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DTA study of preheated kaolinite in the mullite formation region

Akshoy K. Chakraborty*

Central Glass and Ceramic Research Institute, 196 Raja S.C. Mullick Road, 700032 Kolkata, India

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Abstract

Kaolinite usually exhibits a weak second exothermic peak at ∼1250 °C during differential thermal analysis (DTA) due to mullitization. But preliminary study indicates that significant thermal effects occur in the high temperature region when preheated kaolinite is packed by pressing instead of using raw kaolinite and is commonly packed by loose packing technique. A newer decomposition scheme of kaolinite is envisaged.

Keywords: Kaolinite; Packing; Path of mullitization

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1. Introduction

A good variety of china clay contains kaolinite as mineral phase. On differential thermal analysis (DTA) it generally exhibits two endothermic peaks at ∼120 °C due to removal of physically adsorbed moisture, and at 550–650 °C due to loss of structural water and an exothermic peak at ∼980 °C (first exotherm) related to crystallization of Al–Si spinel phase at the medium scale of temperature. This observation is almost well-known and the fact is standard. On the contrary, a little information is available at high temperature region of DTA. Review by West [1] shows that a large number of authors have investigated DTA experiments based on some variables but none has noted any significant exotherm where considerable amount of mullite formation occurs out of heating kaolinite. Bradley and Grim [2], and Glass [3] showed a broad exothermic peak (second exotherm) of very less in magnitude at ∼1250 °C and was explained as due to mullitization. After mullite formation, occasionally another small peak due to cristobalite formation occurs. One question arises: why the second exotherm due to mullitization shows an extremely low intensity in comparison to the sharp and intense first exotherm due to Al–Si spinel formation? This question is obvious since mullite is a quite hard, dense and stable crystalline phase in the binary Al_2O_3–SiO_2 system and its heat of formation value is quite large. The temperature of occurrence and the exhibition of thermal events of kaolinite generally depends upon number of variables. For example, (i) origin of kaolinite and its nature of crystallinity, size distribution and its impurities content. (ii) DTA equipment and its sample holder, thermocouple, sensitivity, furnace and its atmosphere. (iii) Operating conditions—heating rate, sample size, packing, etc. It is largely expected theoretically that mullite formation should exhibit high exothermic energy due to its quantitative yield, large heat of crystallization and it is crystallized out of metastable phase of high energy, i.e. metakaolinite. But no one has reported a large exotherm experimentally due to mullite formation in comparison to Al–Si spinel phase formation. Only Bulens and Delmon [4] noted a comparatively larger

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* Fax: +91-33-473-0957.
E-mail address: AKSHOYC@hotmail.com (A.K. Chakraborty).

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exotherm by using mineralized kaolinite however, at the expense of Al–Si spinel phase. Moreover, a large base line drift is often noticed especially in the high temperature side of the DTA trace. In usual packing condition of kaolinite run in DTA experiment, the analyzed sample generally noted to be very fragile and contained innumerable cracks, pores and large voids. In the present study, some modifications in sample preparation techniques are made in order to show more increase in intensity of mullitization exotherm. As such, Rajmohol kaolinite was preheated first to 1000 °C with a view to complete all three previous thermal changes associated with two endotherms and one exotherm. In this procedure, moisture is eliminated and Al–Si spinel crystallization is completed. As such, it is expected that sample bed in DTA cell would be remain intact without any crack during its run. With this assumption, preheated kaolinite is analyzed for DTA to highlight more information likely related to mullite and cristobalite formations out of decomposition of kaolinite.

2. Experimental

DTA analysis was done at Shimadzu Thermo Mechanical Analyser System having a DTA attachment. Three different sets of experimental condition were used as shown below.

Condition no. 1—About 50 Mg of powdered kaolinite was loosely packed to fill the platinum holder by gently tapping the base of the cup. The reference material was α-Al_2O_3, rate of heating was 10 °C/min, the sensitivity was $\pm 50\,\mu V$ and the thermogram is shown in Fig. 1.

