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Sintering of pre-mullite powder obtained by chemical processing

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The crystallization and sintering behaviour of a premullite powder which had been synthesized from aluminium sulphate [$Al_2(SO_4)_3 \cdot 16H_2O$] and colloidal silicon dioxide have been studied. Calcination of the mixture at 860 °C for 12 h gives a very active powder (surface area = 188 m^2g^{-1}) in the form of spinel and mullite forms via this spinel phase. The non-mullitized powder can be reactively sintered at 1500–1550 °C to 97%–99% density in 3–5 h with a very fine microstructure.

1. Introduction

Mullite ($3Al_2O_3 \cdot 2SiO_2$) has attracted much interest due to its unique combination of properties such as excellent high-temperature strength [1] and creep resistance [2], low thermal expansion coefficient [3], low dielectric constant [4] and good infrared transparency [5]. It is, therefore, considered to be a suitable material for both high-temperature structural and electronic applications.

There have been a number of studies which aimed to produce high-density and purity mullite ceramics either by sintering of crystalline mullite powder or reaction sintering of aluminium silicate mixture in which mullite forms after sintering. Homogeneous molecular scale mixing of aluminium and silicon-bearing compounds using controlled chemical processing (i.e. monophasic precursors) gives fine, crystalline mullite powders via an amorphous phase after calcining at ~ 980 °C [6–8], while colloidal-scale mixtures of alumina and silicon dioxide (i.e. diphasic precursors) crystallize to mullite at higher temperatures (~ 1100–1300 °C) either via a spinel phase [7, 9–12] or δ- or θ-Al_2O_3 [13, 14] depending on the starting materials and processing conditions. Crystalline mullite powders prepared by either method need temperatures around 1600–1650 °C to be able to be sintered to high densities (~ 98%) [6, 7, 11, 15]. However, aluminium silicate mixtures prepared using colloidal boehmite and silicon dioxide (or tetraethylorthosilicate) and, recently, silicon dioxide-coated α-Al_2O_3 can be reaction sintered to high densities (95%–99%) at temperatures as low as 1200–1250 °C [16–19]. This is due to the fact that mullitization, which precludes densification [20, 21], can be retarded in these mixtures up to temperatures > 1250 °C, around which temperature viscous flow of amorphous silica occurs to aid densification. Then mullitization of the dense compacts is carried out at higher temperatures, the degree of which depends on the nature of the starting materials.

In this work, the crystallization and densification of aluminium silicate mixtures with the mullite composition obtained from aluminium sulphate and colloidal silicon dioxide have been studied and the resultant microstructures examined.

2. Experimental procedure

The preparation method of the aluminium silicate mixture was similar to that of Mizuno and Saito [11]. The starting materials were aluminium sulphate, $Al_2(SO_4)_3 \cdot 16H_2O$ and colloidal silica (both BDH Chemicals, Poole, UK). Aluminium sulphate was dissolved in distilled water at a concentration corresponding to 8 wt % Al_2O_3 and the pH after dissolution was ~ 2. A silica sol was prepared by dispersing colloidal silica powder in distilled water and the pH of the sol was ~ 4. The pH was decreased to 2 by the addition of 1 M HCl. The silica sol was slowly added to the alumina solution under vigorous mixing which was carried out for 0.5 h with the final pH of the mixture being 2.2. It was dried at 170 °C for 3 days, crushed and calcined at either 860 or 970 °C for 12 h to decompose the aluminium sulphate. Then, milling of the calcined powders was carried out in heptane (BDH Chemicals, Poole, UK) for 8 h using alumina balls and the powder was dried at 120 °C for several hours followed by sieving through 100 μm mesh. The surface area was measured by the BET method and the alumina content was determined by energy dispersive X-ray analysis (EDX). The crystallization behaviour was observed by X-ray diffraction (XRD) using CuK_α radiation. Lattice parameters of mullite were calculated using (041), (331) and (002) reflections measured by a step-scanning technique with a 2θ intervals of 0.02° in a constant time of 10 s for each step.

In order to study the effect of powder compaction pressures on the green and sintered densities, powders were uniaxially pressed in a 13 mm die at various pressures and sintered at 1650 °C for 5 h. Sintering experiments were performed at various temperatures and times after cold isostatic pressing of the powders at 450 MPa. Also to study the effect of the calcination temperature on the sintered density, the 860 °C calcined and milled powders were further calcined at 1100 and 1350 °C for 5 h, milled by mortar and pestle and sintered at 1550 °C for 5 h. Green and sintered bulk densities were measured from the dimensions of the pellets and by the Archimedes' method, respectively. Relative bulk densities were calculated by taking the theoretical density of mullite as 3.17 g cm^{-3} (JCPDS Card no. 15–776). The specimens were polished and thermally etched (1550 °C, 1 h) and were then examined using scanning electron microscopy (SEM).

