Evolution of Mullite Texture on Firing Tape-Cast Kaolin Bodies

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Kaolin undergoes a series of phase changes on heating to elevated temperature, proceeding through kaolin, metakaolin, \( \gamma \)-Al\(_2\)O\(_3\) spinel, and mullite. The morphologic evolution of the kaolin–mullite reaction series has been investigated in the present study. A highly textured kaolin green body was prepared by a tape-casting technique, and the morphology evolution from kaolin flakes to mullite aciculars on firing from 450°C to 1600°C was then monitored using X-ray diffractometry and scanning electron microscopy. Equiaxed mullite nuclei first appeared at 1000°C; the aspect ratio of the mullite grains then increased with increased firing temperature. The mullite aciculars rearranged their orientation in a glassy phase until they impinged on each other. A highly textured mullite specimen was prepared by firing the kaolin tape at a temperature >1500°C.

I. Introduction

The crystalline product after firing kaolin at a temperature >1100°C is mainly mullite. Although the kaolinite–mullite reaction series has been extensively investigated for many years using various techniques, such as X-ray diffractometry (XRD),\(^1\)–\(^{15}\) differential thermal analysis (DTA),\(^8\),\(^11\),\(^12\),\(^14\),\(^16\)–\(^18\) and transmission electron microscopy (TEM),\(^3\),\(^6\),\(^9\),\(^10\),\(^14\),\(^18\)–\(^23\) controversial issues continue to exist. These issues include (1) the extent of crystallization of metakaolinite, (2) the crystal structure and chemistry of an intermediate, \( \gamma \)-Al\(_2\)O\(_3\) spinel phase, which is formed at \( \sim 1000\)°C, (3) the composition of mullite at the beginning of its formation, and (4) the crystallographic orientation relationships of the kaolinite–metakaolinite–spinel–mullite series. These issues can be related to the presence of impurities, which are intrinsic in the kaolinite extracted from natural resources. Furthermore, the grain size of the crystallized phases involved in the reaction series, such as metakaolinite and \( \gamma \)-Al\(_2\)O\(_3\) spinel phase, is at the nanometer scale, making technical analyses challenging. However, because of the development of high-resolution transmission electron microscopy (HR-TEM), considerable progress has been made recently on these issues.\(^{14,21}\)

Although several groups have investigated the evolution of the crystallographic orientation from kaolinite, metakaolinite, and spinel to mullite,\(^5\),\(^14\),\(^15\),\(^19\)–\(^21\) uncertainties on the orientation relationships between kaolin and mullite remain. Brindley and Nakahira\(^6\) and Comer\(^19\) proposed that a preferred orientation exists between either kaolin and mullite or spinel and mullite. Onike\(^{14,20}\) observed a relationship between kaolin and spinel. Lee \textit{et al.}\(^{14}\) confirmed the existence of the preferred orientation between spinel and metakaolinite, although their study also suggested that no clear orientation relationship exists between kaolinite and mullite. Because the kaolinite particles are flaky in nature, McConville \textit{et al.}\(^{21}\) suggested that the texture development depends strongly on the shaping technique used. Textured mullite specimens were obtained by preparing kaolin powder compacts by an extrusion\(^21\) or a die-pressing technique,\(^15\) then fired at elevated temperature. However, no mullite texture was observed in a fired loose-packaging kaolin powder compact.\(^{21}\)

A textured microstructure can offer many possibilities to improve the performance of ceramics. For example, mechanical,\(^24\) electrical,\(^25\) and piezoelectric\(^26\) properties can be improved by transforming an equiaxied microstructure to a textured microstructure. A recent study has demonstrated that a highly textured mullite can be prepared by templated grain growth,\(^27\) specifically, by doping oriented acicular mullite seeds into a mullite precursor to develop a textured microstructure after firing at elevated temperature. In the present study, a textured mullite has been prepared using kaolin powder as starting material. The evolution of phases and their morphologies in the kaolin–mullite reaction series has been carefully monitored.