Condition no. 2—About 85 Mg of powder Rajmohol kaolinite precalcined to 1000 °C for 2 h was packed fully in the cup in by pressing with tip of forefinger. In the other cup 50 Mg of Al_2O_3 was taken as reference material. Rate of heating and sensitivity were 10 °C/min and $\pm 50\,\mu V$. The thermogram is shown in Fig. 2.

Condition no. 3—With same conditions as above, only the rate of heating is increased from 10 to 20 °C/min. The thermogram is shown in Fig. 3.

3. Result

Due to use of preheated kaolinite and adopting pressing technique a significant observation is noted in DTA curve in comparison to use of loosely packed raw clay sample. For example, DTA trace of Rajmohol kaolinite when loosely packed in the platinum holder, shows two endotherms due to dehydration and dehydroxylation of kaolinite to the formation of metakaolinite and then the usual 980 °C exotherm. On the high temperature side, it exhibits three exotherms. Each of the exotherm is quite small in magnitude

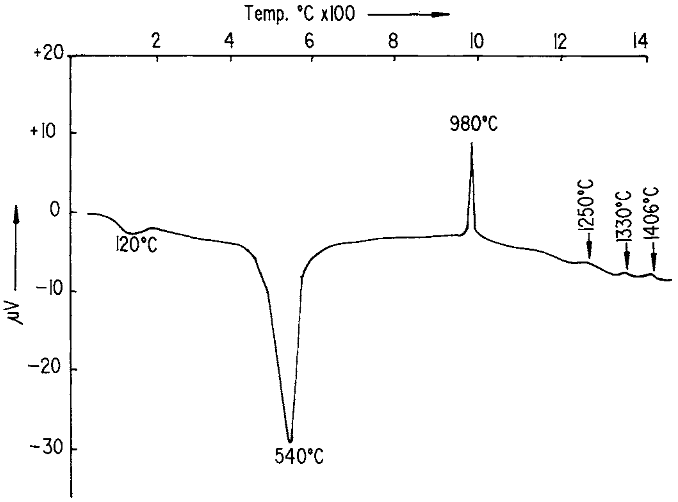

Fig. 1. DTA trace of Rajmohol kaolinite in loose packing condition—sample weight: 50 Mg; heating rate of heating: 10 °C/min; reference: α-Al_2O_3.

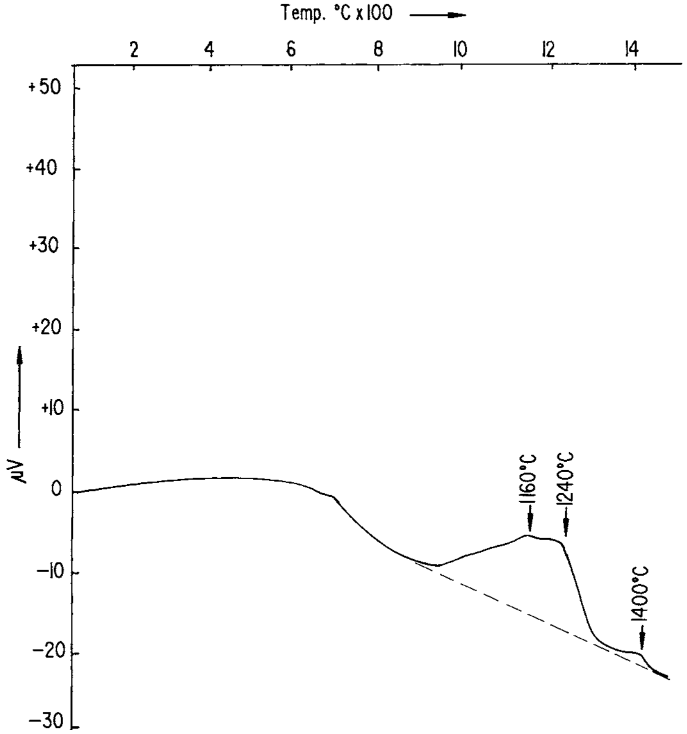

Fig. 2. DTA trace of Raimohol kaolinite pre calcined to 1000 °C for 2 h and then pressed under pressed packing condition—sample weight: 85 Mg; rate of heating: 10 °C/min; reference: α-Al_2O_3.

