Effect of Mixed Grinding of Kaolinite-Gibbsite Mixture on Formation of Mullite*

by Hojin RYU1, Eiki KASAI2 and Fumio SAITO3

Effect of mixed grinding of a kaolinite-gibbsite mixture on formation of mullite has been investigated by the X-ray diffraction method, DTA, SEM and surface area determination of powders. The both structures of individual specimen and their mixture are transformed easily into an amorphous state within about 60 minutes grinding by a planetary ball mill under dry condition. The amount of amorphous phase in the ground specimen increases with increasing grinding time. Accordingly, there has been a rapid decrease in the density of the mixture in the beginning of grinding and a leveling off with the progress of grinding. The specific surface area of the mixture increases sharply at the initial stage of grinding, then decreases gradually with an increase in grinding time, because of the coagulation. The mixed grinding has resulted in the formation of mullite directly from spinel phase without formation of corundum and cristobalite phases during sintering at more than 1223K. The ratio of formation of mullite has increased with an increase of grinding time and sintering temperature.

KEY WORDS: Mullite, Kaolinite, Gibbsite, Planetary Mill, Amorphorization, Mixed Grinding

1. Introduction

Mullite (3Al2O3·2SiO2) has a narrow stability field in the alumina-silica system, and a high melting point (about 2123K)1). Highly pure mullite ceramics are well known as the properties of high bending strength, excellent thermal shock resistance even at high temperature, creep resistance, and chemical stability2,3). Such properties of mullite enable us to use it as heavy-duty refractory materials and a high-temperature ceramic component. To use mullite as an infrared window material and other technological important applications, it is necessary to prepare highly reactive, pure and homogeneous powders which can be sintered to a fully dense ceramic body. Such powders have been mainly prepared by different synthesis methods such as sol-gel4), hydrolysis of mixed alkoxides5), co-precipitation6) and CVD7).

In addition, a study on preparation of mullite by solid-state reaction using kaolinite as one of starting materials has been investigated in recent years9). Such investigations suggest that key to the production of high performance mullite ceramics is the control of their starting powder characteristics. It might be very important for preparation of, especially, the original powders to improve their reactivity in solid-state reaction forming mullite11,12). Little attention has been paid on the effect of mixed grinding of the mixture of a kaolin minerals and gibbsite system of formation of mullite13).

The main purpose of this study is to clarify the effects of mixed grinding of a kaolinite-gibbsite mixture by a planetary mill on their structural change and the purity of mullite after sintering process by using X-ray diffraction, DTA, SEM and surface area determination of powders. The results of mixed grinding is compared with those of mixing, without grinding, of kaolinite and gibbsite by an agate mortar. From the experiment, we have found that the mixed grinding resulted in the formation of mullite directly from spinel phase without forming corundum and cristobalite phases during sintering at more than 1523K. The ratio of formation of mullite increased with an increase in grinding time and sintering temperature.

2. Experimental Procedure

The chemical composition of kaolinite (produced by Engelhard Co. Ltd.: ASP-200) used for the preparation of mullite was given in Table 1. Based on preliminary chemical analysis and structural analysis by X-ray diffraction, a small amount of anatase (TiO2) was included in this kaolinite as the main impurity. Gibbsite employed in this study was a reagent with purity over 97% (KANTO CHEMICAL Co., INC, Tokyo, Japan). According to the data on the size distribution measured by a centrifugal particle size analyzer, SA-CP3 (SHIMADZU Co. Ltd.), the particle size ranges for
Table 1 The chemical compositions of used kaolinite.

<table>
<thead>
<tr>
<th>Composition</th>
<th>mass %</th>
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</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>45.50</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>38.50</td>
</tr>
<tr>
<td>TiO₂</td>
<td>1.60</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>0.50</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.20</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.10</td>
</tr>
<tr>
<td>CaO</td>
<td>0.03</td>
</tr>
<tr>
<td>MgO</td>
<td>0.02</td>
</tr>
<tr>
<td>Ig. Loss</td>
<td>13.86</td>
</tr>
</tbody>
</table>

Fig. 1 Flow chart showing the methods of sample preparation of mullite by solid-state reaction.

kaolinite and gibbsite were below 5 μm and 10 μm, respectively. Their median sizes were 1.4 μm for the kaolinite, and 5.7 μm for the gibbsite.

The schematic diagram of mullite preparation by solid-state reaction is shown in Fig. 1. First of all, the kaolinite and the gibbsite were mixed so as to be the stoichiometric mullite composition (3Al₂O₃·2SiO₂) by the following two different methods. One is only mixing, without grinding, by an agate mortar for 1 hour keeping the crystal structures of kaolinite and gibbsite in acetone, so called unground mixture (0 minute ground specimen). The other is mixed grinding under dry condition by a planetary ball mill with accompanying the structural change of their crystal phases. The specified milling times are 15, 30, 60, 120 minutes and the milling condition is given in Table 2.