II. Experimental Procedure

A kaolin powder (AKIMA 35, Akima Co., Malaysia) was used as the starting material in the present study. Chemical composition of the kaolin powder was determined using induced coupled plasma emission spectroscopy (ICP; Spectro Analytical Instruments, Fitchburg, MA). Kaolin powder and 2 wt% dispersant (sodium hexametaphosphate, Showa Chemical Co., Tokyo, Japan) were mixed together in deionized water in an agitator for 4 h. The solids loading was 20 wt%. After the slurry was left unstirred for 24 h, the sediment from the slurry was discarded to remove the agglomerates. Approximately 60 wt% of the starting powder was removed at this stage. The suspension was then stirred again and heated to 90°C, after which 2.5 wt% binder (poly(vinyl alcohol), PVA; Nacalai Tesque, Inc., Kyoto, Japan) and plasticizer (poly(propylene glycol), PPG; Nacalai Tesque) relative to the slurry were added slowly into the slurry. The ratio of the binder to plasticizer was one to one. The viscosity of the slurry was then adjusted to 400 cP (0.4 N s/m\(^2\)) by removing part of the water by heating at 90°C. Tape casting was conducted after the slurry had cooled to room temperature and had been sieved.

The slurry was cast onto a moving mylar carrier (24.5 cm wide) through a 15 cm wide doctor blade at a rate of 20 cm/min. The blade height was set at 400 \( \mu \)m, and the thickness of the green tape ranged from 100 to 150 \( \mu \)m after drying. Figure 1 gives the definition of the parallel and perpendicular planes of the tape.

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relative to the casting direction. The cast tape was then stamped into 1 cm × 1 cm squares and fired at temperatures varying from 450° to 1600°C for 1 h after removing the organics at 450°C. The heating and cooling rates were 5°C/min.

The viscosity of the slurry was measured using a shear-controlled cylinder viscometer (Model LVDT-II, Brookfield Engineering Laboratories, Stoughton, MA). The phase identification was performed using XRD with CuKα radiation. The microstructure was observed using either SEM or field-emission scanning electron microscopy (FE-SEM). Concentrated hydrofluoric acid (48%) was used as etching solution to reveal the morphology of mullite grains. Many mullite grains were found on the parallel plane, as demonstrated later. Therefore, the size and aspect ratio of mullite grains could be determined by measuring such grains directly from SEM micrographs. At least six micrographs were taken from each firing condition, and more than 100 mullite grains were measured for each firing condition.

III. Results and Discussion

The constituents of the as-received kaolin powder, as determined by ICP, are SiO₂ (48.6 wt%), Al₂O₃ (35.7 wt%), K₂O (1.2 wt%), Fe₂O₃ (0.9 wt%), TiO₂ (0.4 wt%), MgO (0.2 wt%), CuO (0.1 wt%), BaO (0.1 wt%), and an ignition loss of 12.6 wt%. Comparing these constituents with the chemical formula for kaolinite, Al₂O₃·2SiO₂·2H₂O, there is an excess of ~6% SiO₂ in the raw material. The excess SiO₂ exists mainly in the form of quartz in the raw material, as shown in Fig. 2(a). There is also a small amount of mica impurity detected in the as-received kaolin. Figure 3 shows the morphology of as-received kaolin particles, demonstrating the flaky nature of the particles. Figure 4 shows a three-dimensional view of the green tape, indicating that most kaolin flakes are aligned parallel. The texture of the green tape can be further verified using XRD analysis. Figure 2 also shows the XRD patterns of the as-received kaolin powder and of the green tape. The XRD pattern of the as-received kaolin powder is obtained by tapping the powder lightly into the XRD powder holder. Some of the flakes lie flat because of the tapping. Figure

![Fig. 2. XRD patterns of (a) as-received powder and (b) green tape.](image)

![Fig. 3. Morphology of the kaolin particles.](image)

![Fig. 4. Three-dimensional view of a green kaolin tape.](image)

![Fig. 5. XRD patterns of the tapes after firing at the indicated temperatures for 1 h.](image)
2(b) shows the XRD pattern of the green tape, demonstrating the presence of strong peaks of (00l) planes. Kaolinite is a layered structure composed of sequential SiO$_4$ tetrahedral sheets and Al(O,OH)$_6$ octahedral sheets. The morphology of the kaolin particles thus tends to be flaky in shape. The c-axis of the kaolinite crystal is perpendicular to the flake plane. The strong (00l) peaks in Fig. 2(b) indicate that most kaolin flakes are aligned parallel. Thus, the tape-casting technique used in the present study prepares a strongly textured kaolin powder compact. The tape-casting technique is superior to the die-pressing technique in terms of texture control of the green compact. Therefore, the morphologic evolution from kaolin flakes to mullite aciculars can be monitored.

