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NEW DATA ON THERMAL EFFECTS OF KAOLINITE IN THE HIGH TEMPERATURE REGION

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Abstract

DTA study of an Indian Kaolinite has been performed by varying packing density and rate of heating. Both these two parameters influence the intensities of both endothermic and exothermic peaks related to the dehydration, dehydroxylation and then crystallizations of Al–Si spinel, mullite and cristobalite phases. Significantly, the study reveals that mullitization takes place by two separate reactions as indicated by two exotherms in the 1200–1400°C range of DTA trace.

Keywords: heating rate, kaolinite, mullitization, packing density

Introduction

The mechanism of thermal decomposition of kaolinitic clay is of much interest to a large section of ceramist and others. A large number of investigators applied mainly X-ray as the primary tool to study the sequences of the various phases crystallized on heating clay. At high temperature, clay crystallizes to mullite and cristobalite via the formations of some intermediate phases at different stages. Differential thermal analysis (DTA) is an ideal method to investigate the thermochemical change vis-à-vis to corroborate XRD findings. It is obvious that at each cristallo-chemical transformation step some thermal change-effect must occur. At the first step of transformation, DTA exhibits a more or less symmetrical large endotherm due to dehydroxylation of structural –OH groups when kaolinite transforms to metakaolinite with loss of *c*–axis structure. At the second step DTA shows a characteristic sharp exothermic peak at ~980°C and conceived as crystallization of either mullite or Al–Si spinel phase out of metakaolinite. However, differential thermal events at high temperature region are almost scanty. West [1] in his review showed that in between 1200–1450°C there are at least two exothermic peaks for various origins of kaolinite. The natures of them are not much significant. Correlation of the exhibition of thermal events in DTA with phase developments and finally derivation of the decomposition scheme of kaolinite are not properly explored. Examining Zettlitz kaolinite by DTA, Insley and Ewell [2] noted a small second exothermic effect over a broad temperature range. Using Georgia kaolinite, Bradley and Grim [3] showed a broad

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but comparatively more pronounced second exotherm in the temperature range 1200–1300°C. They pointed out the effect of heating rate on the nature of the exhibition of exotherms e.g., slower heating rate in comparison to faster one may reduce peak intensity. Spiel *et al*. [4] showed thermal curves with variation of particle size of clay and heating rate only upto 1000°C. It was shown that the size of the peak and its temperature of formation decrease as the particle size decreases. Secondly slower the heating rate, broader is the peak and occurs at lower temperature. Glass [5] noted two exotherms at the high temperature region at close temperature interval. For example, well crystallized kaolinite showed first peak at ~1250°C of greater intensity and second peak occurred at ~1300°C. On corroborating the exhibitions of these two thermal peaks with X-ray analysis of heated clays, he explained the first exotherm was due to mullitization and last peak might be due to cristobalite formation. Later on using same Georgia kaolinite of well crystallized variety, Wahl and Grim [6] showed comparatively a sharp exotherm in between the temperature range of 1200–1340°C but with absence of last exotherm as shown by Glass [5]. Johnson *et al.* showed the effect of some metal oxides on high temperature exotherms. For example, CaO shifts the exothermic peak from lower to higher temperatures i.e., 1275 to 1300°C, where as K_2O shift it to lower temperature i.e.,1275 to 1250°C. These impurities affect the last exotherm also. Bulens and Delmon [8] showed that MgO promoted spinel formation with large 980°C exotherm, where as CaO exhibited intense 1250°C exotherm with large quantity of mullite formation. Thus, the occurrence and intensity of exotherms vary and are dependent on three main factors e.g., source of kaolinite and its characteristics, associated impurity oxide present or added externally, and conditions of DTA run etc. For example, heating rate and increase in packing density generally known to enhance the peak intensity. However, no such data are available in the high temperature DTA study of kaolinite with packing effect and change of heating rate. Considering the above fact, a particularly well crystallized kaolinite is chosen to study the effect of packing density on its DTA characteristics at the high temperature region.

