Journal of the European Ceramic Society 20 (2000) 2519–2525

Preparation of mullite by the reaction sintering of kaolinite and alumina

C.Y. Chen, G.S. Lan, W.H. Tuan *

Institute of Materials Science and Engineering, National Taiwan University, Taipei, Taiwan 106, ROC

Received 9 December 1999; received in revised form 6 April 2000; accepted 11 April 2000

Abstract

In the present study, mullite specimens and mullite/alumina composites are prepared by reaction sintering kaolinite and alumina at a temperature above 1000°C. The phase and microstructural evolution of the specimens and their mechanical properties are investigated. Primary mullite appears at a temperature around 1200°C. The alumina particles are inert to the formation of primary mullite. Alumina starts to react with the silica in glassy phase to form secondary mullite above 1300°C. The formation of secondary mullite decreases the amount of glassy phase. Furthermore, the addition of alumina reduces the size of mullite grains and their aspect ratio. The strength and toughness of the resulting mullite increase with the increase of alumina content; however, the mechanical properties of the mullite and mullite/alumina composites are lower than those of alumina for their relatively low density. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Al_2O_3; Kaolinite; Mechanical properties; Microstructure-final; Mullite; Reaction sintering

1. Introduction

Kaolinite ($2SiO_2{\cdot}Al_2O_3{\cdot}2H_2O$), an aluminosilicate-based ceramic, is widely used in ceramic industries for many years. The stoichiometric 3:2 mullite ($3Al_2O_3{\cdot}2SiO_2$) is a thermodynamically stable phase in the SiO_2–Al_2O_3 system.[1] The mullite is thus formed after firing kaolinite at elevated temperature.[2,3] Nevertheless, the amount of SiO_2 in kaolinite is much higher than that in mullite; the excess SiO_2 together with the impurities in kaolinite forms a glassy phase and cristobalite to accompany the formation of mullite at a temperature higher than 1000°C.[4] The cristobalite may also transform to a glassy phase as kaolinite is fired above 1500°C.[5] The strength of glass is usually low at room temperature; furthermore, the glass is softened at elevated temperature. The presence of a large amount of glass phase is thus detrimental to the mechanical properties of the mullite prepared from kaolinite.

The amount of the SiO_2 in the glassy phase can be consumed by adding Al_2O_3. Furthermore, the reaction product of the SiO_2 in glass and Al_2O_3 is also a mullite phase. The addition of Al_2O_3 can therefore reduce the amount of glass phase and increase the amount of mullite. In the present study, the interactions between kaolinite and alumina at elevated temperature are investigated. Furthermore, the microstructural evolution of the mullite prepared by the reaction between kaolinite and alumina during sintering is also studied.

2. Experimental

A kaolin (AKIMA 35, Akima Co., Malaysia) powder and various amounts of alumina (AES-11, Sumitomo Chem., Japan, 99.8% Al_2O_3) were milled together in ethyl alcohol with a turbo-mixer. The composition of the kaolin powder was determined with the induced coupled plasma emission spectroscopy (ICP). The grinding media was zirconia balls and milling time was 4 hours. After drying, the dried lumps were crushed and passed through the plastic sieve with an aperture size of 149 μm. The particle size and its distribution were determined with a laser particle-size analyzer (LS 230, Coulter Co., USA). The powder compacts were prepared by the die-pressing technique. The pressure applied was 27 MPa. The firing was carried out at a

---

* Corresponding author. Tel.: +886-2-2365-9800; fax: +886-2-23634562.

E-mail address: tuan@ccms.ntu.edu.tw (W.H. Tuan).

PII: S0955-2219(00)00125-4

temperature varied from 1000 to 1600°C for 1 h. The heating rate and cooling rate were 5°C/min.

