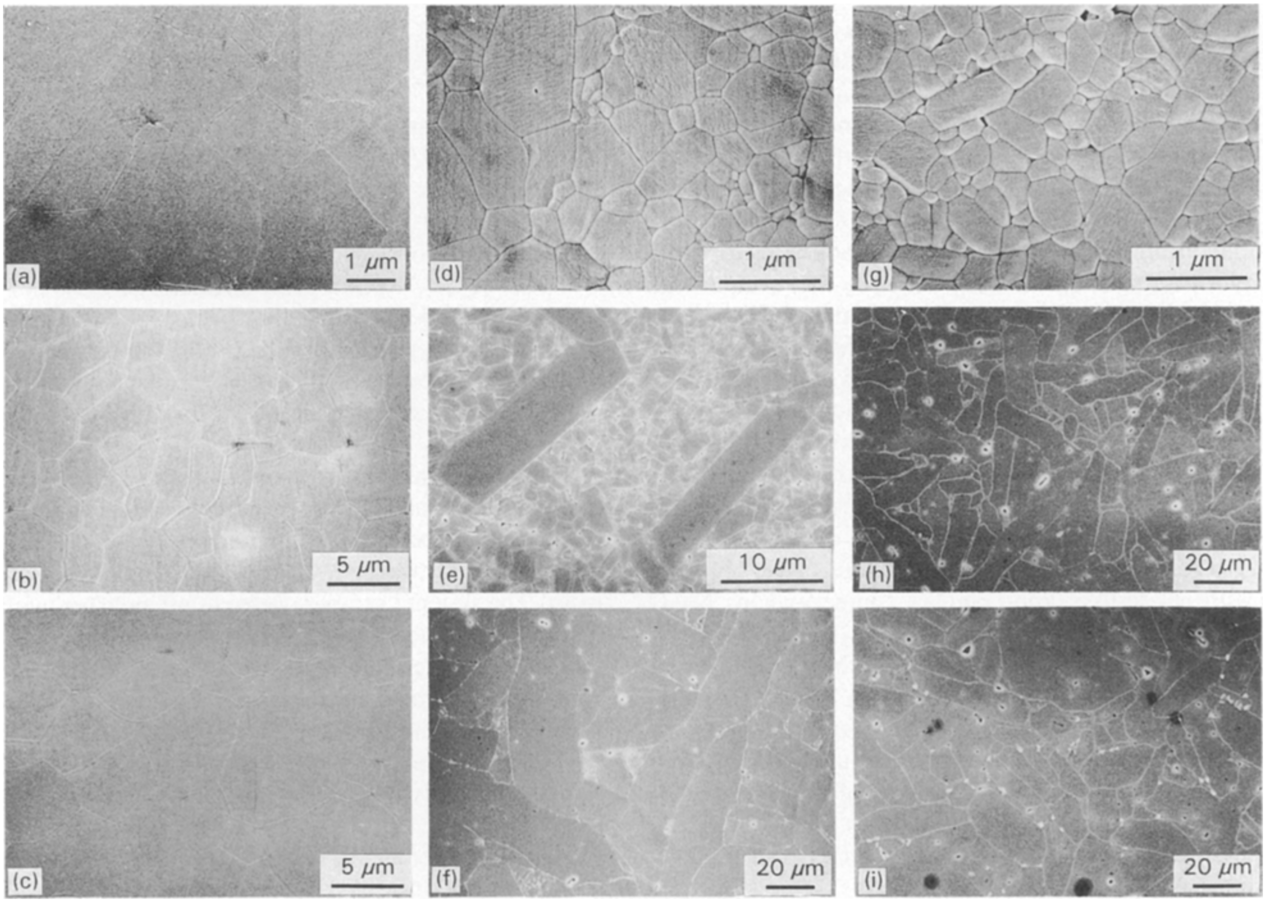

Figure 2 Typical microstructure of Al_2O_3 ceramics doped with CaO + SiO_2. The content of CaO + SiO_2 and the sintering temperature are: (a) 0 mol %, 1400 °C; (b) 0 mol %, 1500 °C; (c) 0 mol %, 1600 °C; (d) 0.05 mol %, 1400 °C; (e) 0.05 mol %, 1500 °C; (f) 0.05 mol %, 1600 °C; (g) 0.25 mol %, 1400 °C; (h) 0.25 mol %, 1500 °C; and (i) 0.25 mol %, 1600 °C.

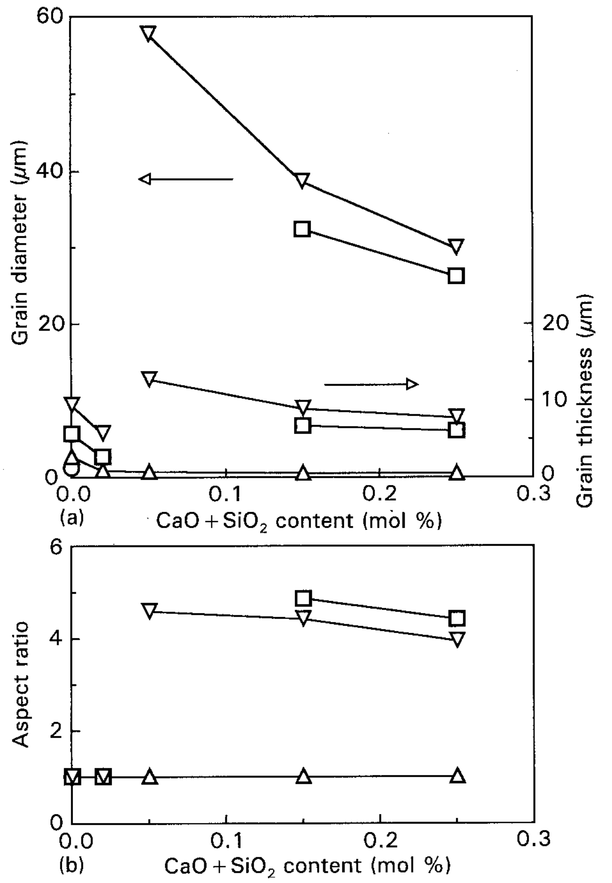

Figure 3 Influence of CaO + SiO_2 content on (a) the grain diameter and the thickness and (b) the aspect ratio of Al_2O_3 ceramics. We chose the grain size measured by a linear intercept method for Al_2O_3 with equi-axed grains, and the grain diameter and thickness calculated using the equation derived by Fullman [7] for Al_2O_3 with platelet grains. (○) 1300 °C, (△) 1400 °C, (□ 1500 °C, (▽) 1600 °C.

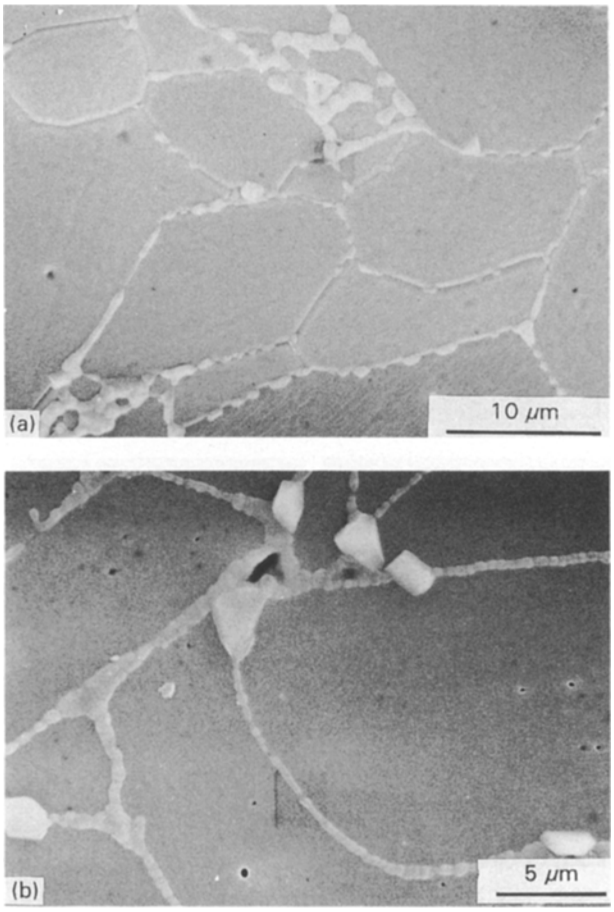

Figure 4 Etched surfaces of Al_2O_3 ceramics observed at higher magnification. The content of CaO + SiO_2 and sintering temperature are: (a) 0.05 mol %, 1600 °C; (b) 0.25 mol %, 1600 °C.