(Fig. 1). In comparison, Fig. 2 shows the exhibition of a large broad exothermic peak in the region 1000–1400 °C which may be related to mullitization from kaolinite. Within the broad peak there are two peak maxima, one occurs at 1160 °C, and the other exhibits at 1240 °C, respectively. Finally, it shows another exotherm at ~1400 °C which may be related to crystallization of free siliceous phase. When heating rate was made faster from 10 to 20 °C/min, the DTA profile in the mullitization region shows asymmetry

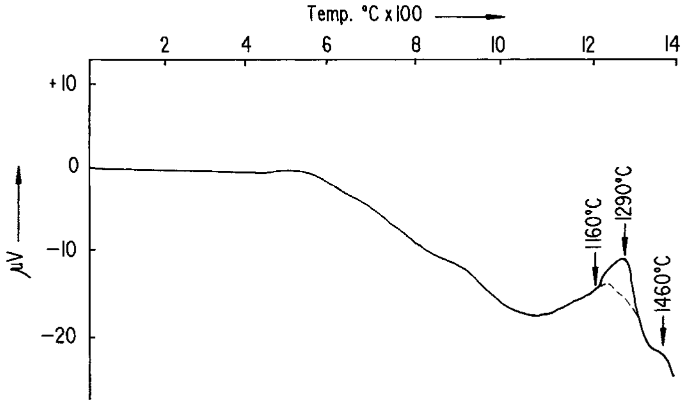

Fig. 3. DTA trace of Rajmohol kaolinite precalcined as above—sample weight: 83 Mg; heating rate: 20 °C/min; reference: α-Al_2O_3.

in the left-hand side of the profile and a peak maxima at 1290 °C within the broad exotherm between 1000 and 1400 °C (Fig. 3). Temperature of the last exotherm increases from 1400 to 1460 °C with rise of heating rate. Thus, it becomes possible to exhibit exotherm(s) of large magnitude in DTA studies in the temperature range where mullite formation occurs.

4. Discussion of previous works

There are four major steps of kaolinite transformation. One could expect thermal change for each step. As expected, by applying DTA tool and corroborating with X-ray diffraction (XRD) technique, five thermal events are observed in the present study. Reasonable explanations for the causes of those related to the decomposition of kaolinite or formation of newer phases are put forward.

4.1. Decomposition of kaolinite to metakaolinite

In the first step of transformation, kaolinite forms metakaolinite with loss of structural hydroxyl groups during the occurrence of endotherm as noted in DTA. It does not show any powder X-ray pattern. Transmission electron microscopic (TEM) evidence indicates that it is not an amorphous oxide mixture but retains a crystalline order from original kaolinite.

4.2. Formation of Al–Si spinel

In the second step, metakaolinite decomposes and forms spinel phase generally during heating around first exothermic peak temperature. The crystallites size of it are very small ∼10 nm as noted in electron microscopy. The X-ray powder diffraction pattern of the spinel phase showed only two broad *d* (nm) peaks partially resembling the pattern of γ-Al_2O_3 as per review of Richardson and Wilde [5]. The composition of this spinel phase was disputed earlier. By radial electron distribution (RED) study, Leonard [6] conjectured that it is pure Al spinel (γ-Al_2O_3). On the contrary, by lattice parameter data and by noting orientation relationship among parent kaolinite to metakaolinite to spinel phase, Brindley and Nakahira [7] predicted this spinel as Si-bearing spinel phase instead of simple γ-Al_2O_3. Subsequent studies show that spinel phase contains silica which may be 10 wt.% according to Okada et al. [8] and Sonuparlak et al. [9] by using analytical TEM and high resolution electron microscopy (HREM). On the other hand Chakraborty and Ghosh [10] by alkali leaching study suggested that composition of spinel is analogous to composition of orthorhombic form of mullite (o-mullite) which was supported later on by Srikrishna et al. [11] by their energy dispersive X-ray spectrum (EDS) studies. The amount of spinel phase formed was estimated semi-quantitatively for different kaolinites heat treated to ∼1000 °C by XRD technique by Okada et al. [8], and later on by Chakraborty and Ghosh [12]. An approximate value of it would lie in the range 20–30 wt.% for kaolinites of different origins. The 980 °C reaction according to Chakraborty and Ghosh [10] was predicted as follows:

$$\text{Metakaolinite} \underset{\text{first exotherm}}{\overset{980\,^{\circ}\text{C}}{\rightarrow}} \begin{array}{l}\text{(i) Al–Si spinel phase (20–30 wt.\%)}\\ \text{(ii) Mullite (weakly crystalline, trace)}\\ \text{(iii) Aluminosilicate phase (amorphous, 30–40 wt.\%)}\\ \text{(iv) SiO}_2\text{ (amorphous, }\sim 36\text{ wt.\%)}\end{array} \qquad (1)$$

4.2.1. Criteria for exhibiting exotherm

Before pointing out the real cause of exothermic peaks in DTA trace of kaolinite, it is necessary to focus first the guideline, i.e., the necessary and sufficient conditions regarding the commencement of DTA peak in general. The following points are to be considered. (i) As the exothermic reaction is due to crystallization phenomenon, then identification of the crystal phase which is forming at the exotherm is to be ascertained first. (ii) The quantitative yield of crystalline phase(s) must be sufficiently high such that liberated heat energy would change the sample's temperature and consequently, the differential emf in a thermocouple circuit so that a most sensitive DTA apparatus could record it. (iii) To produce an exotherm in DTA, the rate of crystallization of a reaction must be sufficiently rapid such that crystallization would take place in the usual heating schedule, e.g., 2, 5, 10 and 20 °C/min as followed in DTA analysis.

Therefore, the present aim is to seek out the phase, which is found to form just at the exothermic peak during heating kaolinite at the same rate as used in DTA analysis. As mullite is started forming during heating at ~980 °C and due to its poorly crystalline nature, contribution of it to the said exotherm should not be much important. On the other hand, Al–Si spinel suddenly forms at first exotherm. Quantitative XRD analysis by Okada et al. [8] and others indicated that an appreciable amount of spinel is rapidly formed during non-equilibrium heating of kaolinites at the rate of 10 °C/min. Although its heat of formation data of spinel is not known, still it would be predicted on the above considerations that Al–Si spinel formation should be the cause of first exotherm. This view verifies the earlier observations of Insley and Ewell [13] and Glass [3] that rapid formation of spinel coincides with maximum of the peak temperature (T_m) of the exotherm. In this context, the combined XRD and DTA experiments carried out by Tsuzuki and Nagasawa [14] is of much convincing. They noted increase of spinel content is coincident with the exothermic peak on the differential thermal curve.

4.3. Crystallization of mullite

Most likely formation of mullite out of the decomposition of metakaolinite and out of tranformation of Al–Si spinel phase is highly expected to exhibit exotherms in DTA trace. The question is: where would the exotherm due to mullite formation occur?

Let us see first the course of mullite formation during heating of kaolinite. By X-ray and electron microscopic observation, it is noted that at 900–1000 °C mullite crystallization ensued and in most cases is formed in association with Al–Si spinel phase. Diffraction peaks characteristics of mullite are not fully observed. Moreover, all peaks are very broad. Patterns of well-crystallized mullite are observed only on heating kaolinite beyond 1200 °C with complete disappearance of broad X-ray pattern due to spinel phase. As far as the growth curve is concerned, the intensity of mullite peak showed increasing from 1100 °C. At ~1200 °C and above increase in both intensity and crystallinity of it are evident as per lattice parameter measurements. There may be two probable regions of mullitization exotherms.

4.3.1. At first exothermic region

There are many speculations in this aspects. A group of researchers suggest mullite formation is the sole cause of first exotherm, while some others believed that as some quantity of mullite is forming along with spinel phase, a part of contribution should be for 980 °C exotherm. Bradley and Grim [2] stated that sudden sharp first exothermal effect might be due to rapid evolution of a hard and dense mullite phase. On the contrary, they discarded spinel formation as a cause of it on the plea that it was a irregularly constituted phase, i.e. ill-crystallized and could not evolve sufficient detectable energy in slow development process. According to Roy et al. [15] the cause of first exotherm was assigned to formation of mullite. They conjectured mullite formed around this temperature seldom yielded X-ray pattern owing to its small particle size. The crystal became large enough (by heating for longer periods or at higher temperature) to give powder X-ray pattern. According to Johns [16], DTA is most sensitive in revealing the first exothermic effect as a result of energy involved in rearrangement of packing of oxygen network. Subsequent reorganization of cations follows thereafter and is detected by the development of appropriate diffraction characteristics of mullite.

However, Slaughter and Keller [17] argued that the formation of extremely small mullite nuclei should preclude a very large heat of reaction for metakaolinite to mullite formation at 980 °C.

The role for cause of first exotherm due to mullitization is least considered because of the two reasons. It is weakly crystalline in nature and secondly low quantitative value forms suddenly during the occurrence of first exotherm. Slaughter and Keller [17] were of the opinion that at least a part of the 980 °C exothermic reaction of kaolinite must be attributed to mullite formation.

4.3.2. At second exothermic region

Various earlier researchers claimed the rapid rise of mullite formation is the cause of second exotherm at ~1250 °C in DTA as per review of Freund [18]. Glass [3] choose to heat various kaolinites dynamically at the

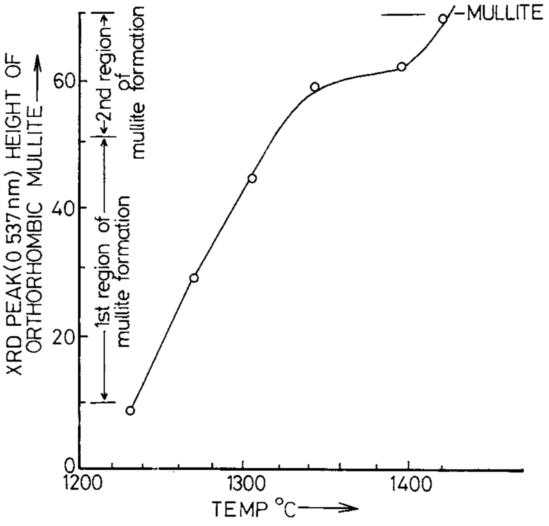

Fig. 4. Mullsite formation out of Rajmohol kaolinite at increasing temperature.

rate of 10 °C/min and showed that the major formation of mullite takes place (by X-ray) at ∼1200–1250 °C where the temperature of second exothermic peak generally lie. Wahl and Grim [19] noted that initial appearance of mullite is noted on the diffractogram at 1180 °C which coincides with the beginning of second exotherm at approximately 1200 °C in DTA curve.

4.3.3. *Newer concept of crystallization phenomenon in the 1200–1400 °C range of thermal curve*

The amounts of o-mullite developed out of Rajmohol kaolinite was semi-quantitatively estimated by measuring the heights of the 0.537 nm peaks from XRD recordings as shown in Fig. 4. This curve shows two distinct temperature regions of mullite formation. In the present study, DTA curve in the temperature range 1000–1400 °C exhibits two exotherms. Therefore, it indicates that these two peaks are related to two paths of mullite formation.