Experimental

A well crystallized Indian kaolinite named Rajmohol analyzed for DTA using Shimadzu thermo mechanical analyzer system having a DTA attachment. DTA run was made at the following sets of experimental conditions.

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^{-1} and the sensitivity was 50±μV and the DTA curve is shown in Fig. 1.

Condition No. 2 – The same amount of sample was packed in the cup first by gentle tapping followed by pressing with tip of fore finger. Other conditions were same as in No. 1 and the DTA curve is shown in Fig. 2.

Condition No. 3 – About 78 mg of sample was packed as per the condition No. 2 to completely fill the cup. Other conditions were same as above and the DTA curve is shown in Fig. 3.

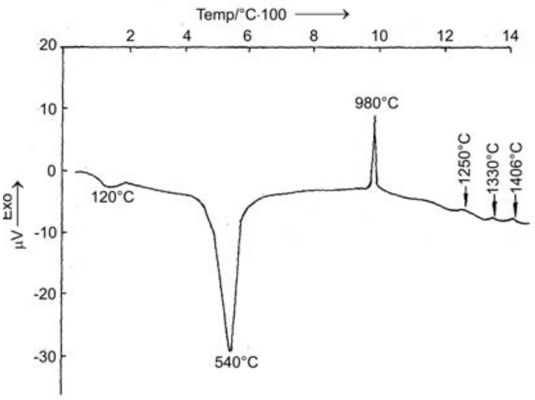


Fig. 1 DTA trace of Rajmohol kaolinite in loose packing condition; sample mass – 50 mg; heating rate – 10°C min^{-1} and reference – α-Al_2O_3

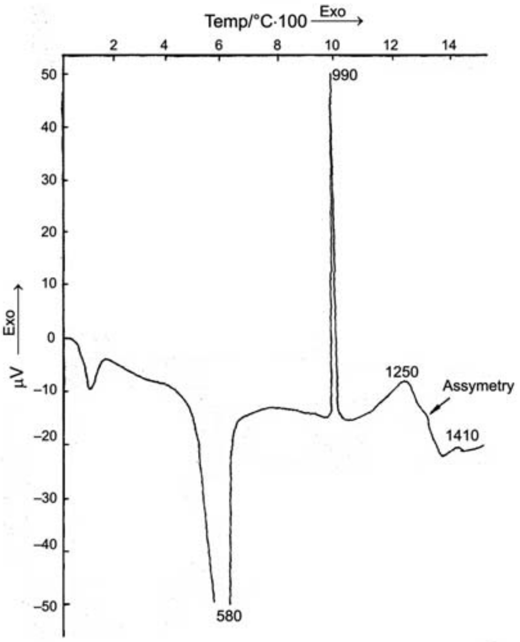


Fig. 2 DTA trace of Rajmohol kaolinite in pressed packing condition; sample mass 50 mg; other conditions are same

Condition No. 4 – Sample amount and packing condition were same as in case of condition No. 3, only the rate of heating was increased from 10^{-1} to 20°C min^{-1} and DTA curve is shown in Fig. 4.

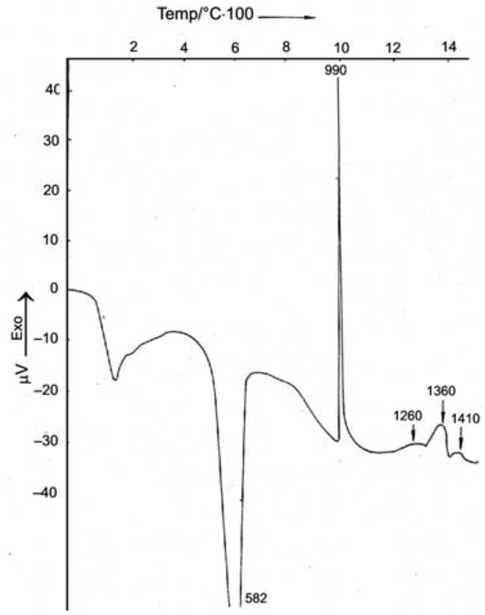


Fig. 3 DTA trace of Rajmohol kaolinite under pressed packing condition ; sample mass –78 mg and other conditions are same as above

