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Improvement of sintering and microstructural homogeneity of a diphasic mullite

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Abstract

Effect of seeding of boehmite–colloidal silica mixture with aluminium sulphate–colloidal silica mixture on its mullite formation and sintering behaviours and microstructural development was studied. It was observed that early forming mullite crystallites from aluminium sulphate–colloidal silica mixture acted as nuclei for boehmite–silica mixture and improved mullite formation behaviour. Although seeding reduced viscous flow sintering behaviour of boehmite–colloidal silica mixture, its solid state sintering behaviour was improved as seeding reduced mullite grain size and prevented the occurrence of fine intragranular pores within mullite grains.

Keywords: Grain size; Mullite; Seeding; Sintering; Sol–gel processes

1. Introduction

Mullite has very attractive high temperature properties such as creep resistance, strength and hardness retention up to high temperatures.[1] Therefore, there has been numereous research on the processing of high density mullite ceramics and these include sintering of crystalline mullite powders[2–6] and reaction sintering of alumina–silica mixtures of varying particle sizes.[7–19]

Due to the low diffusivities of aluminium and silicon in mullite, sintering of even much fine (≈0.1 μm) mullite powders has to take place above 1600°C to get high densities.[4,5] On the other hand, mullite formation and sintering behaviour varies greatly during the reaction sintering, depending on the scale of mixing. Micron scale mixtures (e.g. α-Al_2O_3 and quartz) requires temperatures in excess of 1600°C for both sintering and mullite formation.[19] Meanwhile, colloidal scale boehmite and silica mixtures (also known as diphasic mixtures) were found to sinter to high densities ($>95\%$) at temperatures as low as 1250°C.[7–11,13] In this case, densification was found to be due to viscous flow of amorphous silica (presumably containing some dissolved alumina) before mullite formation. As soon as mullite forms, the densification was observed to stop sharply until high temperatures where further densification, if required, takes place by diffusion. Therefore, it is well established that mullite formation should be avoided as much as possible in order to achieve high densities by viscous flow sintering. Once densification was achieved, the mullitization takes place by continued heat treatment at sintering temperature or by slightly increasing the temperature.

Mullite formation behaviour from the diphasic mixtures depends on their fineness. For instance, using aluminium sulphate solution as the alumina source instead of colloidal boehmite particles (≈20 nm particle size) both with colloidal silica (≈15 nm particle size) caused early mullite formation due to finer nature of the sulphate derived alumina than boehmite.[12,13] This resulted in poor viscous flow sintering behaviour of the powder derived from aluminium sulphate–colloidal silica mixtures in that only 70% density was achieved by viscous flow sintering at 1250°C after 5 h.[12] On the other hand, the boehmite–collodial silica mixture could be sintered to $>95\%$ density after 2 h.[7–10,13] In spite of its poor viscous flow sintering behaviour, denser mullite ceramics ($>98\%$) were obtained from aluminium sulphate–colloidal silica derived powder than boehmite–colloidal silica derived powder when sintered in a solid state at or above 1500°C.[13] This was possibly due to the engulfment of

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fine pores by large mullite grains forming in boehmite–colloidal silica derived powder and these pores were difficult to eliminate.[20]

Engulfment of fine pores by growing mullite grains and their persistence even up to 1600°C during mullite formation in sintered boehmite–colloidal silica mixtures have been observed by Wei and Halloran[21] and Kara and Little[13] in their analysis by transmission electron microscopy. They concluded that these pores were larger interagglomerate pores inherited from the green compacts which could not be eliminated during viscous flow sintering. On heating to high temperatures, the pores were observed to become facetted and aligned parallel to [001] direction of mullite.[22]