The specific surface area of unground and ground mixtures was measured by using a dynamic flow technique, and the calculation of their values was determined by the BET method. The morphology of unground and ground mixtures was observed using 20kV electron beam in a scanning electron microscope (SEM: HITACHI HSS-2R). Density of them was measured by the Archimedes' method with toluene. The differential thermal analysis of unground and ground mixtures each with 20 mg in weight of specimen was made at a constant heating rate of 10 K/min in an atmospheric condition. The mixtures were pressed into a pellet with 13 mm in diameter and 2 mm in thickness by using an uniaxial pressing device under the pressure of 44.1 MPa. The pellets were heated in an electric furnace at 1223~1923K for 1 hour in air. The sintered bodies were quickly removed from the furnace and cooled down to room temperature. The microstructure of sintered body was observed by SEM after thermal etching for 30 minutes at 1623K in air and chemical etching treatment in a 1% hydrofluoric acid solution for 16 hours at room temperature.

The analysis of crystal structure of unground and ground mixtures, and sintered bodies ground by an agate mortar were made by the X-ray diffraction method using CuKα radiation with a singly-bent pyrolytic graphite monochromater in a diffracted beam in range from 2θ = 5° to 60°, where θ is a half of an angle between incident and diffracted beams. Operational condition is fixed 35 kV in voltage and 20 mA in current. The crystal structure for each specimen was analyzed by identifying the diffraction peaks with the JCPDS (Joint Committee on Powder Diffraction Standards) file.

3. Results and Discussion

3.1 Change of Powder's Characters and its Structure by Grinding

Fig. 2 shows the X-ray diffraction patterns of a kaolinite-gibbsite mixture for various grinding times. As can be seen from this figure, as the grinding progresses, a decrease of
intensity is observable. The intensity decreased sharply as compared with that of the unground specimen during the early stage of grinding up to 30 minutes. In the 60 minutes ground specimen, the X-ray diagram has scarcely any distinct diffraction peak except for a weak peak of anatase. Therefore, the amorphous state may be almost attained at 60 minutes grinding. Though the crystallinity of anatase included in kaolinite as impurity decreases slowly with an increase in grinding time, the crystalline of anatase was still remained until 120 minutes grinding. The similar tendency of amorphization of kaolinite and gibbsite was also observed in individual grinding using a planetary mill. It can be readily deduced that, in the progress of the grinding, the structure of the crystalline part of unground mixture approaches to the disordered state. Fig. 3 shows the change of density in the process of the dry grinding of the mixtures. The density sharply decreased at the initial stage of grinding up to 15 minutes, but thereafter it reaches a nearly constant value. The sudden decrease in the density curve is observed for 15 minutes ground mixture. This is consistent with the X-ray diffraction results (Fig. 2) indicating the change of structure of crystalline phase into amorphous state by the grinding. Thus, the density is correlated to the relative degree of crystallinity in the internal and stacking variations, so that the density of a kaolinite-gibbsite mixture could indicate as the degree of the crystallinity.

Fig. 4 shows the scanning electron microphotographs in the course of grinding of a kaolinite-gibbsite mixture. Original kaolinite crystals with a hexagonal plate-like shape can be seen in the unground sample shown in Fig. 4(a). It is observable that, in the early stage of grinding, fine particles are produced by fracturing of the original powders, as shown in Fig. 4(b) and (c). By the further prolong grinding, the fine powders produced by grinding were observed as if they agglomerate into spherical shape with an increase of grinding time (Figs. 4d and 4e).

Fig. 5 shows the specific surface area of the mixture together with their equivalent specific surface diameter as a function of grinding time. As shown in this figure, the specific surface area of ground mixture increases sharply in the initial stage of grinding up to 15 minutes, but thereafter the value falls rapidly then, decreases gradually with increasing grinding time. This result implies that the mixed grinding of original kaolinite and gibbsite powders results in the size reduction in the early stage and then the hard agglomeration of fine particles produced in the prolong grinding.

3.2 Differential Thermal Analysis

Fig. 6 shows the results of differential thermal analysis for unground and ground mixtures at the various periods of grinding. As can be seen from this figure, three main endothermic peaks are observed in the unground mixture at about 480K, 550K and 800K. The former two peaks are caused by the decomposition of gibbsite\(^{15}\), the last peak is caused by the decomposition of kaolinite related to the formation of
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Fig. 6 DTA curves for a kaolinite-gibbsite mixture with grinding time. These endothermic peaks were shifted to the lower temperature side with increasing grinding time. As for the endothermic peak at 800K, a sudden lowering in the peak temperature and a reduction of its height and area are observed. Finally this reaction disappears thoroughly at 60 minutes grinding, where kaolinite becomes the amorphous state. This corresponds with a sudden and complete disappearance of the kaolinite crystal structure due to grinding. The exothermic peak appearing at about 1250K indicates the formation of Al-Si spinel by the condensation of metakaolinite. The relatively sharp exothermic peak can be observed in the mixture after 60 minutes grinding. The peak temperature of this reaction falls a little with an increase in grinding time. The size reduction and mechanochemical effects by grinding make it possible to assist the phase transformation, resulting in a decrease in temperature of the exothermic and endothermic peaks with an increase in grinding time. The exothermic reaction at about 1500K is attributed to the formation of mullite from spinel structure, precise composition not certain, with further discard of silica and addition of alumina from gibbsite.