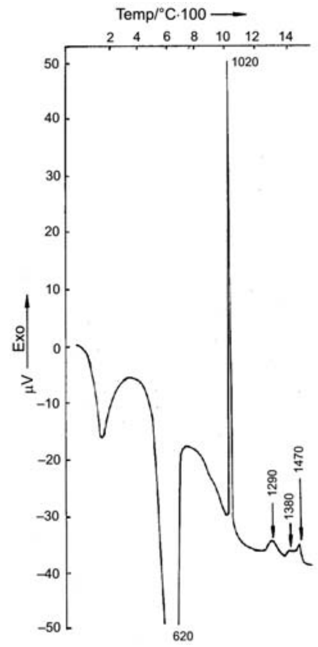


Fig. 4 DTA trace of Rajmohol kaolinite under pressed packing condition; sample mass – 80 mg; rate of heating – 20°C $\min^{-1}$ and reference as above

Result

Effect of packing behavior

Figure 1 shows a usual DTA trace of Rajmohol kaolinite when packed loosely in the sample holder cup. It exhibits two endotherms at ~120, ~540°C and a sharp exotherm at ~ 980°C having peak height of ~12 μV. At the high temperature side, it exhibits three small peaks at ~1250, ~1330 and ~1406°C respectively. The natures of exhibits as shown in Fig. 1 are similar with that of same kaolinite studied by Banerjee and Gupta [9] using Netzsch'409 equipment.

When the nature of the packing is changed from loose packing to comparatively dense packing of the same amount of sample, a pronounced change in thermal effects are noted (Fig. 2). On comparing with Fig. 1 following observations are made. i) Two endothermic peaks are more predominant. ii) Intensity of 1st exotherm at 980°C (peak height) increases from 12 μV to 66 μV. iii) Intensity of 2nd exotherm at 1250°C increases to a great extent. The area of this exothermic profile is asymmetrical and it may be a real effect. This indicates the presence of a new exotherm at the right hand side of the DTA trace. The occurrence of this exotherm may be designated as 3rd exotherm and exhibition of it seems to be possible by packing effect of kaolinite sample in the holder. In other words it is presumed that besides increasing the magnitude of the exotherm, packing technique also helps in resolution of exotherms in the high temperature region. iv) The last exotherm is noted at 1410°C and is designated as 4th exotherm.

Using full cup sample, and with same pressing technique as in condition No. 2, the intensities of thermal effects are increased to a great extent as shown in Fig. 3. Following observations are noted. i) The two endothermic peaks, one due to physically adsorbed moisture at ~120°C and other due to constitutional water at ~540°C increased in intensities in comparisons to earlier conditions of DTA analysis. ii) Peak height of 1st exotherm increases to 72 μV. iii) A broad exothermic peak appears with T_m at ~1260°C to be called as 2nd exotherm. iv) Following the 2nd exotherm, a large exotherm is noted to occur over a long temperature range with its T_m at ~1360°C and now is called as 3rd exotherm. This finding points to believe that the asymmetry region as shown in the Fig. 2 in the temperature is real and resolution is certain. Thus, there are two exotherms in the mullite formation region. v) 4th exotherm is clearly noted in the DTA curve.

Effect of heating rate

Changes in rate of heating of densely packed kaolinite results to the following changes in the temperature of occurrences of thermal peaks as shown in Fig. 4.

i) Dehydroxylation temperature increases from ~582°C in previous cases to 620°C. ii) Intensity of 1st exotherm increases to >80+μV and T_m occurs at 1020°C. iii) Two exotherms in the mullite formation region are clearly discernable. The 2nd exotherm occurs at ~1290°C. At the end of this exotherm, the DTA profile rises and then attains constant. Thereafter, it further increases and exhibits 4th exotherm distinctly. It is to be believed that the nature of the trace between 2nd and 4th exotherms is a peak with its T_m at 1380°C. Thus, it is possible to resolve the asymmetric nature of the 2nd exotherm as shown in Fig. 2 into an additional exotherm by performing DTA with increased rate of heating. iv). The temperature of the 4th exotherm increases from 1410°C as shown in Fig. 2 to 1470°C which is also due to rise in rate of heating.