The phase transformation series from kaolin to mullite can be seen in the XRD patterns shown in Fig. 5. The kaolinite transforms to metakaolinite by removing the hydroxyl groups at a temperature $\leq 600^\circ$C. The crystalline structure of metakaolinite is in a form of short-range order; therefore, the diffraction peaks of metakaolinite are buried in the XRD background. The size of spinel crystals formed after heating at 1000 $^\circ$C is also small, and, therefore, the height of the peaks for the spinel is too low to be identified. Cristobalite and mullite are found after firing at 1000 $^\circ$C for 1 h, suggesting that mullite is formed simultaneously with the formation of spinel. Other groups also have reported this finding. Because the spinel transforms to mullite above 1100 $^\circ$C, the intensity of the mullite peaks increases significantly after heating at 1100 $^\circ$C. The intensity of mullite peaks also increases with increasing firing temperature. The splitting of (120) and (210) peaks after heating to 1600 $^\circ$C can be attributed to the change of the composition from aluminium-rich mullite, $2\text{Al}_2\text{O}_3\text{SiO}_2$, to $3\text{Al}_2\text{O}_3\cdot2\text{SiO}_2$ mullite.

The microstructure of the kaolin tape after firing at 1100 $^\circ$C for 1 h is shown in Fig. 6. The micrograph for the green tape is also shown for comparison purposes. The flaky nature of the starting particles remains after firing up to 1100 $^\circ$C. From the perpendicular plane, small particles in the range of 0.5–1 $\mu$m are found on the edge of the flakes above 1100 $^\circ$C (see Fig. 7(a)). Even smaller nuclei, ~50 nm, are revealed in the particles after etching with hydrofluoric acid for a few seconds (see Fig. 7(b)). From XRD analysis, these nanosized nuclei are determined to be mullite. The mullite nuclei are roughly equiaxed. The morphologies of the mullite grains in the specimens fired at 1200 $^\circ$C and 1400 $^\circ$C for 1 h are shown in Fig. 8, indicating that the mullite grains are no longer equiaxed after firing above 1200 $^\circ$C. Figure 9 shows the morphology of mullite aciculars after firing at 1500 $^\circ$C and 1600 $^\circ$C for 1 h. The mullite aciculars undergo considerable grain growth after heating at 1600 $^\circ$C, and there are many aciculars aligned parallel, as shown in Figs. 8 and 9. Therefore, the length, width, and aspect ratio of the mullite aciculars can be monitored.
determined by measuring such grains in Fig. 10. The points show the average values, and standard deviation is also shown. The aspect ratio of mullite aciculars is 10 after firing at 1600°C for 1 h. The standard deviation of the aspect ratio increases with increasing firing temperature, indicating that the distribution of the aspect ratio of aciculars is broadening with increasing temperature. Figure 11 shows the three-dimensional view of the tape after firing at 1600°C. The three-dimensional micrograph demonstrates a strongly textured microstructure.

The XRD patterns of specimens fired at 1600°C are shown in Fig. 12. The XRD pattern of a loose-packing specimen prepared by simply placing the kaolin powder (without packing or tapping) into an alumina crucible and then firing at 1600°C is shown in Fig. 12(a). Here, the intensity of the mullite \((hkl) l \neq 0\) peaks in the kaolin tape after firing at 1600°C is significantly lower than that of the peaks in the loose-packing specimen. The \(c\)-axis of the mullite is parallel to the long axis of the aciculars. The XRD analysis in Fig. 12(b) confirms the microstructural observation that many mullite aciculars are aligned in parallel. Although the intensity of mullite \((hkl) l \neq 0\) peaks does not decrease to zero, Fig. 11 shows that those aciculars that are not lying on the parallel plane deviate only a few degrees from the parallel plane.

The intensity ratio of \((100)\) to \((220)\) planes of mullite can be taken as an index for preferred orientation. The mullite specimen used to determine the intensity ratio shown in the Powder Diffraction File is presumably randomly oriented. The index for

![Fig. 8. Microstructures of the specimens fired at (a) 1200°C and (b) 1400°C for 1 h. Specimens were treated with hydrofluoric acid for a few seconds.](image)

![Fig. 9. Microstructures of the specimens fired at (a) 1500°C and (b) 1600°C for 1 h. Specimens were treated with hydrofluoric acid for a few seconds.](image)

![Fig. 10. Width, length, and aspect ratio of mullite grains as a function of firing temperature. Dwell time was 1 h.](image)
the preferred orientation for the ratio from the Powder Diffraction File is thus taken as zero. The index is shown as a function of firing temperature in Fig. 13. The intensity ratio for the loose-packing specimen is similar to that taken from the Powder Diffraction File, indicating that the mullite aciculars in the loose-packing specimen are randomly oriented. Figure 7 indicates that the nanosized mullite nuclei formed at 1100°C are equiaxed. The mullite nuclei then transform to aciculars with an aspect ratio of 2 after firing at 1300°C for 1 h, as shown in Fig. 10. Figure 13 suggests that the mullite aciculars are randomly oriented at 1300°C. The intensity ratio then decreases with increasing firing temperature, indicating that the extent of the preferred orientation increases.

A small amount of K₂O is present in the starting material. The eutectic temperature of the K₂O-Al₂O₃-SiO₂ system is as low as 985°C. The mullite nuclei formed at 1100°C are random oriented (see Fig. 7(b)). The presence of the liquid phase facilitates the formation of mullite aciculars. These mullite grains grow in size within the liquid phase through a dissolution and reprecipitation process. After the formation of mullite aciculars due to the presence of liquid phase, the aciculars can then accommodate their orientation with each other to grow in size. Because kaolin flakes are packed flake by flake, these flakes tend to stick to each other after being fired at elevated temperature. The perpendicular growth of aciculars in the kaolin tape is constrained because of the limited space in that direction. The growth of aciculars is, nevertheless, relatively easy parallel to the tape; therefore, a textured mullite is formed after firing the kaolin tape at elevated temperature. Furthermore, these mullite aciculars, which are not in parallel and difficult to grow, can dissolve into the liquid and then precipitate onto the large aciculars. The extent of preferred orientation, therefore, increases with increasing sintering temperature, as shown in Fig. 13. The texture is not noted in the loose-packing specimen, which indicates that the rearrangement process is not significantly affected by gravity, but depends strongly on the packing of kaolin flakes.

Figure 14 shows that the intensity ratio as a function of firing time at 1600°C tends to remain constant at that temperature. The size and aspect ratio of mullite aciculars are relatively large after firing to 1600°C (see Figs. 9(b) and 10). Because the mullite aciculars can easily impinge on each other, the reorientation process is restricted at 1600°C.

IV. Conclusions

The morphologic evolution of the kaolinite–mullite reaction series is monitored in the present study. A highly textured kaolin powder compact is first prepared using a tape-casting technique. The kaolin particles are flaky in shape, tending to align parallel to the tape plane during casting. The flaky nature of the starting
particles remains approximately the same up to 1100°C, and the
mullite nuclei formed at this temperature are equiaxed. Mullite
aciculars formed above 1200°C are caused by the presence of a
glassy phase. The mullite aciculars tend to develop parallel to the
tape plane because of the space constraint in the perpendicular
direction. The aspect ratio of the mullite aciculars increases with
increasing firing temperature. The reorientation process is prohib-
ited, because the mullite aciculars are too large and impinge on
each other. Most mullite aciculars not on the parallel plane deviate
only a few degrees from the parallel plane; thus, the mullite
specimen prepared by firing kaolin tape is textured. The present
study demonstrates that there is a preferred orientation between
kaolin flakes and mullite aciculars, although the extent of preferred
orientation depends strongly on the processing conditions.

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