difficult to form the liquid at this temperature because CaO and SiO_2 were added in the form of powder and their content was remarkably small. As shown in Fig. 4, the surfaces etched at 1300 °C were observed at higher magnification. It was observed that the intergranular phase of the samples with 0.05 and 0.25 mol % CaO + SiO_2 spread from the Al_2O_3 grain boundary. From observations using EPMA (Fig. 5), this phase contained both calcium and silicon. These phenomena indicated that this phase was formed by the reaction between CaO, SiO_2 and Al_2O_3 at 1500 °C or above, and changed to liquid phase when the samples were etched at 1300 °C. Therefore, it was considered that liquid-phase sintering occurred when Al_2O_3 ceramics contained a small amount of CaO + SiO_2. On the other hand, the intergranular phase was not seen in the samples sintered at 1400 °C, and the additives played a role as obstacles which prevented grain growth, because the content was insufficient to produce liquid phase or the viscosity of the liquid phase was too high.

As already mentioned, the formation of these platelet grains was affected by the existence of liquid phase produced during sintering. The phase diagram of the CaO–SiO_2–Al_2O_3 system shows that the liquid content increase when samples with larger content of additives are sintered at higher temperature. On the other hand, the diffusion coefficient increases by one order from 1400 °C to 1500 °C [8]. The increase of both liquid content and diffusion coefficient had a large influence on the formation of these platelet grains. The morphology of platelet grains was also affected by the formation of liquid phase. It was considered that the formation of liquid phase along grain boundaries made the interfacial energy of basal planes low and the difference of the energy between the basal planes and the other planes controlled the morphology.

The liquid phases did not form uniformly in this study because $CaCO_3$ and SiO_2 powder were used as additives. Liquid phase was formed around SiO_2 particles because the size of SiO_2 particles was larger. SiO_2 reacted with CaO and Al_2O_3 to produce liquid phase which increased the rate of grain growth. Therefore, it was considered that platelet grains were formed at some position where SiO_2 particles were distributed, as shown in Fig. 2e (0.05 mol % CaO + SiO_2 doped samples sintered at 1500 °C), even if it was unknown if the nuclei, where platelet grains were formed, were either a part of Al_2O_3 powder added initially or nuclei formed by solution/precipitation. Fig. 6 shows the relationship between the content of additives and the grain volume. Assuming that SiO_2 particles produced the same number of platelet grains, the size of the platelet grains decreased as the content