Discussion

First step of transformation

During heating kaolinite first loses its physically adsorbed moisture at the 1st endotherm at ~120°C. Thereafter, it loses its constitutional –OH groups in the 2nd endothermic peak temperature range and forms metakaolinite.These endothermic peaks (Figs 1–4) are quite comparable with the reported DTA curve shown by previous authors for well crystallized Zettlitz, and Georgia kaolinites. Moreover, the present study shows the enhancement of intensities of these two endotherms which are obvious due to increase of packing density and weight of clay taken for DTA analysis.

Second step of transformation

Metakaolinite in this step first decomposes and then crystallizes. The intensity of the 1st characteristic exothermic peak at ~980°C is found to be sharp and its magnitude increased due to similar effect as mentioned. The cause of the occurrence of this peak was explained earlier as due to formation of Al–Si spinel phase rather than pure γ-Al_2O_3 spinel. It may contain 10–28 mass% SiO_2 according to compositional analysis given by Okada *et al*.[10]: Sonuparlak *et al*. [11] and Chakraborty and Ghosh [12]. Only a trace of weakly crystalline mullite appears at the formation of 980°C exotherm. Accordingly, mullite formation as the cause of any exotherm has been shifted to occurrence to other exotherm may be in the higher temperature region.

Third step of transformation

This step of thermal evolution is the formation of mullite. A large number of authors believe that solid state reaction between spinel phase with associated silica phase is responsible for mullitization as evidenced by the exhibition of a broad and small 2nd exotherm in DTA. In contrast Chakraborty and Ghosh [12] predicted polymorphic transformation of Al–Si spinel as an alternative explanation for occurrence of 2nd exotherm to mullite formation.

A significant observation is that tight packing enhances the magnitude of the broad 2nd exotherm as shown in Fig. 2 in comparison to the less intensity peak usually noted by several researchers. Secondly, it also exhibits two peak maxima within the broad peak. Thirdly, the exothermic peak occurs over a long range of temperature from 1000–1400°C instead of a short temperature range as noted by Bradley and Grim [3], Moya *et al*. [13] in their DTA traces. Further, these authors did not mention the ordinate (Δ*T*) scale except Insley and Ewell [2], who noted (Δ*T*) in terms of galvanometer deflection. Thus, it is very difficult to compare the intensity of the 2nd exotherm shown by them for Georgia kaolinite with the data presented in Fig. 2 for Rajmohol kaolinite. None of the previous researchers observed either such broad peak or two peaks (T_{ms}). Even using highly crystallized variety of kaolinite, Insley and Ewell [2] observed a broad exotherm in the high temperature region. Now, what happens in such temperature range ? Formation of mullite is the only alternative, since crystallization exotherm of amorphous silica to β-cristobalite occurs at the last stage of the DTA trace at 1400°C. Chakraborty and Ghosh [16] noted a large amount of residual aluminosilicate phase during Al–Si spinel phase formation at the occurrence of 1st exotherm (Fig. 5). This amorphous phase might be a source of mullitization and if nucleation of mullite takes place into it, evolution of heat of crystallization of mullite is legitimate. The exhibition of the broad exotherm as noted in Figs 2 and 3 may be speculated as due to mullitization in the said temperature region where abundant quantity of mullite crystallizes during heat treatment of kaolinite as usually seen by XRD. Thus, by considering the DTA profile, it is interpreted that mullitization starts as early as in aluminosilicate phase at ~1000°C and proceeds continuously, shows rapid crystallization where T_m=1360°C due 3rd exotherm occurs and lastly drops at ~1400°C (Fig. 3). Within this crystallization zone, the associated spinel phase transforms with exhibition of 2nd exotherm at 1260°C. Thus, there are two ways of mullitization path, each exhibits separate exotherms and both lie in the temperature region where abundant quantity of mullite crystallizes. Obviously, first path constitutes transformation of Al–Si spinel at 2nd exotherm and second path constitute nucleation cum crystallization in aluminosilicate phase at 3rd exotherm.