3.3 Formation of Mullite

Fig. 7 shows the X-ray diffraction patterns for sintered bodies of the unground specimen heated at various temperatures. The diffraction patterns of mullite, corundum, cristobalite, Al-Si spinel and anatase included in the sintered bodies agree well with the JCPCS cards 15-776, 10-173, 4-359, 10-425 and 21-1272. As can be seen from this figure, below 1423K, only Al-Si spinel phase together with anatase is detected. In the temperature between 1523K and 1823K, the mullite phase with corundum and cristobalite phases appears in the sintered body. Beyond 1923K, only the mullite phase is barely detected, although the temperature for complete formation of mullite from the unground mixture is not specified. It is well known that mullite is synthesized from kaolinite under some high temperature by a solid-state reaction via two intermediate phases, metakaolinite and Al-Si spinel phase. Brindley and Nakahira noted that this sort of solid-state reaction forming mullite from kaolinite progressed with the structural continuity. It can be readily deduced that the formation process of mullite from the unground mixture is

Fig. 7 X-ray diffraction patterns for sintered bodies of the unground mixture heated at various temperatures.

Fig. 8 X-ray diffraction patterns for sintered bodies of the 120 minutes ground mixture heated at various temperatures.
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somewhat similar to that from only kaolinite under the temperature between 1523K and 1823K.

Fig. 8 shows the X-ray diffraction patterns for sintered bodies of the 120 minutes ground mixture fired at various temperatures. It is clear that the phase formation for the ground mixture is considerably different from that for the unground mixture. Especially, even relatively low temperature, 1523K, the mullite phase only appears in the sintered body except for anatase without forming any crystalline substances. It can be deduced that the mullite starting from the ground mixture is directly synthesized via Al-Si spinel phase under the temperature beyond about 1523K. Such difference in phase formation between the unground mixture and 120 minutes ground mixture may be due to the degree of mixing. It is reported that the mullite prepared by a chemical reaction such as co-precipitation, which enables us to attain the homogeneous mixing state in microscale of atomic level, is formed directly from the spinel phase without forming the cristobalite and corundum phases. Although the degree of mixing for the ground mixture is not achieved such the ordered mixing state in microscale, there may be a tendency to approach such condition.

Fig. 9 shows the variation of the relative amount of mullite in various sintered bodies, in case of the amount of mullite of sintered body for 120 minutes ground mixture heated at 1923K for 1 hour.

![Graph showing variation of relative amount of mullite](image)

**Fig. 9** Variation of the relative amount of mullite in various sintered bodies, in case of the amount of mullite of sintered body for 120 minutes ground mixture heated at 1923K for 1 hour.

The improvement of reactivity between kaolinite and gibbsite caused by the reduction of the particle sizes and activating their surface characteristics by the mixed grinding.

Fig. 10 shows SEM photographs of microstructure of sintered bodies fired at 1923K for 1 hour for the unground and 120 minutes ground mixtures. Only the mullite phase is detected by X-ray diffraction in both sintered bodies fired at 1923K, but there are significant difference in the amounts of mullite between them, as mentioned above. The presence of amorphous phases as glass pockets surrounded by grains has been reported using TEM analysis. It is also apparent from Fig. 10(a) that a certain amount of an unreacted amorphous phase (A) remains at the portions among the grain boundaries in the microstructure of the sintered body from the unground mixture. On the other hand, a relatively small amount of such phase is apparent in the microstructure of sintered body from the ground mixture, as shown in Fig. 10(b). Furthermore, it appeared to be that a higher densification was estimated for the sintered body from the ground mixture comparing to that from the unground mixture by a microscopic observation.

4. Concluding Remarks

The effect of mixed grinding of a kaolinite-gibbsite mixture by a planetary ball mill on formation of mullite through the solid-state reaction was studied with aids of mainly X-ray diffraction analysis, DTA, SEM and specific surface area determination. The following conclusions of this study can be obtained:

1. The amorphorization of a kaolinite-gibbsite mixture is improved with an increase in grinding time. The almost perfect amorphorization of them is attained after 60 minutes grinding. The density of mixture varies almost inversely in comparison with the amount of amorphorization.

2. The specific surface area of mixture increases sharply
in the initial stage of grinding up to 15 minutes. However, thereafter, it falls gradually and then tends to approach to a certain value.

(3) Mullite is formed more effectively from the ground kaolinite-gibbsite mixture than that from the unground mixture. The amount of mullite in the sintered body of the mixture increases with an increase in sintering temperature and grinding time.

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References