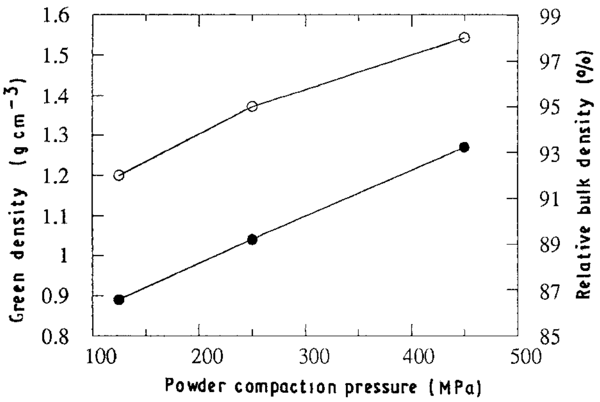

Figure 2 Dependence of the (●) green and (○) sintered density on compaction pressures in a die press. Sintering condition is 1650 °C for 5 h.

3. Results and discussion

The surface area of the powder calcined at 860 °C was 188 m^{2}g^{-1} and the Al_2O_3/SiO_2 weight ratio determined by EDX was about 2.88 (74.25 wt % Al_2O_3).

3.1. Formation of mullite

Fig. 1 shows the development of crystalline phases as determined by X-ray diffraction. After calcination at 860 °C for 12 h, the main phase present is spinel and on further calcination of the 860 °C calcined product at 1100 °C for 5 h the spinel phase is preserved but with increased intensity. Although the composition of the spinel phase was not studied, formation of Al–Si spinel has been observed from colloidal-scale mixtures of aluminium salts and silicon-bearing compounds [7, 9, 10, 12]. Mullite forms via the spinel phase and it was almost complete at 1200 °C (5 h). No formation of δ- or θ-Al_2O_3 was observed. At higher temperatures, only traces of α-Al_2O_3 were detected as a second phase.

3.2. Densification behaviour

Owing to the very fine nature of the powder, high compaction pressures were needed to obtain a relatively high green density. Green densities of the compacts after 450 MPa isopressing were about 1.40 g cm^{-3}. Fig. 2 shows the dependence of sintered density on compaction pressure. Lower compaction pressures resulted in lower green densities and, in turn, lower final sintered densities and observed higher shrinkages.

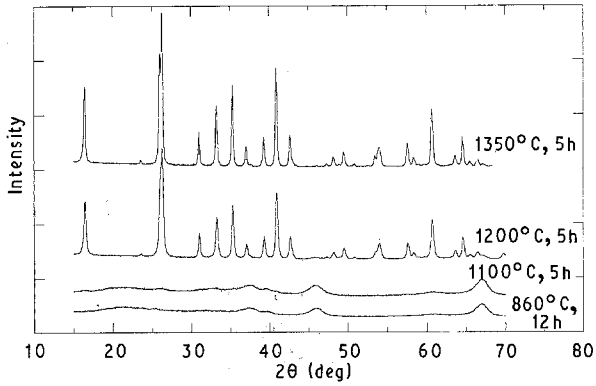

Figure 1 Development of the crystallization of the mixture. Temperatures higher than 860 °C are the further calcination temperatures of the 860 °C calcined powder.

The dependence of the final density on sintering temperature and time are shown in Figs 3 and 4, respectively. It can be seen that high-density mullite bodies (> 98%) can be produced by sintering the green compacts at 1550 °C for 3–5 h and that the density is further increased by calcining the powder at higher temperatures. The densities of the compacts prepared from 970 °C calcined powder were 97.3% and 99.1% after sintering at 1500 and 1550 °C for 5 h, respectively. The reason for the increased density with increasing calcination temperature is due to a decrease in weight loss, because weight losses during sintering tend to increase the pore volume of the compacts which decreases densification. Powders calcined at 860 and 970 °C showed weight losses of about 10% and 6.5%, respectively, after sintering. Weight loses are due to incomplete decomposition and some organics from the milling media.

Fig. 5 shows the dependence of the sintered density on the calcination temperature. It is clearly seen that when using the crystalline mullite powder which was obtained by calcining the mixture at 1350 °C densification decreases dramatically. Similar observations were reported by Hirata and Shimada [22].

As the mullite formation was almost complete at 1200 °C, the viscous flow of the amorphous phase for densification could not be utilized or could have a limited use, and therefore no great densification occurred at such low temperatures, unlike in the boehmite–silica system [16–18]. However, as is seen from the Fig. 3, the densities of the compacts sintered at 1400 °C are as high as 80% due to the high activity of the powder and/or limited viscous flow sintering. In contrast, crystalline mullite powders do not show a great deal of densification up to 1400 °C [6, 7] mainly due to low interdiffusion rates of silicon and aluminium in crystalline mullite, i.e. their bulk density is nearly the same as their green density. Therefore, the higher densities of the reactively sintered compacts

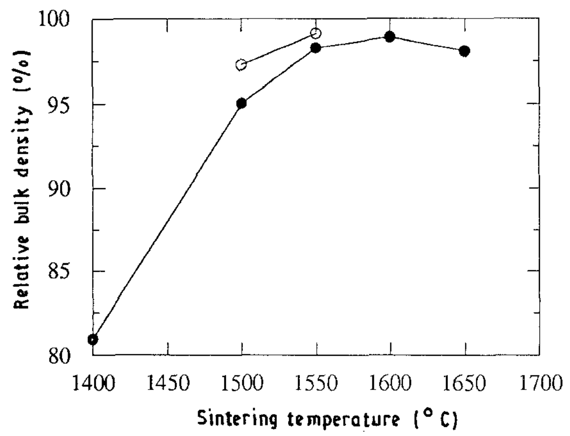

Figure 3 Change in relative sintered density with sintering temperature (sintering time is 5 h). (●) calcined at 860 °C, (○) calcined at 970 °C.

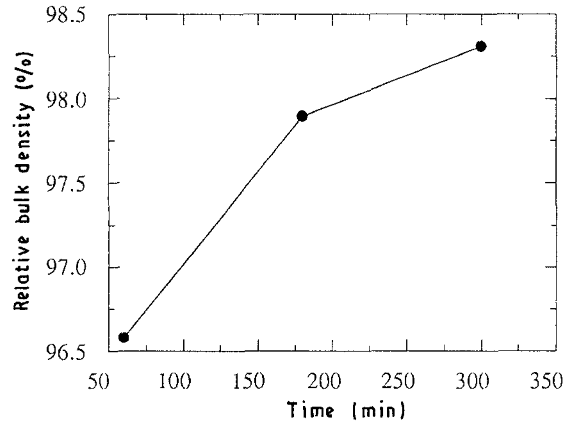

Figure 4 Change in relative sintered density with time (sintering temperature is 1550 °C).

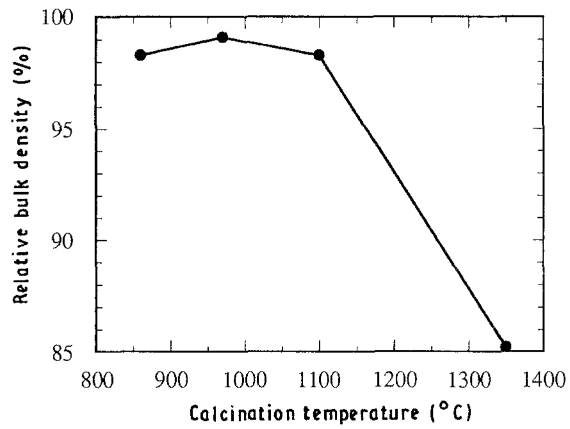

Figure 5 The effect of calcination temperature on the sinterability of the powders (sintering condition is 1550 °C for 5 h).

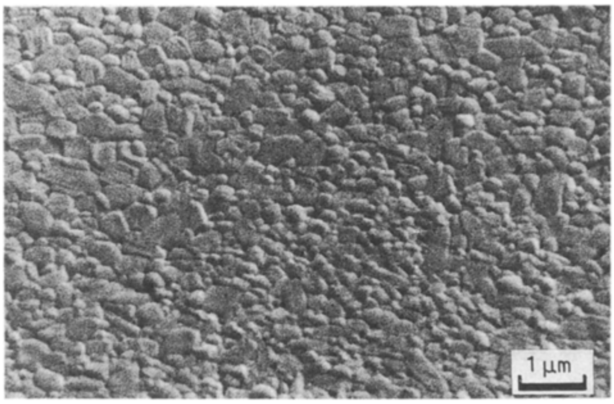

Figure 6 Microstructure of the specimen sintered at 1500 °C for 5 h.