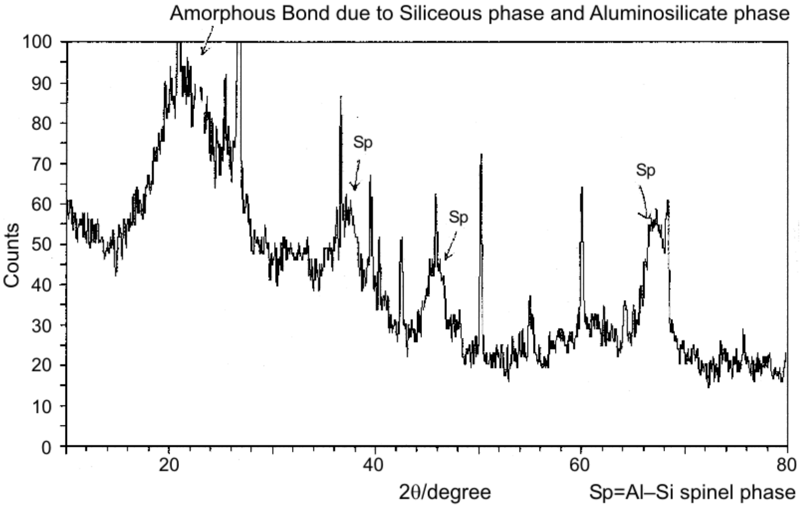


Fig. 5 XRD pattern of Rajmohol kaolinite heated to 1000°C band at ~22° 2θ due aluminosilicate phase and siliceous phase besides Al–Si spinel phase and traces of mullite

Similar thought of mullite growth was conceived earlier by Comeforo *et al.* [14] who predicted that generation of mullite nuclei might took place in the collapse of a skeletal anhydride. John [15] was of opinion that mullitization in kaolinite took place by two steps. Rearrangement of the packing of oxygen network of metakaolinite occurred at the first stage. Nucleation of mullite took place thereafter by reorganization of cations. However, both the authors ignored the formation of any intermediate spinel phase and likely its role in the subsequent mullite formation process.

When the rate of heating is increased from 10 to 20°C min^{-1} and with same condition of packing, the T_{ms} of the 2nd and 3rd exotherms automatically rise as expected. For example, 2nd exotherm increases from 1260 to 1290°C and 3rd exotherm rises from 1360 to 1380°C. So the same phenomena are occurring in both cases of DTA run. Packing effect increases the intensity of 1st exotherm e.g. from +12 to +66 mV (Figs 1 and 2). Same packing condition but with use of more quantity of kaolinite and increase in heating rate the resolution of the mullite exotherm becomes possible.

Fourth step of transformation

Just after two exotherms related to two ways of mullite formation as discussed above, one more exothermic peak at ~1410°C is noted. XRD of heated kaolinite showed cristobalite formation besides mullite formation (Fig. 6). Glass [5] and Johnson *et al.* conjectured that the formation of cristobalite out of amorphous silica liberated during the decomposition of metakaolinite might be the reason for this exotherm in DTA trace. By dynamic X-ray diffraction studies on heating poorly crystallized Illinois kaolinites, Wahl and Grim [6] observed that cristobalite formation matched with temperature of last exotherm in DTA. By chemical leaching technique, Chakraborty and Ghosh [12] showed the liberation of 35–37 mass% amorphous SiO_2 during decomposition of metakaolinite at 1st exotherm. Later on Chakraborty [17] corroborate the thermal effects observed in DTA with the dimensional changes noted in

