Effect of prolonged sintering time at 1200 °C on the phase transformation and reactivity with moisture of fired kaolinite

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Abstract

Fired clay-based ceramics react continuously with moisture from their surroundings which causes long-term expansion which, if not accommodated, results in cracking. Studies of the reactivity of fired kaolinite with moisture are important as a simple model material for the behaviour of fired clay ceramics. In this study, kaolinite compact powders were sintered at 1200 °C for between 2 and 12 hours. Following this, high accuracy mass measurements were carried out using a recording microbalance. Fractional mass gain was plotted against time 1/4 and the reactivity defined as the gradient. XRD and SEM were employed to identify and examine the crystalline phases developed during firing. The results show that increasing sintering time at 1200 °C reduces the subsequent reactivity of fired kaolinite with moisture. An exponential decay of reactivity with sintering time was found. Longer sintering time enhances the crystallinity of mullite and converts the amorphous silica, which accompanies the formation of mullite, into cristobalite.

Keywords: Sintering; Kaolinite; Mullite; Cristobalite; Moisture expansion; Traditional ceramics.

1. Introduction

Fired clay-based ceramics expand slowly over time as a result of exposure to atmospheric moisture. This expansive behaviour is caused by the very slow chemical combination of moisture with the fired material. This moisture induced expansion can cause problems for ceramic bodies over long periods of time, e.g. crazing on glazed ceramics, and can even cause structural failures. Information about long term moisture expansion is therefore important from a durability point of view.

It is known that moisture induced expansion is accompanied by an increase in mass of the material. Milne studied the expansion of fired...
kaolinite following autoclaving for 96 h at 200 °C and recorded both the expansion and the gain in mass. However, at high firing temperatures the samples were badly cracked and expansion could not be measured. Recently, it has been proposed that the kinetics of moisture expansion and mass gain in fired clay ceramics can be described by a (time$^{1/4}$) law. Moreover, it has been demonstrated that both moisture expansion and mass gain in freshly fired clay bricks (manufactured from a mixture of carbonaceous shale and Etruria marl) follow a two-stage process, each stage being linear with (time$^{1/4}$).

Traditional ceramics such as whitewares are formed from natural raw materials of which the major component is clay. A (ceramic) whiteware is defined as “a fired ware consisting of a glazed or unglazed ceramic body that is commonly white and of fine texture, designating such product classifications as tile, china, porcelain, semivitreous ware, and earthenware.” For such whitewares, firing at high temperatures is required to develop glassy and crystalline phases.

Kaolinite (2SiO$_2$.Al$_2$O$_3$.2H$_2$O) is the major clay mineral used in manufacturing whitewares. On heating, kaolinite dehydroxylates in the temperature range 450 - 600 °C forming metakaolinite. As heating continues a spinel-type phase crystallizes within the metakaolinite, beginning at around 900 °C. At about 1100–1200 °C spinel is lost and mullite crystals begin to develop. Kaolinite fired at 1200 °C has been shown to exhibit the least reactivity with moisture compared to that fired at lower temperatures. However, the effect of prolonged sintering time at 1200 °C on the reactivity of fired kaolinite with moisture has not previously been studied.

Kaolinite has been chosen as a simple model material to investigate the reactivity of fired clay-based ceramics with moisture. In this study kaolinite was fired at 1200 °C and kept at different holding or sintering times and its subsequent reaction with moisture was measured by continuous recording of the mass of samples with time. A high accuracy recording microbalance was used for mass measurements.

2. Materials and methods

The kaolinite used in this study was supplied in the form of light acid-washed kaolin powder by Fisher Scientific Ltd, UK. The chemical composition was determined by X-ray fluorescence (XRF) using an Axios Sequential Spectrometer manufactured by PANalytical, The Netherlands. The XRF analysis of the kaolinite used, given in table 1 as
the oxide equivalent, shows the presence of very small amounts of alkali (Na, K) and alkaline earth (Ca, Mg) metals. The loss on ignition was found to be 14.45 %.

The average particle size of kaolinite was determined using a Mastersizer Micro Plus V2.19, manufactured by Malvern Instruments Ltd, UK. The average particle size of the kaolinite was found to be 7 µm. The specific surface area of sintered samples was measured using a Gemini 2360 surface area analyzer, manufactured by Micromeritics Instrument Corporation, USA.

The kaolinite powder was uniaxially pressed by a hydraulic pellet maker in a 4 cm diameter die at 120 MPa. Samples of approximately 2 g were cut for microbalance measurements from the resulting compact kaolinite powder disc. An electric muffle furnace model Carbolite CWF 1200 fitted with a type 3216 temperature controller was used for sintering. Samples were heated at a rate of 10 °C/min and sintered at 1200 °C for 2, 4, 6, 8 and 12 hours. Following sintering, samples were removed from the furnace and allowed to cool in air for 5 min and then held under vacuum for 30 min to avoid reaction with moisture before being transferred to a microbalance for continuous mass measurements.

The microbalance measurements were carried out using a CiSorp water sorption analyzer manufactured by CI Electronics Ltd., Salisbury, UK. This equipment can measure the mass increase of a sample to an accuracy of ± 1µg plus 0.001% of the suspended mass. Measurements were carried out in the microbalance weighing chamber under controlled relative humidity (RH) and temperature conditions. Here 55% RH (± 2%) and 30 °C (± 0.2 °C) were used. Mass was recorded at increments of 0.001% mass increase, typically every 5-40 s.

XRD analysis was performed on powdered samples of sintered material at values of 2θ = 5° to 85°, at a step size of 0.05° 2θ and scan step time 10 s, using a Philips X’-Pert APD diffractometer (CuKα radiation, λ = 0.154 nm) at 50 kV and 40 mA. The percentage of crystalline phases developed during firing was estimated from the areas of the crystalline reflections and the amorphous halo. These areas were determined by profile fitting using PC-APD version 3.6. These areas were then expressed as a ratio.

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<th>Component</th>
<th>Weight percent</th>
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3. Results and discussion

3.1 Microbalance study

The freshly fired kaolinite sintered at 1200 °C starts to react with moisture once it is cooled and its mass increases correspondingly. Fig. 1 shows the fractional mass gain of freshly fired kaolinite sintered at 1200 °C for times from 2 to 12 hours plotted versus time $^{1/4}$. Each line in fig. 1 represents thousands of data points recorded over about 30 hours (~2.35 $^4$ hours). Previous work has shown that there are two stages representing the reaction of moisture with freshly fired kaolinite.$^{11}$ The first stage (Stage I) finishes within about an hour from the time of first exposure to moisture. The second stage (Stage II) continues thereafter. Mass gain during Stage I can be attributed to both physisorption and chemisorption processes. However, the mechanism controlling mass gain in Stage II is chemisorption only. In the current study, a distinct Stage I is not clear and is of little interest. However, it is clearly seen from fig. 1 that the Stage II fractional mass gain varies systematically with the sintering time and reduces as sintering time is increased. Stage II is clearly linear with time $^{1/4}$. It is the Stage II mass gain that is related to the long-term moisture expansion of the material.

The reactivity of freshly fired kaolinite is defined here by the gradient of the Stage II mass gain versus time $^{1/4}$ graph. Fig. 2 represents the so

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<tr>
<td>SiO$_2$</td>
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<tr>
<td>TiO$_2$</td>
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<td>K$_2$O</td>
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<td>CaO</td>
<td>0.02</td>
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<tr>
<td>MgO</td>
<td>0.08</td>
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<tr>
<td>Loss on ignition</td>
<td>14.45</td>
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Table 1. Chemical composition and loss on ignition of washed kaolinite.
calculated Stage II gradients plotted against sintering time. From fig. 2 it can be seen that the Stage II gradient decreases exponentially with sintering time.

![Fig. 1 Fractional mass gain plotted against time^{1/4} for kaolinite fired at 1200 °C and sintered for times from 2 to 12 hours.](image)

![Fig. 2 Stage II fractional mass gain rate (Stage II gradients obtained from the data in fig.1) plotted against sintering time for kaolinite fired at 1200 °C.](image)

### 3.2 X-ray analysis

Fig. 3 shows the X-ray diffraction patterns of kaolinite sintered at 1200 °C for the sintering times examined. It can be seen that mullite is the major crystalline phase developed. Amorphous free silica phase can be
seen as a hump at about $\theta = 21 - 22^\circ$, also shown in fig. 3. With increased sintering time, cristobalite starts to develop and increases gradually up to 8 hrs sintering time. A dramatic increase in cristobalite is observed for kaolinite sintered for 12 h at 1200 °C. This suggests that prolonged sintering time converts the amorphous free silica into cristobalite which in turn reduces the amount of amorphous phase present. The reactivity with moisture decreases as a consequence of this since the reaction is attributed to the amorphous phase. Prolonged sintering enhances also the crystallinity of mullite. Increase in mullite content and development of cristobalite with increasing firing temperature in the range 1200 – 1500 °C of kaolinitic clay has been reported elsewhere.\textsuperscript{12}

Fig. 4 shows the percentage of crystalline phases developed with sintering time. It can be seen from this figure that the proportion of crystalline phases increases exponentially with sintering time. The exponential growth relationship between the percentage of the crystalline phases, \textit{i.e.} cristobalite and sintering time could be attributed to the grain growth kinetics. The results above summarize that both the variation of Stage II gradient and therefore reactivity to moisture and the variation of the amount of the crystalline phases exhibit exponential behaviour with sintering time: the reactivity decreases whereas the crystallinity increases.

![XRD analysis of kaolinite fired at 1200 °C and sintered for 2, 4, 6, 8 and 12 hours (* = mullite and o = cristobalite).](image-url)
3.3 Surface area measurements

Specific surface area measurements were carried out to investigate the changes in this property with sintering time. Fig. 5 shows the specific surface area values plotted against sintering time. Specific surface area decreases exponentially with sintering time as does the Stage II gradient. Stage II mass gain and consequently long-term moisture expansion of a ceramic body is related to an active phase in the body which reacts with moisture. It would be expected that the larger the surface area of that phase the higher the reactivity with moisture of the ceramic body and consequently the greater the increase in mass and moisture expansion. The surface of the amorphous or glassy phase represents an active surface whereas that of the crystalline phase represents an inactive surface. However, because it is difficult to differentiate between the specific surface area associated with active surfaces and that associated with inactive surfaces, correlating the moisture expansion of a ceramic body with its specific surface area is difficult.\textsuperscript{13}

For ceramic bodies fired above 1000 °C, moisture expansion and specific surface area both decrease in direct proportion to each other.\textsuperscript{13} The results reported here on surface area of kaolinite fired at 1200 °C and sintered for different times support this.

Fig. 4 the percentage of crystalline phase developed during sintering of kaolinite at 1200 °C plotted against sintering time.
It is known that porosity and surface area are linked and previous work\textsuperscript{14} has demonstrated that the role of crystalline phases in reducing moisture expansion can be greater than the role of porosity in these bodies.

![Graph showing specific surface area vs. sintering time](image)

Fig. 5 The specific surface area of kaolinite fired at 1200 °C and sintered for different times.

### 3.4 Scanning electron microscopy

Electron micrographs of sintered kaolinite fired at 1200 °C for different times are shown in fig. 6. The secondary electron (SE) images of polished and then etched samples reveal that primary mullite dominates the microstructure. Primary mullite formed directly from the clay decomposition has a fine, cuboidal or scaly morphology.\textsuperscript{15} The morphology of mullite is controlled by the silicate liquid formed on firing and its chemical composition. The chemical composition of silicate liquid affects the liquid viscosity which in turn affects the morphology of mullite formed. The silicate liquid formed from clay alone will be more silica-rich and viscous compared to that formed from a feldspar material. Therefore, in pure clay systems the mullite formed is smaller cuboidal primary mullite. However, in pure clay systems the composition and viscosity of the liquid formed on firing can be complex. Clays can contain various levels of impurities such as alkalis and iron-containing compounds which can also influence mullite formation.\textsuperscript{16}

As shown in fig. 6 (a-c), increasing the sintering time at 1200 °C of kaolinite from 4 to 8 and then 12 hours produces coarser mullite particles.
The small mullite particles observed for kaolinite sintered at 1200 °C for 4 hours, shown in fig 6(a), appear to coalesce forming coarser particles with increasing sintering time and this is shown clearly in kaolinite sintered for 8 hours (fig. 6(b)). With further increased sintering time, coalesced mullite particles tend to begin a spherodisation process as shown in fig. 6(c). In kaolinite sintered for 12 hours, regions containing crystalline phases appear to be dense compared to those of lower sintering time. This may be due to the large reduction of amorphous silica phase by formation of cristobalite.
Fig. 6 SEM/SE images of sectioned, polished, etched and coated kaolinite following sintering at 1200 °C for (a) 4 hours, (b) 8 hours and (c) 12 hours.
4. Conclusion

The present work can be concluded into three points:

1. The results show that increasing the sintering time of kaolinite at 1200 °C reduces its subsequent reactivity with moisture. An exponential decay of reactivity with increased sintering time was found and it has been shown that prolonged sintering time enhances the crystallinity of mullite and converts the amorphous silica, which accompanies the formation of mullite, into cristobalite. In addition, increasing sintering time may produce a more densified ceramic body as demonstrated by the gradual reduction in specific surface area with sintering time and shown by scanning electron microscopy images.

2. It is apparent from surface area measurements and SEM images that reduction of specific surface area with sintering time is largely due to coalescing and coarsening of crystalline phases, i.e. mullite which in turn reduce the exposed surface area to be measured.

3. It may be concluded that using the time$^{1/4}$ kinetics to describe the reaction of freshly fired and sintered kaolinite with moisture yields an excellent correspondence between the reactivity of the freshly fired material and the associated microstructural and physical changes during sintering.

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References