The reaction as following was taken place during the sintering of the powder mixtures of kaolinite and alumina,

$$2SiO_2 \cdot Al_2O_3 \cdot 2H_2O + 2Al_2O_3 \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 2H_2O \quad (1)$$

The phase identification was performed by X-ray diffractometry (Philips PW1710, Philips Co., Netherlands) with CuK_α radiation. In order to determine the amount of mullite and alumina phases in the sintered specimens, a high-purity mullite was used to mix with the alumina powder. The mullite/alumina powder mixtures with the ratio of 1/4, 2/3, 3/2 and 4/1 were prepared with the same procedures as those for the kaolin/alumina powder mixtures. A slow scanning speed, 0.005° 2θ/s, was used to determine the integral intensity of the (120) plane of mullite and of the (012) plane of alumina within the 2θ ranged from 25 to 27°. Three runs were conducted to determine the reproducibility of the XRD analysis. The calibration curve was then established by correlating the intensity ratio to mullite/alumina ratio. The ratio of mullite and residual alumina in the sintered kaolinite/alumina specimens could thus be determined. Since the amount of SiO_2 and Al_2O_3 in the starting materials was known; mullite, alumina and glass phase were the major phases in the fired specimens. The amount of mullite, residual alumina and glassy phase in the sintered specimens could therefore be determined after the mullite/alumina ratio was measured. The final density was determined by Archimedes' method. By using the theoretical density of 3.16 g cm^{-3} for mullite, 3.98 g cm^{-3} for alumina and assuming 2.5 g cm^{-3} for glass, the relative density of the fired specimens could then be estimated. Since the composition of stoichiometric 3:2 mullite formed at elevated temperature varied in a rather small range[1] and the density of Al_2O_3–SiO_2–K_2O glass was very close to 2.5 g cm^{-3},[6] the error that may thus be caused by using the above values to calculate the relative density should be relatively minor.

The flexural strength of the rectangular specimens was determined by the three-point bending technique at ambient, room-temperature condition. The lower span for the flexural testing fixture was 30 mm. The loading rate was 0.5 mm/min. The fracture toughness was determined by the three-point single-edge-notched-beam (SENB) technique. The notch was generated by cutting with a diamond saw. The width of the notch was around 0.45 mm. The microstructure was observed by scanning electron microscopy (SEM). To reveal the grain boundaries of mullite, a concentrated hydrofluoric acid was used as etching solution. The mean size of mullite grains was determined with the line intercept technique. The line intercept was taken randomly from several SEM micrographs for each composition. Furthermore, more than 800 grains were counted. A statistical procedure[7] to determine the aspect ratio, the length/width ratio, of elongated Si_3N_4 grains in the in-situ reinforced silicon nitride was adopted in the present study to evaluate the aspect ratio of mullite grains.

3. Results and discussion

The mean size of kaolinite and alumina particles is 1.7 and 0.3 μm, respectively. The morphology of the kaolinite particles and of a powder mixture of kaolinite and alumina is shown in Fig. 1. Fig. 1(b) shows that fine alumina particles are mixed uniformly with the coarse kaolinite particles after milling and drying. Fig. 2 shows the XRD patterns of the powder mixture of kaolinite and alumina. A minor phase, quartz, is detected in the starting kaolin powder. The XRD patterns of the kaolin/42 wt.% alumina powder compact at elevated temperature are also shown in Fig. 2. Mullite is first noticeable in the specimen fired at the temperature of 1200°C. At the temperature, the amount of Al_2O_3 is not reduced, indicating that alumina remains inert chemically until 1200°C. This finding is the same as the result

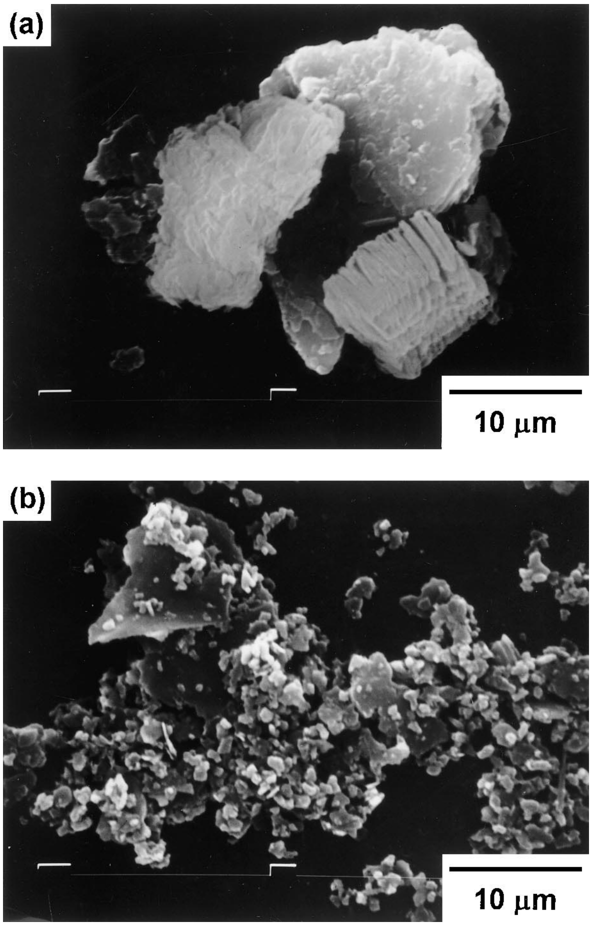

Fig. 1. Morphology of (a) kaolin powder and (b) kaolin + 52 wt.% alumina powder mixtures.

reported by Liu et al.[8] As the temperature is raised to 1400°C, the amount of alumina is decreased considerably, the amount of mullite increased instead. The mullite formed at 1200°C is termed as primary mullite;[8,9] the mullite formed above 1300°C as secondary mullite. The formation of secondary mullite is mainly contributed by a solution and precipitation mechanism through the glassy phase.[9] The formation of secondary mullite consumes the SiO_2 in the glassy phase. The amount of glassy phase is thus decreased.

The ICP analysis indicates that the composition of the kaolin used in the present study is 48.6 wt.% SiO_2, 35.7 wt.% Al_2O_3, 1.2 wt.% K_2O, 0.9 wt.% Fe_2O_3, 0.4 wt.% TiO_2, 0.2 wt.% MgO, 0.1 wt.% CaO, 0.1 wt.% BaO and 12.6 wt.% ignition loss. Assuming that the SiO_2 in the kaolinite is reacted completely with Al_2O_3 to form mullite as the reaction shown in Eq. (1); since there is 48.6 wt.% SiO_2 in the starting kaolin powder, an excess amount of 41.7 wt.% alumina is needed to react all SiO_2 in the kaolin powder to form mullite. Therefore, there is no Al_2O_3 found in the kaolin/32 wt.% alumina and kaolin/42 wt.% alumina powder compacts after firing at high temperature (Fig. 2). However, residual alumina can be detected in the specimens containing more than 52 wt.% Al_2O_3. Therefore, the specimens containing 52, 62 and 72 wt.% Al_2O_3 are virtually mullite/alumina composites after sintering at a temperature above 1400°C.

The calibration curve to correlate the XRD intensities to mullite/alumina ratio is shown in Fig. 3. The results between the three tests for each composition are very close, indicating the reproducibility is high. The ratio of mullite/(mullite + alumina) is shown as a function of sintering temperature in Fig. 4. Fig. 5 shows the amount of residual alumina after reacting with kaolinite as a

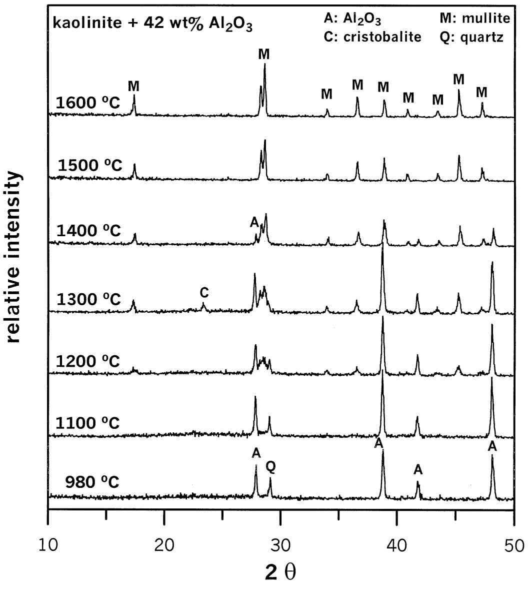

Fig. 2. XRD patterns of the kaolinite + 42 wt.% alumina powder compacts at elevated temperatures.

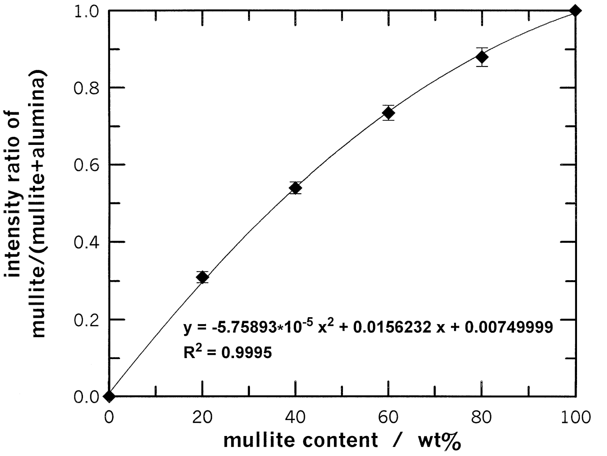

Fig. 3. Calibration curve for the determination of mullite in the fired specimens.

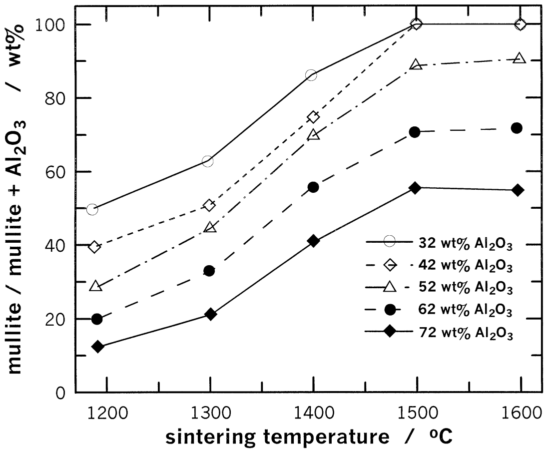

Fig. 4. Ratio of mullite to (mullite + alumina) in the sintered specimens as a function of sintering temperature.

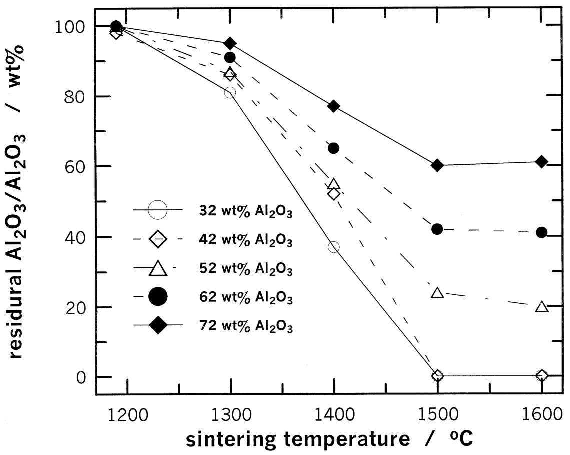

Fig. 5. Amount of residual alumina in the sintered specimens as a function of sintering temperature.

function of sintering temperature. The mullite formed at 1200°C is attributed to the formation of primary mullite. The amount of alumina remains approximately the same at the temperature of 1200°C, suggesting that alumina is inert to the formation of primary mullite. In the temperature ranges from 1300 to 1500°C, the amount of mullite increases rapidly, the amount of alumina decreases rapidly instead. The increase in mullite amount in this temperature range is contributed by the formation of secondary mullite through the solution of alumina particles and precipitation of mullite grains.[9] The amount of mullite is not increased any further above 1500°C. Fig. 6 shows the amount of glassy phase as a function of sintering temperature. The amount of glass phase in the kaolinite specimen is also shown in the figure for comparison. The amount of glass phase is reduced as alumina is added into kaolinite. The amount of glass phase decreases rapidly between 1300 and 1500°C. The glass in the specimen containing 72 wt.% Al_2O_3 is consumed nearly complete. However, due to the existence of impurities in the starting materials, glass phase will always present at the grain boundaries. From Figs. 5 and 6, the alumina and glass are consumed rapidly to accompany the formation of secondary mullite in the temperature region from 1300 and 1500°C.

The absolute density of the (kaolin + alumina) powder compacts after sintering is shown as a function of sintering temperature in Fig. 7. The density of the kaolin powder compact and alumina powder compact is also shown in the figure for comparison. The relative density of the powder compacts is shown as a function of alumina content in Fig. 8. The relative density of the alumina-containing specimens is higher than 90% as the specimens are sintered at 1600°C. In the temperature ranges between 1300 and 1500°C, the densification rate is relatively slow (Figs. 7 and 8). Secondary mullite is formed within this temperature region, suggesting that the reaction between the glass phase and alumina to form mullite is detrimental to the densification.

The density of kaolin powder compact is decreased above 1500°C. The Fe_3O_4 is formed at a temperature above 1500C.[10] The formation of Fe_3O_4 from Fe_2O_3 can generate oxygen as

$$3Fe_2O_3 \rightarrow 2Fe_3O_4 + 1/2O_2 \tag{2}$$

large holes are formed consequently in the sintered compact.[5] The density of the kaolin specimen thus decreases considerably above 1500°C. In the alumina-containing specimens, the amount of iron oxide is diluted due to the addition of alumina. Furthermore, iron oxide can dissolve into alumina at elevated temperature (the solubility of Fe_2O_3 in Al_2O_3 is higher than 15 wt.% above 1400°C),[11] the decrease of density in the alumina-containing specimens above 1500°C is thus not observed.

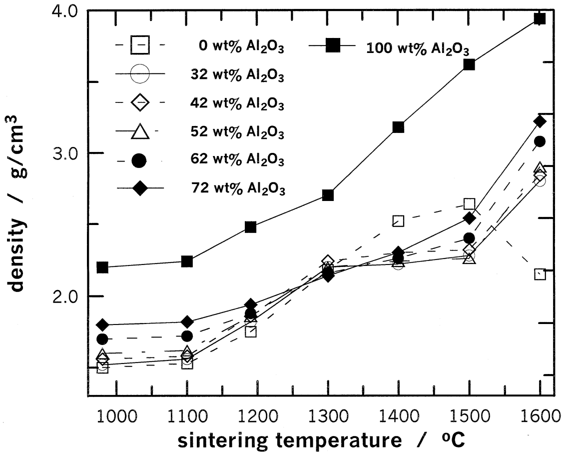

Fig. 7. Absolute density of the sintered specimens as a function of sintering temperature.

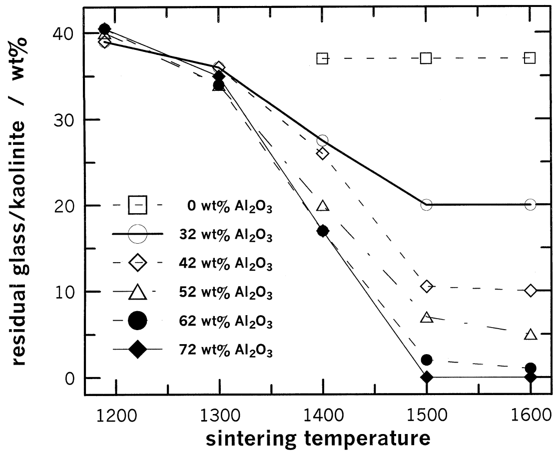

Fig. 6. Amount of glassy phase in the sintered specimens as a function of sintering temperature.

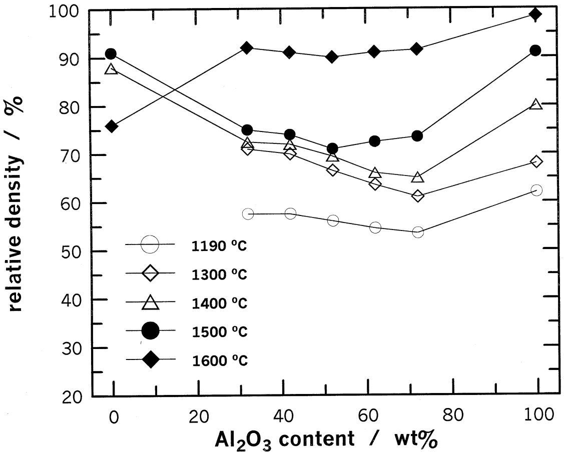

Fig. 8. Relative density of the sintered specimens as a function of alumina content.

The fracture surfaces of the specimens containing 42 wt.% Al_2O_3 are shown in Fig. 9. In the specimen sintered at 1400°C, large holes are observed [Fig. 9(b)]. Such large holes are not found in the green compact and in the specimens sintered below 1300°C [Fig. 9(a)]. These large holes are nearly spherical in shape. Furthermore, the fracture path around the large holes is very much flat, indicating the surface of large holes is covered with glass phase. The holes are no longer spherical in shape in the specimen sintered at 1600°C [Fig. 9(c)]; mullite grains intrude into the large holes. The density of the kaolinite, alumina and mullite is different, a shrinkage is accompanied with the reaction between kaolinite and alumina. The formation of mullite is mainly taken place between 1300 and 1500°C. Large holes are thus formed in this temperature region. Glass phase can flow to the surface of holes, the holes are thus covered with glassy phase. More glassy phase is consumed by alumina to form mullite at higher temperature; furthermore, mullite grains grow in their size at 1600°C. The holes are thus no longer spherical at the temperature. Nevertheless, the presence of the large holes renders the density of the kaolin-containing specimens lower than that of alumina (Fig. 8).

The microstructures of the specimens sintered at 1600°C for 1 h are shown in Fig. 10. The average intercept and the aspect ratio of mullite grains are shown in Fig. 11. As 32 wt.% Al_2O_3 and 42 wt.% Al_2O_3 are added into kaolin, both the average intercept and aspect ratio of mullite decrease with the increase of alumina content. In the specimens containing more than 52

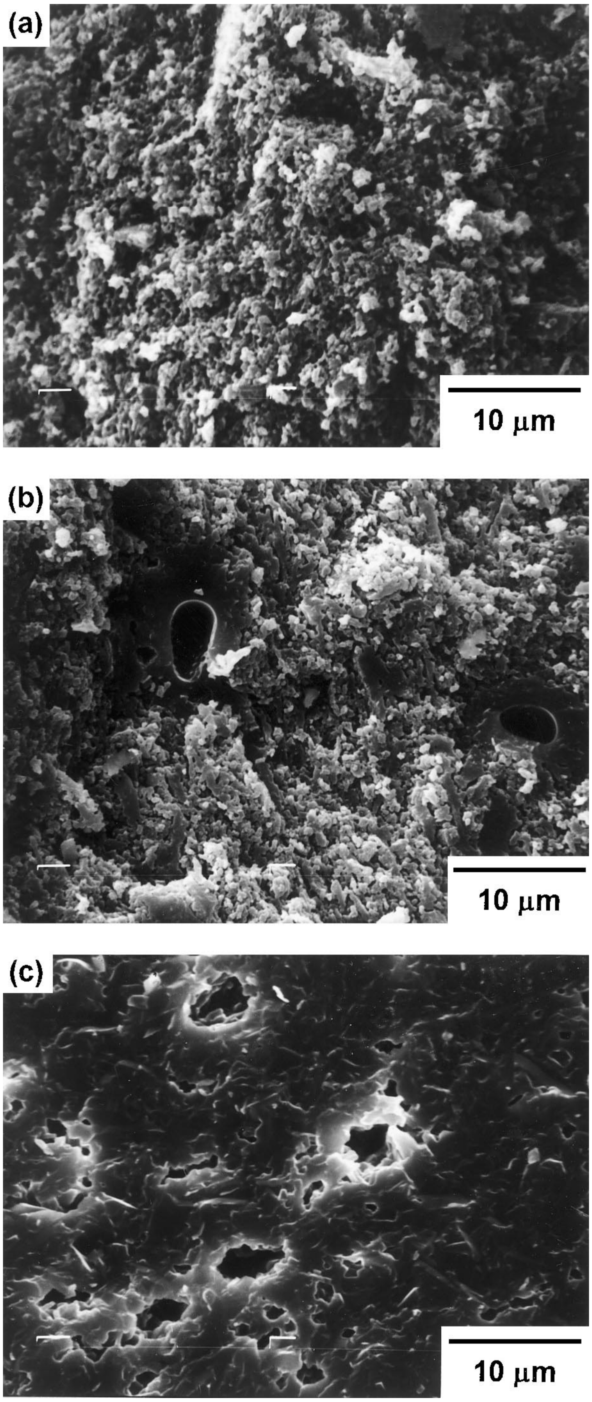

Fig. 9. Micrographs of the fracture surface of kaolinite + 42 wt.% alumina specimen sintered at (a) 1200°C, (b) 1400°C and (c) 1600°C.

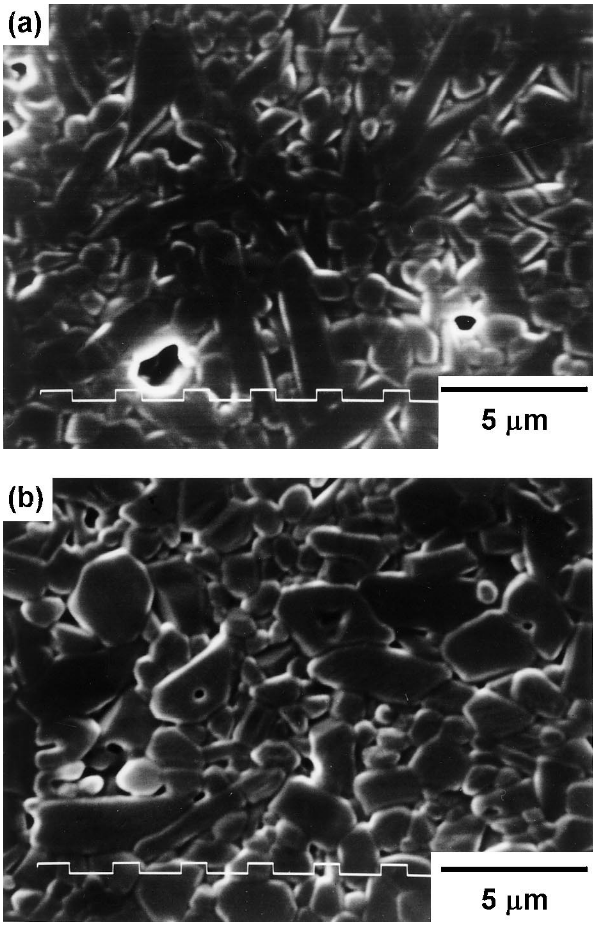

Fig. 10. Microstructures of the sintered specimens containing (a) 42 wt.% and (b) 72 wt.% Al_2O_3. The sintering temperature is 1600°C.

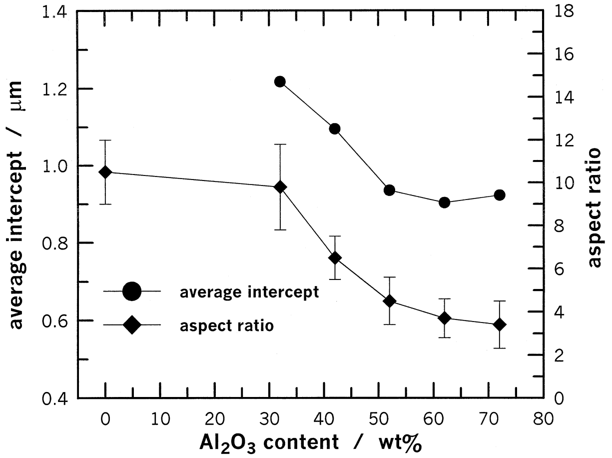

Fig. 11. Average intercept and aspect ratio of the grains in the specimens sintered at 1600°C for 1 h as a function of Al_2O_3 content.

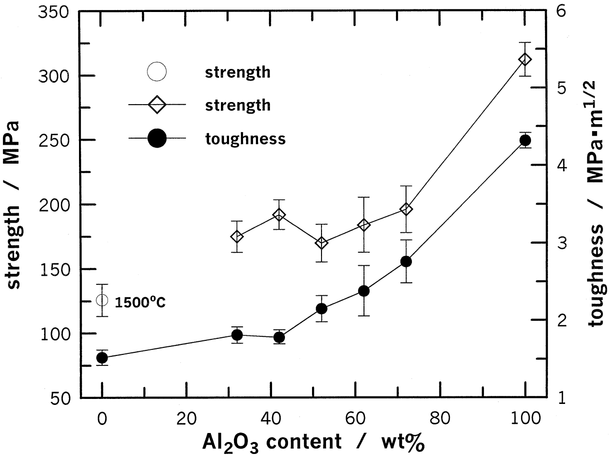

Fig. 12. Strength and toughness of specimens sintered at 1600°C as a function of Al_2O_3 content. The strength of the kaolin specimen (i.e. 0% Al_2O_3 specimen) sintered at 1500°C is also provided in the figure.

wt.% Al_2O_3, mullite and alumina are coexisted. Therefore, the intercept and aspect ratio in Fig. 11 are virtually the values for both mullite and alumina grains. The alumina grains can act as the nuclei for the formation of mullite grains.[10] The increase of alumina particles increases the amount of nuclei and decreases the amount of glass, the size and aspect ratio of mullite grains are thus reduced.

Fig. 12 shows the strength of the specimens sintered at 1600°C for 1 h as a function of alumina content. The strength of the kaolinite specimen sintered at 1600°C is low for its low density. Therefore, the strength of the kaolinite specimen sintered at 1500°C is also shown in the figure for comparison. The strength of the (kaolin + alumina) specimens is in a rather small region from 170 to 195 MPa, indicating that the size of the critical flaws in the kaolin-containing specimens is more or less the same. The strength of the (kaolin + alumina) specimens is higher than that of kaolin specimen due to the decrease of glassy phase, and lower than the strength of alumina specimen due to the presence of large holes. The toughness of the specimens sintered at 1600°C is also shown in Fig. 12. The presence of rounded holes has little influence on toughness. Due to the amount of brittle glass is reduced, the toughness of the specimens thus increases with the increase of alumina content.

4. Conclusions

The present study demonstrates that mullite can be prepared by reaction sintering kaolinite and alumina. The advantage of this process is its economic feasibility. The disadvantage is its relatively high sintering temperature, low density and consequently low strength. The alumina particles are inert to kaolinite until 1200°C. The reaction between alumina and the glass phase to form mullite starts from 1300°C. The sintering temperature of the (kaolin + alumina) powder compacts has therefore to be higher than 1300°C. Nevertheless, this disadvantage can be coped with by adding flux such as feldspar into kaolin.[12] The reaction between kaolinite and alumina is accompanied with a shrinkage. The presence of glassy phase facilitates the formation of large holes. Fully dense mullite specimens are thus difficult to prepare by using the process employed in the present study. The strength of the specimens is therefore low. However, the toughness of the specimen increases with the increase of alumina content.

Acknowledgement

The present study was supported by the National Science Council, Republic of China, through contract number NSC88-2216-E002-027.

References

1. Aksay, I. A. and Pask, J. A., Stable and metastable equilibrium in the system SiO_2–Al_2O_3. *J. Am. Ceram. Soc.*, 1975, **58**, 507–512.
2. Carty, W. M. and Senapati, U., Porcelain — raw materials, processing, phase evolution, and mechanical behavior. *J. Am. Ceram. Soc.*, 1998, **81**, 3–20.
3. Brindley, G. W. and Nakahira, M., The kaolinite–mullite reaction series: III, the high-temperature phases. *J. Am. Ceram. Soc.*, 1959, **42**, 319–323.
4. Pask, J. A. and Tomsia, A. P., Formation of mullite from sol–gel mixtures and kaolinite. *J. Am. Ceram. Soc.*, 1991, **74**, 2367–2373.
5. Chen, C. Y., Lan, G. S. and Tuan, W. H., Microstructural evolution of mullite during the sintering of kaolin powder compacts. *Ceramics International*, in press.
6. Doremus, R. H., In *Glass Science*, John Wiley & Sons, New York, 1973.
7. Wotting, G., Kanka, B. and Ziegler, G., Microstructural development, microstructural characterization and relation to mechanical properties of dense silicon nitride. In *New Oxide Technical and*

Engineering Ceramics, ed. S. Hampshire. Elsevier Applied Science, London, 1986, pp. 83–96.

8. Liu, K.-C., Thomas, G., Caballero, A., Moya, J. S. and Aza, S., de, Time–temperature–transformation curves for kaolinite-α-alumina. *J. Am. Ceram. Soc.*, 1994, **77**, 1545–1552.
9. Liu, K.-C., Thomas, G., Caballero, A., Moya, J. S. and Aza, S., de, Mullite formation in kaolinite-α-alumina. *Acta Metall.*, 1994, **42**, 489–495.
10. Papargyris, D. and Cooke, R. D., Structure and mechanical properties of kaolin based ceramics. *Brit. Ceram. Trans.*, 1996, **95**, 107–120.
11. Muan, A., Stability of the phase $Fe_2O_3 \cdot Al_2O_3$. *Am. J. Sci.*, 1958, **256**, 413–422.
12. Kobayashi, Y., Ohira, O., Satoh, T. and Kato, E., Compositions for strengthening porcelain bodies in alumina–feldspar–kaolin system. *Brit. Ceram. Trans.*, 1994, **93**, 49–52.