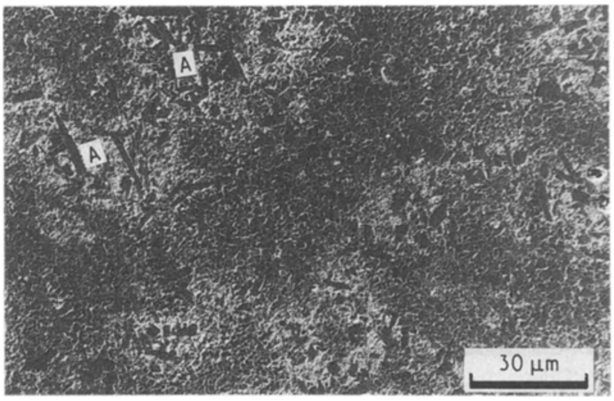

Figure 7 Microstructure of the specimen sintered at 1600 °C for 5 h. Notice the local formation of elongated grains (e.g. at A).

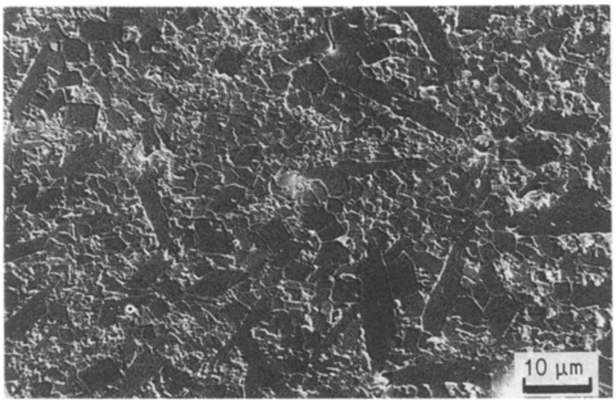

Figure 8 Microstructure of the specimen sintered at 1650 °C for 5 h. The presence of elongated grains is an indication of the presence of a liquid phase which is due to the decomposition of mullite into alumina-rich mullite and a liquid phase.

before high-temperature treatment to attain full density, enable them to be sintered at lower temperatures compared to crystalline mullite powders.

The microstructures of the compacts sintered at various temperatures are shown in Figs 6–8. Specimens sintered at 1500 °C have a very fine equiaxed grain morphology, and only a few large grains 2–3 µm in size with equiaxed or elongated morphology are present (Fig. 6). The small proportion of elongated grains shows that there is little or no liquid phase during sintering because elongated grains can only grow in the presence of a liquid phase [23]. As the sintering temperature increases to 1550 °C, some areas show local formation of elongated grain clumps and at 1600 °C the number of these areas increases (Fig. 7, A). This is probably due to the fact that in these regions

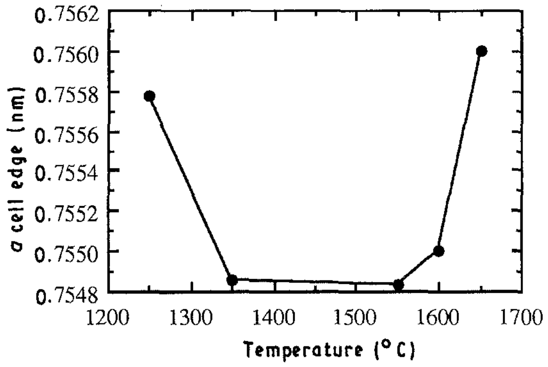

Figure 9 Change of *a* cell parameter of the mullite with temperature.

mullite contains less alumina within the solid solution region, compared to the regions where the grain morphology is equiaxed, and decomposes to a liquid phase and richer alumina mullite with increasing temperature due to the bending of the solid solution region according to the phase diagram proposed by Klug *et al.* [24].

The reason some regions contain more silica may be due to the irreversible coagulation of silica particles during the lowering of the pH of the silica sol to 2, because repulsive forces on the surfaces of the silica particles decrease and, as a result, relatively poorer mixing results. Massive coagulation, however, does not occur due to the formation of a hydration layer on the silica particle surfaces which provides steric protection [25]. Our microstructural observations revealed that heat treatment of the compacts at 1500 °C (before higher temperature treatments) increases the homogeneity of the microstructure which is probably due to the enrichment of mullite solid solution in alumina in these regions via diffusion of aluminium ions and as a result the decomposition is delayed to higher temperatures.

As the sintering temperature increases, grain growth takes place and the degree of decomposition of mullite into an alumina-rich mullite and a liquid phase increases at 1650 °C. Large elongated grains become the main feature of the microstructure (Fig. 8) and the *a* cell parameter increases (Fig. 9) which is an indication that mullite is richer in alumina as suggested by Cameron [26]. The decrease in the final sintered density at 1650 °C is also due to this reason, i.e. the presence of a low-density glassy phase in the microstructure (Fig. 3).

It should be noted here that for the measured *a* cell edge of 0.7548 nm the Al_2O_3/SiO_2 ratio calculated from Fig. 3 [26] is ~ 2.66 (72.7 wt% Al_2O_3) compared to 74.25% wt % Al_2O_3 of the EDX result.

4. Conclusion

Mullite forms from the mixture of aluminium sulphate and colloidal silicon dioxide via the spinel phase and it is almost complete at 1200 °C. Calcination of the mixture below the mullitization temperature gives a very active powder in the form of spinel which can be reactively sintered to 97%–99% relative density with a very fine microstructure at 1500–1550 °C which is somewhat lower compared to that of crystalline mullite powders. Coagulation of silica particles affects the degree of mixing and in turn the microstructural development during sintering.

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Reference

1. S. KANZAKI, H. TABATA, T. KUMAZAWA and S. OHTA, *J. Amer. Ceram. Soc.* **68** (1985) C6
2. P. C. DOKKO, J. A. PASK and K. S. MAZDIYASNI, *ibid.* **60** (3–4) (1977) 150.
3. H. SCHNEIDER and E. EBERHARD, *ibid.* **73** (1990) 2073.
4. B. H. MUSSLER and M. W. SHAFER, *Bull. Amer. Ceram. Soc.* **63** (1984) 705.
5. S. PROCHAZKA and F. J. KLUG, *ibid.* **66** (1983) 874.
6. S. MITACHI, M. MATSUZAWA, K. KANEKO, S. KANZAKI and H. TABATA, *Ceram. Trans.* **6** (1990) 275.
7. T. KUMAZAWA, S. OHTA, S. KANZAKI and H. TABATA, *ibid.* **6** (1990) 401.
8. J. A. PASK, X. W. ZHANG, A. P. TOMSIA and B. E. YOLDAS, *J. Amer. Ceram. Soc.* **70** (1987) 704.
9. K. OKADA and N. OTSUKA, *ibid.* **69** (1986) 652.
10. *Idem., Ceram. Trans.* **6** (1990) 375.
11. M. MIZUNO and H. SAITO, *J. Amer. Ceram. Soc.* **72** (1989) 377.
12. F-S. YEN, C. S. HSI, Y. H. CHANG and H. Y. H. Y. LU, *J. Mater. Sci.* **26** (1991) 2150.
13. W-C. WEI and J. W. HALLORAN, *J. Amer. Ceram. Soc.* **71** (1988) 166.
14. G. KLAUSSEN, G. S. FISCHMAN and J. L. LAUGHNER, *Engng Sci. Proc* **11** (1990) 1087.
15. M. G. M .U. ISMAIL, Z. NAKAI and S. SOMIYA, *J. Amer. Ceram. Soc.* **70** (1987) C-7.
16. S. KOMARNENI, Y. SUWA and R. ROY, *ibid.* **69** (1986) C-155.
17. M. N. RAHAMAN, L. C. De. JONGHE, S. L. SHINDE and P. H. TEWARI, *J. Amer. Ceram. Soc.* **71** (1988) C-338.
18. B. SONUPARLAK, *Comp. Sci. Tech* **37** (1990) 299.
19. M. D. SACKS, N. BOZKURT and G. W. SCHEIFFELE, *J. Amer. Ceram. Soc.* **74** (1991) 2448.
20. M. S. GANI and R. McPHERSON, *J. Aust. Ceram. Soc.* **13** (1977) 21.
21. P. D. D. RODRIGO and P. BOCH, *Int. J. High. Tech. Ceram.* **1** (1985) 3.
22. Y. HIRATA and K. SHIMADA, in "Mullite", edited by S. Somiya (Uchida Rokakuho, Tokyo, Japan, 1985) pp. 89–122.
23. W. LOHRE and H. URBAN, *Ber. Dtsch. Keram. Ges.* **37** (1960) 249.
24. F. J. KLUG, S. PROCHAZKA and R. H. DOREMUS, *J. Amer. Ceram. Soc.* **70** (1987) 750.
25. J. C. HULLING and G. L. MESSING, *Ceram. Trans.* **6** (1990) 221.
26. W. E. CAMERON, *Bull. Amer. Ceram. Soc.* **56** (1977) 1003.

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