Elimination of intragranular pores requires that pores should first travel through lattice to grain boundaries, which act as vacancy sink, and then through the grain boundaries to the surface.[20] Diffusion through lattice, especially in mullite,[23] is very slow and thus elimination of such pores requires high temperatures (>1600°C).[13] Similar engulfment of fine pores by growing grains at the later stages of sintering is also observed in solid state sintering of pure alumina and prevents the attainment of full density.[20] This problem in pure alumina is successfully overcome by doping with a small amount of MgO which reduces the grain growth. By doing this, the pores are kept at three grain junctions and at or near grain boundaries and thus are easily eliminated because diffusion through grain boundaries where defect population is high is faster. In a similar analogy to pure alumina ceramics, the aim of this study is to reduce grain size in a mullite produced from boehmite–colloidal silica as a way to remove intragranular pores within mullite grains and thus to improve final density. It is thought that grain size reduction can be achieved by seeding boehmite–colloidal silica derived powder by aluminium sulphate–colloidal silica derived powder because early forming mullite crystallites in the latter should act as in-situ seeds. The effect of this seeding on mullite formation, sintering behaviour and microstructural development of boehmite–colloidal silica derived powder will be reported.

2. Experimental

Preparation of powders obtained from pseudo-boehmite–colloidal silica (hereafter referred to as powder A) and from aluminium sulphate–colloidal silica (hereafter referred to as powder B) has been described elsewhere in detail.[13] Briefly, powder A was prepared by calcining the boehmite–silica gel at 550°C and milling in methanol for 24 h. Powder B was prepared by mixing the silica sol with aqeuous aluminium sulphate solution. The mixture was gelled, calcined at 1000°C to decompose the sulphate and milled in methanol for 24 h. Powder A and B had surface areas of 220 and 160 $m^2\ g^{-1}$, respectively. They both had an average particle size (rather agglomerate size) of $\approx 2\ \mu m$ after milling.

Powder B (1% and 10%, by weight) was added to powder A by milling the mixture in methanol for 3 h in a ball mill using ZrO_2 balls (1 and 10% powder B seeded powder A will be denoted powder A1 and powder A10, respectively in the following text). The milled powders were dried in an oven at 60°C. For sintering experiments, powders were pressed into pellets in a 13 mm diameter die at 100 MPa which were subsequently isopressed at 300 MPa. The pellets were sintered between 1300 and 1700°C for 2 h in still air and the heating rate during sintering was 5°C min^{-1}. Sintered densities were measured by the water displacement method based on the Archimedes' principle. At least five samples were measured and an average was taken. Relative bulk densities were calculated by taking the theoretical density of mullite as 3.17 g cm^{-3} (JCPDS Card No: 15-776).

The effect of addition of powder B into powder A on mullite formation was studied by X-ray diffraction (Rigaku D-Max 2200, Tokyo, Japan). Microstructural examinations were carried out by scanning electron microscopy [(SEM), CamScan S4, Cambridge, UK] and transmission electron microcopy [(TEM), Philips 400ST, Eindhoven, Holland]. Samples for SEM examinations were thermally etched at 1450°C for 0.5 h after polishing. Grain size of the sintered specimens were measured by linear intercept method on SEM micrographs. At least 50 grains were measured at each condition.

3. Results

Sintering behaviour at various temperatures of powder A together with 1 and 10% of powder B seeding is shown in Fig. 1. Powder A sinters to 92% relative density at 1300°C but the addition of 1 and 10% powder B reduces the density to 89 and 84%, respectively, at the same temperature. However, at higher temperatures (>1400°C) powder A10 shows better sintering behaviour than powders A and A1 in that powder A10 sinters to 97% at 1600°C whereas powders A and A1 sinters to just over 95%.

Fig. 2 shows the extent of crystallization of mullite in the mixtures after 2 h of isothermal treatment at 1250°C. Only the highest intensity peak of mullite (26° 2θ) are barely visible in powder A which indicates that no substantial amount of mullite is formed. However, additions of 1 and 10% powder B cause progressively larger amount of mullite formation in powder A.

Fig. 3(a)–(c) show SEM microstructures of powders A, A1 and A10, respectively, after sintering at 1500°C while Fig. 3(d) gives TEM microstructure of powder A sintered at 1600°C. Many fine pores (30–40 nm in size) visible within mullite grains at 1500°C in powder A [Fig. 3(a)] still remain there even at 1600°C [Fig. 3(d)].

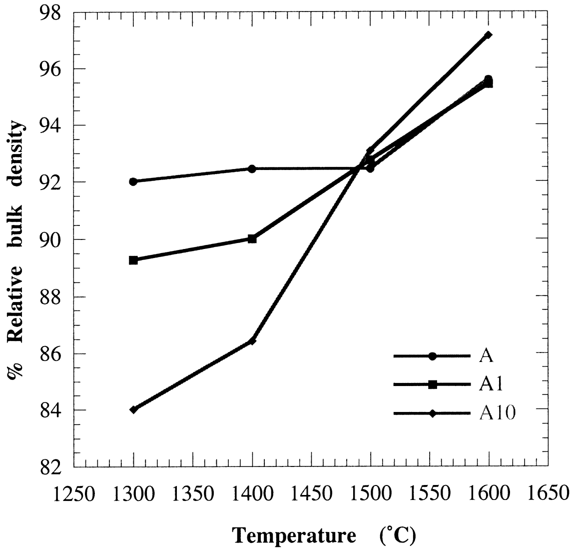

Fig. 1. Change in relative bulk density of powders A, A1 and A10 with sintering temperature. Sintering time is 2 h.

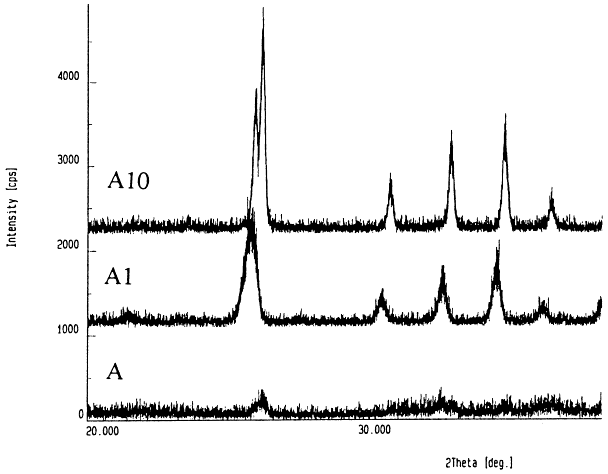

Fig. 2. Crystallization behaviour of powders A, A1 and A10 after calcination at 1250 for 2 h.

Similar to powder A, powder A1 also has fine intragranular pores but less in quantity [Fig. 3(b)]. However, in powder A10, great majority of the pores are located at three grain junctions, not inside mullite grains [Fig. 3(c)].

It can also be seen in Fig. 3(a)–(c) that mullite grain size is reduced dramatically with the amount of powder B addition and this is illustrated in graphic form in Fig. 4 after sintering at 1500 and 1600°C. Grain size of powder A sintered at 1500°C is about 1.2 μm whereas that of powder A10 is about 0.4 μm.

4. Discussion

Previous work on crystallization and early stage sintering behaviour of powder A and powder B by Kara and Little[13] showed that both powders sinter in two dinstinct stages (Fig. 5). In the first stage (before mullite formation), sintering takes place by visocus flow of an amorphous phase and this starts at about 1100°C. While viscous flow sintering helps achieve near full density in powder A at 1250°C, it results in much lower densities in powder B due to early mullite formation in this power (it is to be noted that due to its finer scale mixing, powder B forms mullite at 1200°C, about 50°C lower than powder A at the same isothermal conditions[13]). In the second stage, after the reaction of alumina and silica to form mullite, solid state diffusion has to occur for further densification to take place.[13] Although Fig. 1 shows solid state sintering behaviour of powders A, A1 and A10 at high temperatures, densities attained at 1300°C can mainly be attributed to viscous flow sintering since no significant solid state sintering is expected to occur at this temperature due to very low diffusivity in mullite.[23] As early forming mullite crystallites in powder B enhance mullite formation in powder A by acting as seeds, as seen in Fig. 2, decreased densities with the addition of powder B at 1300°C are expected.

Mullite formation from diphasic aluminosilicate mixtures was shown to occur by self-nucleation from an intermediate amorphous aluminosilicate phase after reaching a critical alumina concentration.[24,25] After the nucleation, the growth of the nuclei takes place with no secondary nucleation. Therefore, the nucleation frequency determines the initial mullite grain size, being higher causes finer mullite grains. Generally, 1–1.5 μm grain size was observed from boehmite–colloidal silica mixtures (e.g. powder A) after crystallization[13,22,26] and this size remains stable up to 1600°C,[22,26] as also seen in Fig. 4. On the other hand, in powder B, nucleation frequency is much higher and thus much finer mullite grains (≈100 nm) were observed to form.[13] Due to its higher nucleation frequency as well as earlier mullite formation behaviour, powder B acts in-situ seeds for powder A to reduce its grain size as observed in Figs. 3 and 4. Since no secondary crsytallization was observed,[24] nucleation frequency and thus mullite grain size in powder A can be controlled by the amount of powder B addition. The minimum mullite grain size achievable should be equivalent to that observed in powder B. Pure powder B grain size when sintered at 1400°C was observed to be ≈130 nm.[13] Similar grain size was also observed in A10 sintered at 1400°C (not shown here). This indicates that 10% is about maximum to get minimum grain size.

Better sintering behaviour of powder A10 than powders A and A1 during solid state sintering (>1400°C) can be understood by comparing the sintered microstructures of these specimens. Powders A and A1 have pores engulfed in mullite grains at 1500°C although the extent is less in A1 [Fig. 3(a) and (b)]. In contrast, due to very fine grain size, the pores are located at three grain

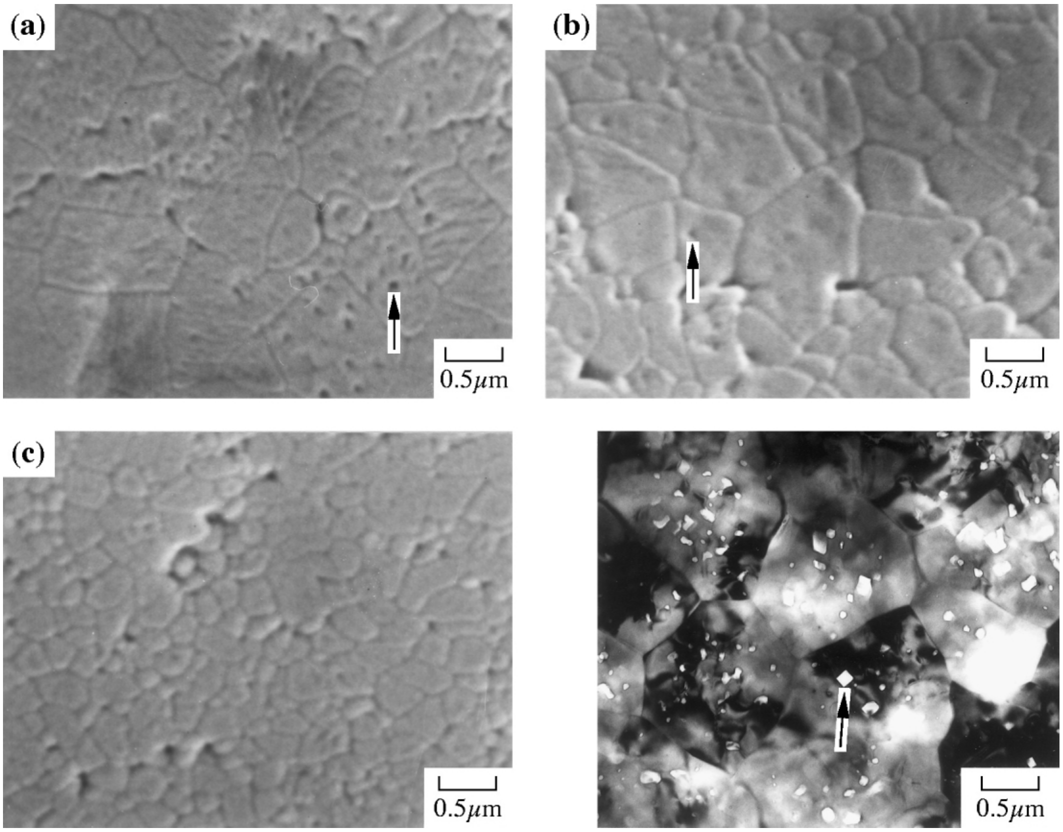

Fig. 3. SEM microstructures of powders (a) A, (b) A1 and (c) A10 after sintering at 1500°C for 2 h; (d) TEM microstructure of powder A after sintering at 1600°C for 2 h. Arrows indicate examples of fine pores.

junctions in powder A10 [Fig. 3(c)] and even if they are located inside mullite grains they will have a very short distance to reach the grain boundaries. Pores located at three grain junctions will diffuse through the grain boundaries to the surface much easier than those located inside mullite grains. This is because pores inside mullite grains will have one extra difficult job to do: to get to the grain boundaries through mullite lattice which have very low diffusivities.[23] Pores visible inside mullite grains even at 1600°C [Fig. 3(d)] further reveals the difficulty of diffusion through mullite lattice. Although, in Fig. 3(d), pores close to grain boundaries are sunk by the grain boundaries, those which are close to grain centres still remain there. The advantage of reducing the grain size of mullite to eliminate intragranular pores and to increase density can thus be realized.

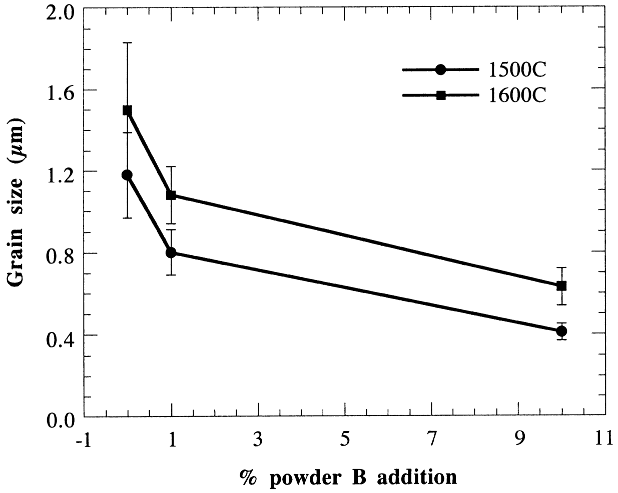

Fig. 4. Change in mullite grain size in powder A with the additions of powder B after sintering at 1500 and 1600°C for 2 h.

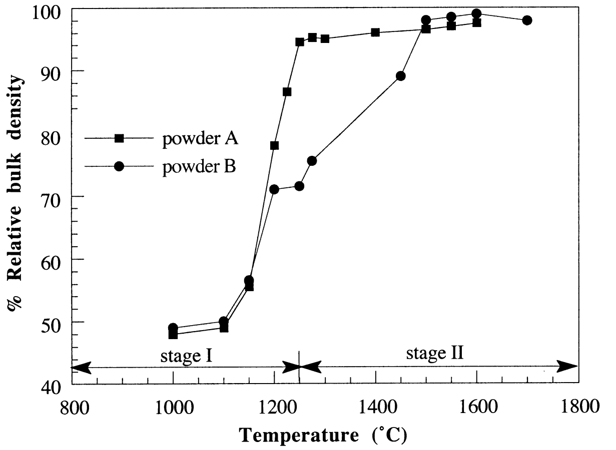

Fig. 5. Comparison of sintering behaviour of powder A and powder B. Redrawn from Ref. 13.

Previous work[26] on detailed microstructural characterization of mullites produced form powder A and powder B has shown that powder B derived mullite is more homogeneous in terms of mullite grain chemistry and glassy phase distribution in that glass present at triple junctions does not wet grain boundaries. Therefore, since powder B seeded powder A produces mullite microstructure very similar to that of powder B, futher advantage with regard to more homogeneous microstructure of mullite can be expected when powder A is seeded with powder B.

5. Conclusions

Grain size in mullite produced from boehmite–colloidal silica (powder A) can be reduced extensively by seeding with aluminium sulphate–colloidal silica derived powder (powder B) because early forming mullite crystallites in powder B act as seeds. This also enhances mullite formation in powder A. The enhanced mullite formation reduces the viscous flow sintering behaviour of powder A. However, reducing the grain size was a way to avoid the occurrence of intragranular pores which were commonly observed in mullites produced from powder A and to obtain denser mullite ceramics with homogeneous microstructure.

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