Densification behaviour and microstructure of gel-derived phase-pure mullite in the presence of sinter additives

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Abstract

Gels with high pure mullite composition have been synthesized using aluminum nitrate nanohydrate and ethyl silicate. Pure mullite has been sintered to 88.5% of the T.D., when sintered at 1600°C for 3 h. Suitable sintering aids such as SrO (0.5 wt.%) and clay (2 wt.%) have tremendous effect in promoting the densification behavior of mullite to attain density to 98 and 95% of T.D. respectively at relatively low temperatures by pressureless sintering. SrO promotes the densification of pure mullite via liquid phase sintering and also does clay assist the viscous flow sintering. Clear differences found in the microstructures of mullite could be related to the different sintering aids, which have apparent effect on the densification behavior. SrO doped samples show a duplex microstructure of fine equiaxed and elongated grain morphology, while the clay doped samples show equiaxed and acicular morphology. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Grain growth; Mullite; Sintering; Sol-gel processes

1. Introduction

Dense mullite ceramics have been produced by various methods including reaction sintering of an alumina–silica mixture and solid state sintering of fine crystalline mullite powders. Similar to other crystalline ceramics with a high degree of covalent bonding, mullite also requires a high temperature (> 1600°C) for densification.[1] This is due to the low inter-diffusion rate of aluminum and silicon ions in mullite and low grain boundary diffusion coefficients. Reaction sintering temperatures of mullite precursors vary widely depending on the scale of mixing. The application of the sol-gel technique to mullite science and technology brings new possibilities in synthesizing high purity single phase mullite at relatively low temperatures ranging from 850 to 1250°C.[2,3] The single-phase gel crystallizes to mullite at lower temperatures than the diphasic gel. The rapid crystallization of mullite in the former gel is not conducive for densification while the diphasic gel leads to enhanced densification apparently due to densification and crystallization in a very narrow temperature range.[4] Therefore, the sintering of stoichiometric pure mullite is very difficult, often necessitating pressure assisted sintering like hot-pressing and hot-isostatic pressing, to achieve a higher densification. Hirata and Shimada[4] have clearly demonstrated that the calcined crystalline mullite powders needed either hot pressing or temperatures above 1650°C to achieve good density. It has also been reported that pure mullite, presumably free of glassy phase, can retain more than 90% of its room-temperature strength up to 1500°C.[5–7] Thus, for high-temperature use, there is an interest commercially in producing engineering ceramic components from mullite with little or no glassy phase.

Although reaction sintering between zircon and alumina to produce zirconia-toughened mullite has been largely investigated,[8–12] not much research was devoted[12,13] to the sintering behavior of mullite itself. A close compositional and microstructural control is necessary in order to maximize the densification.[4,14] Though the mullite used in the later studies has been obtained through the sol-gel technique, it mainly concerns the effect of sintering temperature on the microstructure

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and strength of dense mullite. Recently, much interest has been focussed on the sintering aids of mullite.[15–18] Hence, the aim of the proposed work is to study the sintering behavior of a sol-gel mullite with the help of suitable sintering aids, which were not reported elsewhere, and to analyze the microstructure of the respective samples.

2. Experimental procedure

Aluminum nitrate nanohydrate (E-Merck, 99.99% purity, crystalline form) and ethyl silicate, TEOS (Chemplast, Mettur, India) were used as the starting materials for preparing mullite by the sol-gel process. The details of the experimental procedure and the powder characteristics were described previously.[3] The sintering aids such as SrO (0.5, 1.0, 2.0 and 3.0 wt.%) and clay (1.0, 1.5, 2.0 and 2.5 wt.%) were added to the mullite precursor during the wet milling stage. The aqueous solution of $Sr(NO_3)_2 \cdot 6H_2O$ was added to mullite in the sol stage, whereas the clay, which was obtained from Carborundum Company, Chennai, India, (95% purity, $d_{50} = 0.5–1.0$ μm) was added to mullite precursor during the wet milling stage. The wet milled slurry was dried at room temperature. The dried mullite precursors with and without sintering aids were calcined at different temperatures ranging from 600 to 1300°C. The calcined powders were then uniaxially pressed at a pressure of 150 MPa into compacts of dimension 15×10 mm. All the samples were sintered at different temperatures 1400, 1450, 1500 and 1600°C for 3 h. The density of the sintered samples was determined using Archimede's method. The microstructure of the sintered specimens was observed using SEM (LEICA STEREOSCAN S440).

3. Results and discussion

The bulk density of the mullite compacts, without any sintering aids, with respect to sintering temperatures for different calcined precursors of this study are shown in Fig. 1. It is observed that the precursor calcined at 600°C and sintered at 1600°C for 3 h shows highest densification of 88.5% of T.D., compared to the precursor powder calcined at both higher and lower temperatures. This is attributed to the high surface area of the powder calcined at 600°C.[3] In studying the effects of powder calcination temperature on subsequent sintering behavior, Hirata et al.[4] also presented evidence that amorphous powder show enhanced densification. At higher calcination temperatures, the surface area decreases rapidly to very low values, reflecting the negative effect of particle growth and aggregate formation. However, at very low calcination temperature, the
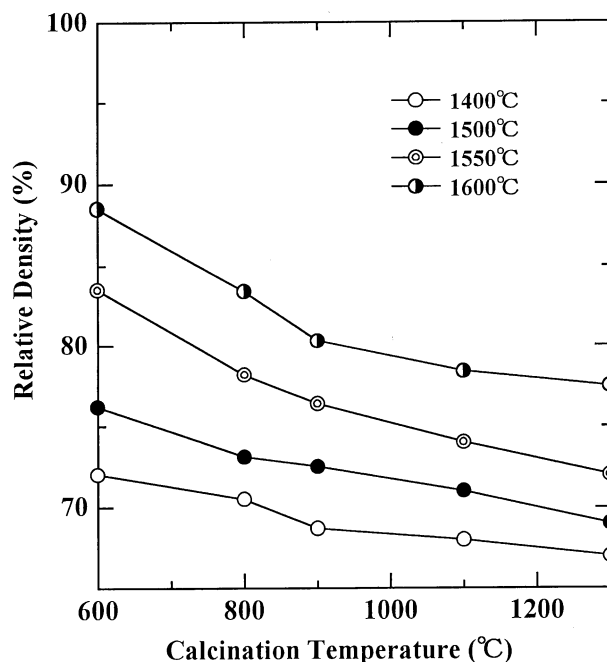

Fig. 1. Effect of calcination temperature on the densification of mullite.

weight loss is accompanied by a large amount of shrinkage. This leads to crack formation on the surface of the compacts during sintering due to the decomposition of the residual.[14] Therefore, it is necessary to have calcination of the precursor powder above the decomposition temperature in order to reduce the weight losses and also to avoid the crack formation.

Farenholtz and Smith[19] have found that when the pellets were sintered at 1600°C for 2 h, the final relative bulk density was 73% for monophasic gel and 90% for diphasic gel. The single-phase gel, which crystallizes to mullite at relatively low temperatures, does not sinter effectively without the application of very high temperatures or very high pressures. Hence, the sintering of stoichiometric pure mullite is very difficult often necessitating pressure assisted sintering. Hence, the alternate to make mullite more sinterable is to exploit the advantage of the addition of suitable sintering aids.

Fig. 2 shows the density of the samples with various SrO concentrations as a function of sintering temperature of the extended hold. From Fig. 2, it is observed that the sintering density increases with the increase in the amount of SrO up to 0.5 wt.% and then decreases for further SrO addition. The addition of 0.5 wt.% of SrO enhanced the sintering density of pure mullite from 88.5 to 98% of T.D. at 1500°C for 3 h. The strong SrO addition on the densification of mullite may be explained by its effect of SrO dissolution into the glass and subsequent decrease in glass viscosity. That is, as the SrO concentration increases, the dissolution rate increases and thus reduces the glass viscosity more effectively. As a divalent material, SrO has strong tendency to
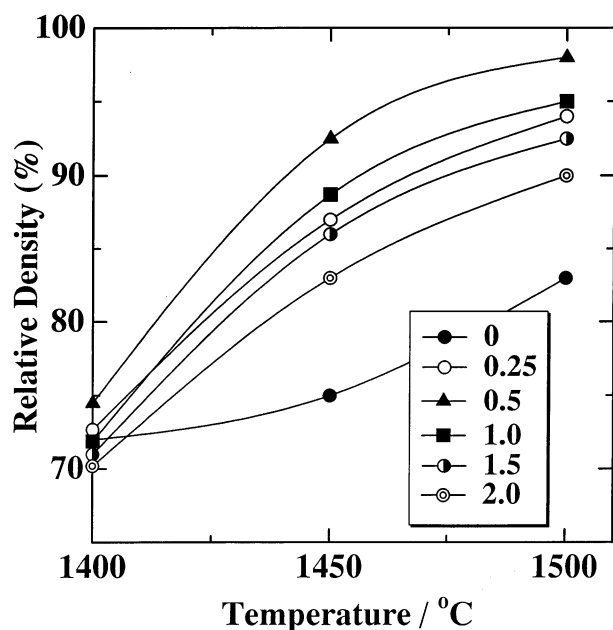
Fig. 2. Effect of SrO addition on densification of mullite precursors calcined at 600°C.

Fig. 3. Effect of clay addition on densification of mullite precursors calcined at 600°C.

grow as a platelet. At 0.5 wt.% doping, highly anisotropic grain microstructure develop, elongated mullite grains start to impinge, and grain thickening is observed (Fig. 4b). When there is further increase in the SrO addition, the density decreases (Fig. 2). This suggests that the process of anisotropic grain growth might be responsible for dedensification. Considering Al^{3+} and Sr^{2+} ionic radii, though, the substitution of Al^{3+} ions by Sr^{2+}, in the mullite lattice position is the most probable solid solution mechanism, it is not well understood. Nevertheless, in the present study, the sintered density increases up to a certain temperature and further remains constant. This is due to the exsolution of SiO_2 from mullite grain with increased temperature forming a liquid phase along the grain boundary and partly vaporizing as SiO.[18] Similar complexity was observed with the addition of MgO and TiO_2 as sintering aids for mullite. Ismail et al.[15] have shown that the addition of MgO above 0.5 wt.% has no effect in controlling the grain growth of mullite. Baudin and Moya[18] have reported that the addition of TiO_2 within the solubility limit enhances the sintering density of mullite. When the amount of titanium di-oxide exceeded the solubility limit, the sintering density decreased with the formation of Al_2TiO_5 at the grain boundary with complex sintering mechanism. The plateau, which has been observed after 1500°C in Fig. 2, for all the dopant concentrations may be attributed also to the anisotropic grain growth of mullite at higher temperature, which further retards the densification process.

Fig. 3 shows the effect of clay addition on sintering density of mullite. From the figure, it has been observed that 2.0 wt.% of clay addition enhances the sintering
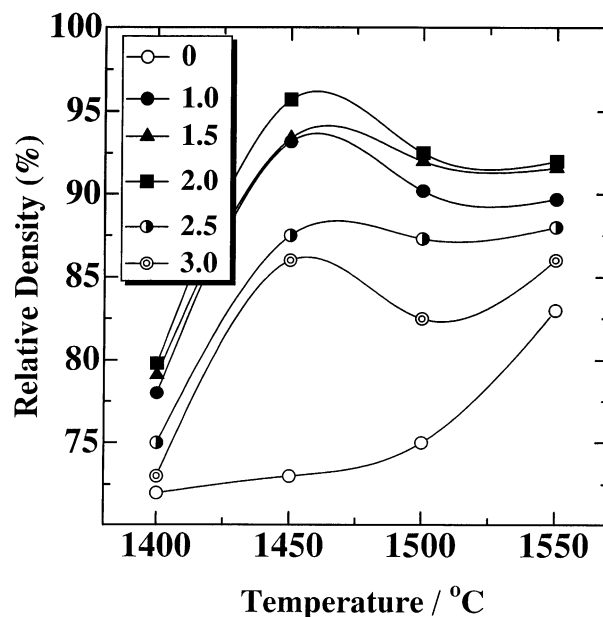
density tremendously to 95% of T.D. at very low temperature, 1450°C by pressureless sintering. This effect is mainly attributed by the free silica present in the clay, which aids for liquid phase sintering, which normally vitrifies around 1450C. Hence, the increase in densification has been achieved prior to the decomposition of clay into mullite and SiO_2. Also, the early densification in clay doped mullite gels believed to be primarily a result of the decrease in glass viscosity with clay doping. The densification occurs through a mechanism similar to viscous flow sintering.[3] In clay, the mullitization starts above 1450°C and the transformation of amorphous SiO_2 to cristobalite occurs at this temperature and reacts with Al_2O_3 to form mullite. This causes a gradual decrease in the semi-viscous-flow sintering which is activated by the existence of softened glass particles. The decrease in the densification rate is enhanced by mullite formation and hence the densification has to take place in the presence of mullite via solid-state diffusional process[14,20] and hence retards the sintering process.

4. Microstructure

Fig. 4 shows the sintered microstructure of pure mullite samples and samples of mullite added with sintering aids. The polished specimens are thermally etched at 1400°C for 30 min. The microstructure of the pure mullite shows bimodal distribution of mullite grains having both very fine and exaggerated grain growth. The large grains are often isolated by surrounding smaller grains. Intergranular pores were observed in the
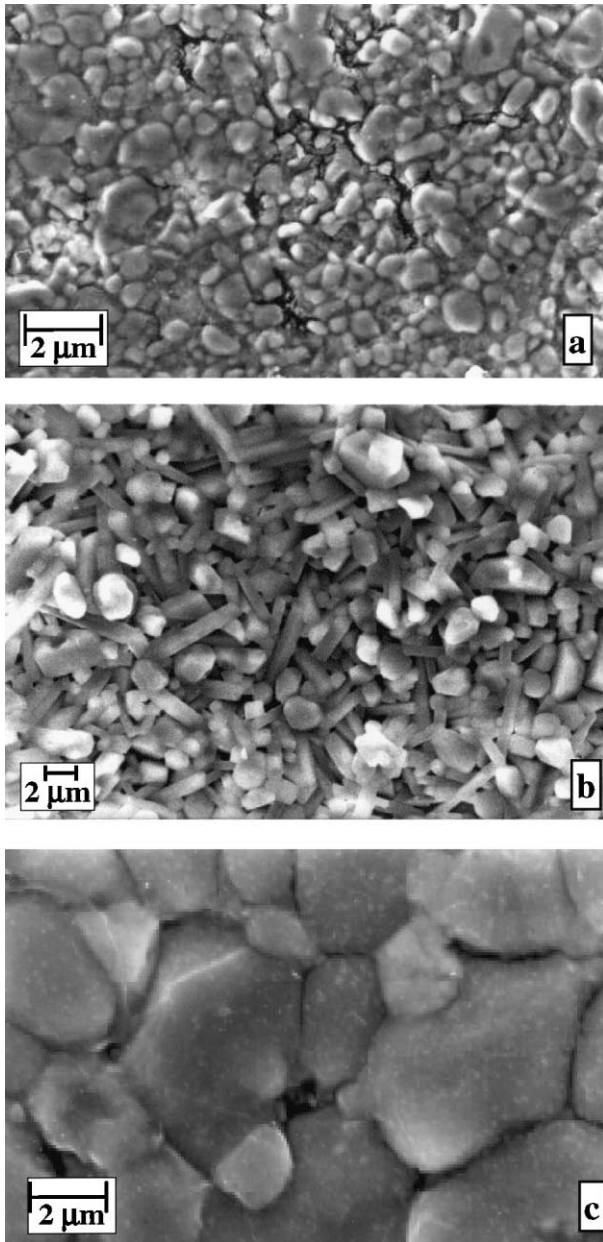
Fig. 4. Microstructure of the sintered specimen. (a) Pure mullite — 1600°C, (b) SrO — 1550°C (0.5 wt.%) and (c) clay — 1450°C (2.0 wt.%).

sample. The sintered microstructure of mullite added with SrO (0.5 wt.%) is shown in Fig. 4b. The specimen sintered with SrO as the additive shows duplex microstructure consisting of very fine equiaxed and elongated grains. Even at 0.5 wt.% of SrO doping, interpenetrating highly anisotropic grain microstructures develop, elongated mullite grains start to impinge, and grain thickening is observed. The aspect ratio, a measure of the degree of anisotropy, of the SrO doped mullite grains is ~4 μm length and ~1 μm width and the average size of the equiaxed grains is ~2 μm. As mullite is composed of octahedral AlO_6 chains aligned in the c-direction and

cross linked by the corner shared AlO_4 and SiO_4 tetrahedra, it has strong tendency to grow as rods. Hence, the anisotropic mullite grains are c-axis oriented with either hexagonal or rectangular cross section. The anisotropic microstructure development in SrO doped mullite is attributed to a lower glass viscosity and thus higher mobility of the diffusing species. Large elongated grains become the main feature of the microstructure, which is one of the indications that mullite is richer in alumina. The clay doped sample show coarser particles with equiaxed morphology (Fig. 4c). Excess SiO_2 composition leads to an equiaxed microstructure.[20] In addition, in the clay doped mullite, the grain size increased to around 10 μm and the grains appeared to be platelets. The large increase in the size of the mullite grains in these samples is probably due to the significant decrease in the viscosity of the glassy phase due to clay content. This would allow for more rapid transport of materials and hence much more rapid grain growth. Therefore, it is obvious and interesting to note that the microstructure of pure sintered mullite is composed of submicron equiaxed grains, the one with SrO was elongated with large increase in the grain size and the clay doped mullite with exaggerated grain growth.

5. Conclusion

Single-phase mullite powder has been sintered to 88.5% of T.D. at 1600°C for 3 h under pressureless sintering. Density >98% of T.D has been obtained for mullite by the addition of 0.5 wt.% of SrO and >95% of T.D. for 2.0 wt.% of clay by pressureless sintering at 1550 and 1450°C for 3 h respectively. Both SrO and clay take part in lowering the viscosity of the liquid phase and thereby increase the diffusing species. Clear differences were found in the microstructures of mullite that could be related to the different sintering aids, which have apparent effect on the densification behavior. SrO doped samples show a duplex microstructure of fine equiaxed and anisotropic grain morphology, while the sintered clay doped samples show equiaxed and acicular morphology.

Acknowledgements

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