4.3.3.1. First path. In this path there are two possibilities. Spinel phase may react in solid-state with silica (A) to develop mullite during the occurrence of exotherm, at ∼1250 °C as per the conjecture of Okada et al. [8], Leonard [6] and Sonuparlak et al. [9]. The second exothermic reaction according to them is as follows:

$$\gamma\text{-Al}_2\text{O}_3 \text{ or Al–Si spinel } (\text{SiO}_2 = 10\,\text{wt.\%}) + \text{SiO}_2\ (\text{A}) \xrightarrow[\text{second exotherm}]{\sim 1250\,^{\circ}\text{C}} \text{o-mullite} \quad (2)$$

In the second possibility, Al–Si spinel polymorphically transform to mullite during second exotherm as per the suggestion of Chakraborty and Ghosh [10] and Srikrishna et al. [12]:

$$\underset{\text{Al–Si spinel cubic (25–30 wt.\%)}}{3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2} \xrightarrow[\text{second exotherm}]{\sim 1240\text{–}1260\,^{\circ}\text{C}} \underset{\text{mullite orthorhombic}}{3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2} \quad (3)$$

As the composition of spinel concept is different from earlier authors, the mullitization reaction is obviously a separate reaction.

4.3.3.2. Second path. To explain the cause of mullite formation by other path, one must have to account the large quantity of aluminosilicate (A) phase that amounts to ∼40 wt.% left as residue during formation of Al–Si spinel phase at 980 °C as shown in Eq. (1). It is expected that mullite formation occurs over a wide range of temperatures from 1000 to 1400 °C during heating. This mode of crystallization corresponds exactly with the broad exothermic peak in the same temperature range. This indicates that mullite crystallization proceeds early by nucleation in aluminosilicate (A) phase, it continues and shows maximum crystallization at ∼1160 °C within the temperature range of 1000–1400 °C where the third exotherm also lies. Meanwhile, the associated Al–Si spinel phase polymorphically transforms at ∼1240 °C and adds to the growth of o-mullite. Thus, during the heating of kaolinite, two mullitization processes occur simultaneously instead of solid-state reaction as assumed by earlier researchers.

4.4. *Crystallization of silica*

Just after two exotherms related to two ways of mullite formation as discussed above, one more exothermic peak (to be called as fourth exotherm) at ∼1400 °C is noted. XRD of heated kaolinite showed β-cristobalite formation besides mullite formation. Glass [3], and Johnson et al. [20] conjectured that the

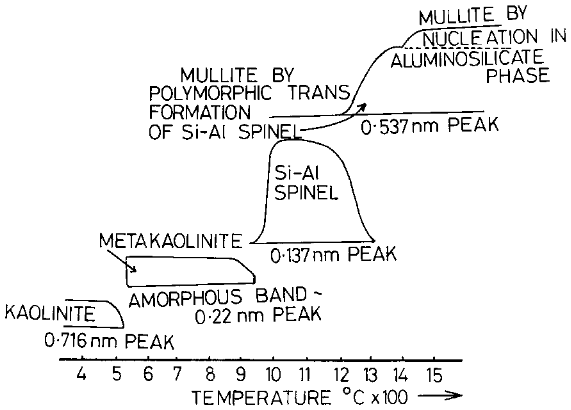

Fig. 5. A scheme of transformation steps of kaolinite to mullite.

formation of cristobalite out of silica (A) liberated during the decomposition of metakaolinite might be the reason for this exotherm in DTA trace. By dynamic XRD studies on heating poorly crystallized Illinois kaolinites, Wahl and Grim [19] observed that cristobalite formation matched with temperature of last exotherm in DTA. By chemical leaching technique, Chakraborty and Ghosh [10] showed the liberation of 35–37 wt.% SiO_2 (A) during decomposition of metakaolinite at first exotherm. Later on Chakraborty [21] corroborated the thermal effects observed in DTA with the dimensional changes noted in TMA/DTMA. Further by semi-quantitative XRD data, he explained that SiO_2 (A) to β-cristobalite accounts for the 1400 °C exotherm in DTA.

Thus, kaolinite changes to mullite ultimately by three separate transformation steps. The sequence of steps of transformation is shown schematically in Fig. 5. The amorphous silica phase exolves out of decomposition of metakaolinite at first exothermic peak temperature finally crystallizes beyond 1400 °C.

5. Conclusion

Mullite formation in a kaolinitic clay occurs by the exhibition of two high temperature exotherms. Accordingly, it is concluded that there are two simultaneous paths of mullitization reaction instead of a single solid-state reaction process assumed earlier.

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