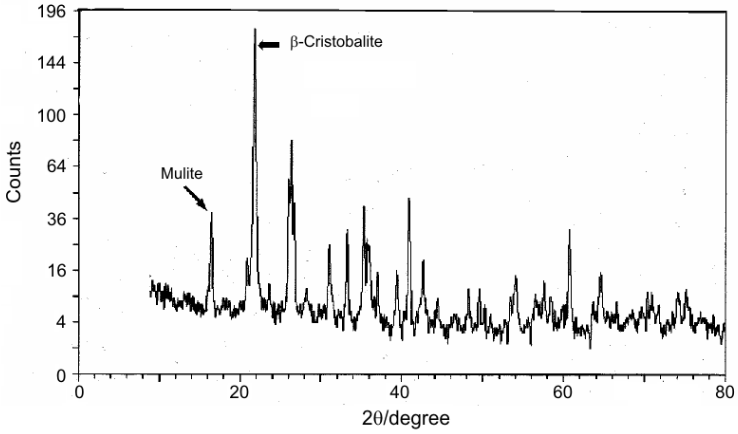
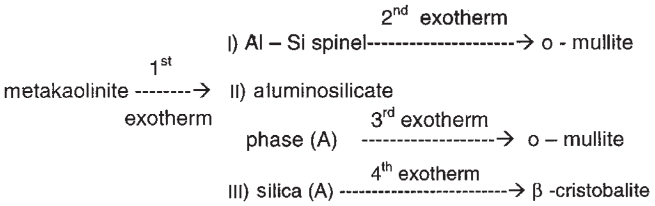


Fig. 6 XRD pattern of Rajmohol kaolinite heated to 1400°C showing cristobalite formation besides usual mullite formation

TMA/DTMA. Further by semi-quantitative XRD data, he explained that amorphous SiO_2 to β-cristobalite accounts for the 1420°C exotherm in DTA. Therefore, the decomposition scheme of metakaolinite at the high temperature range is given below.



Conclusions

The present study mainly concludes that mullitization in kaolinite occur by two simultaneous reaction paths.

In first path, the broad exotherm over a long range of temperature from 1000–1400°C with its T_m at ~1380°C is due to mullite formation out of amorphous aluminosilicate phase.

In the second path, within the broad exotherm as said another small exotherm appears with its T_m at 1260°C is due to mullitization out of Al–Si spinel phase. Thus, there are two exotherms for mullite formation in the high temperature region. Finally, the last exotherm is due to β-cristobalite formation.

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References

1 R. R.West, Differential Thermal Analysis, Vol. 2., Ed. by R. C. Mackenzie, Academic Press, London 1970.

2 H. Insley and R. H. Ewell, J. Res. Natl. Bur. Standards, 14 (1935) 615.

3 W. F. Bradley and R. E. Grim, Am. Miner., 36 (1951) 182.

4 S. Spiel, L. H. Berkelheime, J. A. Pask and B. Davis, U. S. Mines. Tech. Paper, (1945) 664.

5 D. Glass, Am. Miner., 39 (1954) 193.

6 F. M. Wahl and R. E. Grim, Proc. of the 12th Natl. Conf., Vol. 19, Ed. by W. F. Bradley, Pergamon Press 1964, p. 69.

7 J. A. Pask and J. S. Moya, J. Am. Ceram. Soc., 65 (1982) 31.

8 M. Bulens and B. Delmon, Clays and Clay Minerals, 25 (1977) 271.

9 J. C. Banerjee and M. M.Gupta, Cent. Glass & Ceram. Res. Bull., 16 (1969) 1.

10 K. Okada, N. Otsuka and J. Ossaka, J. Am. Ceram. Soc., 69 (1986) C-251.

11 B. Sonuparlak, M. Sarikaya and I. A. Aksay, J. Am. Ceram. Soc., 70 (1987) 837.

12 A. K. Chakraborty and D. K. Ghosh, J. Am. Ceram. Soc., 74 (1991).

13 J. S. Moya, C. J. Serna and J. E. Igresias, J. