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# The processing of kaolin powder compact

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#### Abstract

Powder processing is crucial to the final properties of porcelain bodies. In the present study, a kaolin powder was used as the starting material, water or organic solvent was employed as the milling medium, and subsequently dried and formed by the diepressing technique. The final phase, mullite, is obtained by sintering kaolin powder compacts. By using an organic solvent instead of water, the density, microstructure and mechanical properties show a better performance due to the avoidance of agglomerates formation. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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### 1. Introduction

Mullite  $(3Al_2O_3 \cdot 2SiO_2)$  is an important constituent of refractories, white-wares and structural clay products. Due to its excellent high temperature stability, mechanical properties, low creep rate, low thermal expansion coefficient and low thermal conductivity, mullite ceramics is widely used as thermal insulator and electric resistor. Because of the very low interdiffusion rates of  $Si^{4+}$  and  $Al^{3+}$  within the mullite lattice, the kinetics and mechanism of forming mullite by reaction depend strongly on the precursor mixing [1].  $SiO_4$  tetrahedral layer and Al(O,OH)<sub>6</sub> octahedral layer are in sequential series in kaolinite. The Si and Al are mixed in atomic order in the kaolinite. Therefore, even though there are many different approaches to the production of high purity mullite powders, kaolinite is commonly used to form mullite in white-wares and refractories.

In the present study, a kaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>·2H<sub>2</sub>O) powder is employed as the starting material. The detailed sequence of chemical reactions during the sintering of kaolin bodies is very complicated, depending on the compositions of raw materials, characteristics of powders, and fabrication conditions. However, for a commonly used kaolin powder containing a small amount of quartz, the

general reaction steps can be roughly outlined as follows [2]. Firstly, the dehydroxylation of kaolinite to metakaolin (Al<sub>2</sub>O<sub>3</sub>·2SiO<sub>2</sub>) occurs at ~550°C [3–7]. Metakaolin transforms to a metastable phase of spinel-type structure and releases a large amount of amorphous free silica at ~950–1000°C [8–10]. The spinel phase then transforms to mullite above 1075°C [5]. As the temperature reaches ~1200°C, the phase transformation of quartz to cristobalite begins, then cristobalite disappears above ~1400°C [11].

In conventional processes, however, industrial kaolincontaining products are frequently fabricated by using wet processing such as slip casting or extrusion. Dry processing is less commonly used at present in the industry. Furthermore, though many studies have involved the mechanical properties of triaxial whiteware [12–15], the effect of powder preparation on the properties of mullite developed from kaolin has attracted little attention. In the present study, the effect of kaolin powder preparation for dry processing on sintered mullite bodies is investigated.

## 2. Experimental procedures

The chemical composition reported by the manufacturer of the kaolin powder (AKIMA 35, Malaysia), used in this study was SiO<sub>2</sub> (48.5 wt.%), Al<sub>2</sub>O<sub>3</sub> (35.5 wt.%), K<sub>2</sub>O (1.5 wt.%), Fe<sub>2</sub>O<sub>3</sub> (1.0 wt.%), TiO<sub>2</sub> (0.4

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wt.%), MgO (0.35 wt.%), Na<sub>2</sub>O (0.07 wt.%), CaO (0.05 wt.%) and an ignition loss of 12.6 wt.%. The X-ray diffraction (XRD) pattern of as-received powder is shown in Fig. 1. From the XRD analysis, the kaolin powder consists of kaolinite, quartz, and a small amount of muscovite (mica) phase.

The specimens were formed by die-pressing, by using two different routes, A and B (Fig. 2). The precursor powders were prepared by attrition milling with 2–3 mm zirconia balls for 1 h. The milling liquid used for route A and B were deionized water and ethyl alcohol, respectively. The capacity of the milling tank was 750 cm<sup>3</sup>, and the impeller rotation rate was 300 rpm. A milling batch



Fig. 1. The XRD pattern of kaolin powder.



Fig. 2. Flowchart of the experimental procedures.

for route A consisted of  $\sim 250$  g of powder at 60 wt.% solid loading (relative to deionized water), 5 g of sodium hexametaphosphate (Showa chem. Co., Japan) and  $\sim$ 1.6 kg of milling ZrO<sub>2</sub> balls. The sodium hexametaphosphate could dissolve in water to act as a dispersant for kaolin powder. A milling batch for route B consisted of  $\sim$  50 g of powder at 20 wt.% solid loading (relative to alcohol). No dispersant was added in route B. The slurries were then stirred and dried slowly to remove water and alcohol. After drying, the lumps were crushed and passed through a plastic sieve with aperture size of 100 µm. Powder compacts were formed by uniaxially pressing at 25 MPa. The final dimension of green compacts was  $\sim 4.5 \times 7 \times 50$  mm<sup>3</sup>. The compacts were then sintered in a closed alumina crucible at various temperatures for 1 h in air. The heating rate and the cooling rate were 5°C/min.

The sintered specimens were machined longitudinally with a 325-grit resin-bonded diamond wheel at a cutting depth of 5  $\mu$ m/pass. The final dimensions of the specimens were  $3 \times 4 \times 36$  mm<sup>3</sup>. The flexural strength of specimens was determined by the three-point bending technique at ambient, room-temperature condition. The mechanical testing was carried out with a desktop universal machine (CK10, Engineering System Co., U.K.) with lower spans of 30 mm at a loading rate of 0.5 mm/ min. The fracture toughness was determined by the 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 phase identification was performed by X-ray diffractometry (XRD, Philips PW1710, Philips Co., The Netherlands) with  $CuK_{\alpha}$  radiation. The green density and final density were determined by Archimedes' method. The characteristics of the mechanical failure of the specimens were investigated by examining the fracture surfaces with scanning electron microscopy (SEM, Philips 515, Philips Co., Netherlands). The adsorption of chemicals on the dried powders was determined by the Fourier transform infrared spectroscopy (FTIR, FT/IR-300E, JASCO).

#### 3. Results

Fig. 3 shows the morphology of the powders prepared from route A and B. It is found that powder A and B exhibit strong and weak extent of agglomeration, respectively. Furthermore, the flaky nature of the particles can also be noted. The particle size of powder A is significantly larger than that of powder B. The FTIR spectra of dried powder A and B are shown in Fig. 4. Comparing with the powder A, a small amount of C–H bond remains after the powder dried from route B. Fig. 5 shows the pore size distribution in die-pressed green compacts. It reveals that many large pores existed in sample A in comparison with that in sample B. The





Fig. 3. The morphology of the dried (a) powder A and (b) powder B.



Fig. 4. The FTIR spectrum of dried powder A and B.

XRD patterns of samples developed from routes A and B at various temperatures for 1 h in air are shown in Fig. 6. They indicate that the sample A and B sintered at 1500°C are both composed of mullite phase. The tap density of powders prepared from route A and B was also determined. The tap density of powder A ( $21.5\pm1.5\%$ ) almost double that of powder B ( $9.5\pm1.2\%$ ). Whereas, after die-pressing, the green density of sample A



Fig. 5. Pore size distribution of green compact of sample A and B.



Fig. 6. The XRD patterns of (a) sample A and (b) sample B sintered at various temperatures for 1 h.



Fig. 7. The apparent density of samples A and B as a function of sintering temperature.

 $(63.8\pm0.3\%)$  is slightly higher than that of sample B  $(58.2\pm0.25\%)$ . The apparent density of both samples sintered for 1 h is shown as a function of temperature in Fig. 7. The density of sample A and B is increased with the increase of sintering temperature. They both reach their highest values as the sintering temperature is 1400°C, and then drop with the increase of sintering temperature. It can also be found that the highest density of sample B (sintered at 1400°C) is higher than that of sample A.

The flexural strength of samples A and B sintered for 1 h is shown as a function of sintering temperature in Fig. 8. It indicates that the flexural strength of both samples is increased with the increase of sintering temperature. Both the strength of samples A and B reach their highest values as the sintering temperature is 1400°C. Furthermore, the flexural strength of sample B is pronouncedly higher than that of sample A. Fig. 9 shows the fracture toughness of samples A and B sintered for 1 h as a function of sintering temperature. It also indicates that the fracture toughness of both samples increase



Fig. 8. The flexural strength of samples A and B as a function of sintering temperature.



Fig. 9. The fracture toughness of samples A and B as a function of sintering temperature.

with the increase of sintering temperature. Similarly, both the toughness of sample A and B reach their highest values as the sintering temperature is 1400°C. The fracture toughness of sample B is higher than that of sample A. Fig. 10 shows the typical microstructures for fracture surfaces of both samples sintered at 1400 and 1500°C for 1 h. The pore size of both samples, A and B, sintered at 1500°C is larger than that of the samples sintered at 1400°C. The pores of sample B are almost spherical in shape. The morphology of pores in sample A is more irregular. It can also be found that the pore distribution in sample B is more uniform than that in sample A.

## 4. Discussion

Kaolin powder is one of the most commonly used raw materials in the conventional ceramic industry, and wetprocessing method is frequently employed. In the present study, therefore, kaolin powder is used as the starting material for mullite bodies. Though wet-processing method can fabricate products of complicated shapes, it takes a long time for the drying process and needs a large space to store the green parts during drying. Therefore, dry processing has the merit of mass production in industry.

The details of phase transformation regarding the development of kaolin to mullite are very complicated and remain unclear [2]. From the results of phase analysis, shown in Fig. 6, the mullite formation of sample A and B begins as the sintering temperature is above  $1100^{\circ}$ C.

On quartz-to-cristobalite transformation, sample A occurs below 1190°C, but sample B delays the formation to a temperature above 1190°C. Finally, both samples A and B show only mullite as the sintering temperature reaches  $1500^{\circ}$ C.



Fig. 10. Microstructures of fracture surfaces of sample A sintered at; (a) 1400 and (b) 1500°C for 1 h, sample B sintered at (c) 1400 and (d) 1500°C for 1 h.

Liquid phase sintering is the dominant mechanism during densification in porcelain bodies. The density of both samples (Fig. 7), is increased dramatically during the liberation of glassy phase as the sintering temperature is above 1000°C. The densification data suggest that the density of sample A is higher than that of sample B as the sintering temperature is below 1300°C. As the sintering temperature is higher than 1300°C, the density of sample A is lower than that of sample B. Comparing the densification data with the results of phase analysis, the cristobalite formation of sample A occurs at a lower temperature which owes to the higher density achieved than that of sample B as the sintering temperature is below 1300°C. It implies, therefore, that the transformation temperature of quartz to cristobalite tends to decrease with the increase of density of porcelain body.

As the sintering temperature is above  $1400^{\circ}$ C, the density of both samples is decreased with the increase of temperature. This density decrease, a common phenomenon related with porcelain bodies, has been reported to be due to the impurity of Fe<sub>2</sub>O<sub>3</sub> in clay minerals [14–16]. According to thermodynamic analysis [17,18], the reaction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> can take place to liberate O<sub>2</sub> gas as the temperature reaches ~1500°C. Therefore, the so-called "bloating", is owing to the release of O<sub>2</sub> gas from the reaction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub>.

microstructure of fracture surface, Fig. 10, reveals that the pore size of both samples sintered at 1500° C is significantly larger than that of samples sintered at 1400°C.

The density of sample B is higher than that of the sample A as the sintering temperature is above 1300°C. This is also supported by the microstructure observation, Fig. 10. Powder A reveals a strong agglomeration of stacked kaolin flakes. Powder B, however, is weakly agglomerated with flakes separated from each other. The difference of the powder characteristics between A and B, is resulted from the different milling liquid used during attrition milling. Because of the strong capillary force of water (72.75 dynes/cm, at 20°C) [19] used in route A for milling, a capillary force occurs between flakes during drying, which can lead the flakes to stack on each other to form hard agglomerates. Contrarily, due to the low capillary force of alcohol (23.04 dynes/ cm, at  $20^{\circ}$ C) [19] used in route B, the flakes can hardly attract each other to form agglomerate during drying. The FTIR data (Fig. 4) suggest the existence of C-H bond in powder B after drying. It can be assumed that there is some residual alcohol in powder B even after drying. Therefore, alcohol used as milling medium can prevent the flakes from stacking to form agglomerates. This phenomenon can also be verified by the data of tap density. Because most of the flakes of powder A are closely stacked together, the structure of powder compact is very dense, leading to high tap density. Whereas, the particles of powder B are well separated from each other, exhibiting a low tap density. From the result of pore distribution (Fig. 5) many large pores are formed in the green compact A owing to the existence of hard agglomerates. Therefore, the presence of agglomerates affects the properties of porcelain body significantly.

Furthermore, comparing the microstructures of sample A and B prepared by sintering at the same temperature (Fig. 10) the irregular pores in sample A is due to the agglomeration from the powder preparation. Whereas, an uniform microstructure and the presence of a glassy phase in sample B tend to generate nearly spherical pores. The pore morphology of sample B is, therefore, more regular.

For the mechanical properties of porcelain bodies, intrinsic flaw size is perhaps the predominant factor affecting the strength, and depends very much on the microstructure [2]. Although the density difference between sample A and B above 1400°C is less than 5% (Fig. 8) shows that the flexural strength of sample B is 1.6 times that of sample A. The size of irregular flaws due to the agglomeration in sample A is large, and the flexural strength is thus low. In addition to the higher density of sample B, both the uniform pore size and pore distribution lead the sample B to a higher strength. Furthermore, the shape of pores in sample B, due to the presence of glassy phase, tends to be nearly spherical, leading also to increased strength.

As the sintering temperature is above  $1300^{\circ}$ C, the fracture toughness of sample B is higher than that of sample A. For a glass system, the increase in porosity has little effect on the value of toughness [15]. In the present study, the dominant mechanism operated in toughness development can be related to the shape of pores. The toughness data imply that the pore shapes of both sample A and B become more spherical due to the viscous flow of glassy phase as the sintering temperature is above 1200°C. However, comparing their pore shapes, the pore shapes of sample B is nearly spherical, leading the crack front to become blunter and therefore enhancing the K<sub>IC</sub> values.

## 5. Conclusions

In powder preparation, the selection of milling liquid affects significantly the properties of mullite bodies. In the present study, route A using deionized water as milling liquid leads to the formation of strong agglomerates due to the strong capillary force. The presence of agglomerates in kaolin powder compact is detrimental to densification. Contrarily, route B using organic solvent, ethyl alcohol, as milling liquid leads to the formation of weak agglomerates, exerting positive effect on sintered mullite. Owing to the more homogeneous microstructure of sintered mullite prepared from route B, the flexural strength and fracture toughness are 1.6 and 1.2 times than for the sintered bodies prepared from route A, respectively.

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