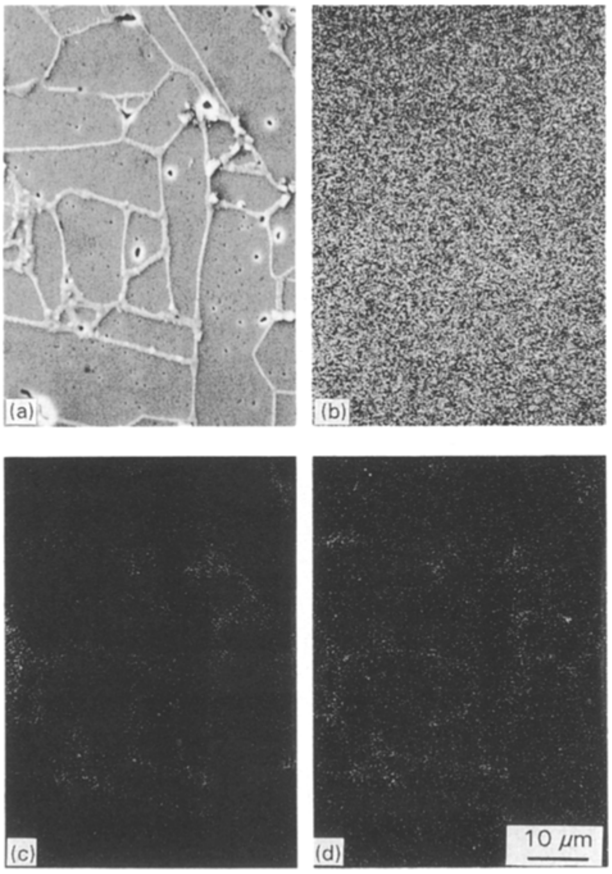

Figure 5 EPMA of 0.25 mol % CaO + SiO_2-doped Al_2O_3 ceramics. (a) SEI, (b) the distribution of aluminium, (c) the distribution of calcium and (d) the distribution of silicon.

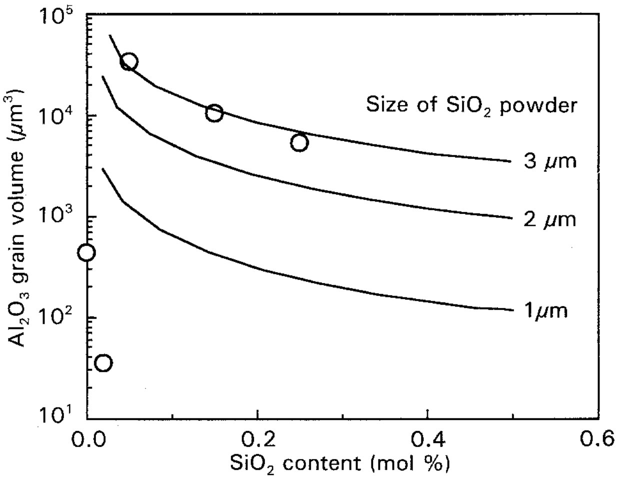

Figure 6 Effect of CaO + SiO_2 content on platelet grain volume of Al_2O_3 ceramics. Lines indicate the grain volume when it is assumed that the number of SiO_2 powder particles is equal to the number of Al_2O_3 platelet grains.

increased, and lines indicate the grain volume when the size of SiO_2 particles is 1, 2 or 3 μm. From these lines, the size of SiO_2 particles in the powder mixes was thought to be about 3 μm. This result indicated that the size and the distribution of SiO_2 particles affected the distribution of liquid phase during sintering and controlled the formation of platelet grains, i.e. the microstructure of Al_2O_3 ceramics. When the size of the SiO_2 particle is sub-micrometre, however, it is considered that liquid phase is formed at the position where a couple of SiO_2 particles react with CaO and Al_2O_3 particles to produce one platelet grain and the number of platelet grains is less than the number of SiO_2 particles. Therefore, the size of platelet grains does not change when the size of the additives is extremely fine. In order to facilitate further consideration precise experimentation on the sintering behaviour of doped Al_2O_3 ceramics and the observation of the intergranular phase are required.

4. Conclusions

The sintering behaviour and the microstructure of Al_2O_3 ceramics without additives and with 0.02–0.25 mol % CaO + SiO_2 ($CaO/SiO_2 = 1$) were investigated. The results are summarized as follows.

1. When Al_2O_3 bodies were sintered at 1400 °C, the sinterability of Al_2O_3 ceramics decreased and the grain size decreased as the content of CaO + SiO_2 increased.
2. When Al_2O_3 ceramics doped with 0.05–0.25 mol % CaO + SiO_2 were sintered at 1500 °C and 1600 °C, both CaO and SiO_2 reacted with Al_2O_3 to produce the liquid phase along grain boundaries, and exaggerated platelet Al_2O_3 grains, with an aspect ratio of about 4.5, were formed. Because the size of platelet grains decreased as the CaO + SiO_2 content increased, it was considered that the distribution of additives which controlled the distribution and the character of this intergranular phase, controlled the formation of platelet grains, i.e. the microstructure of Al_2O_3 ceramics.

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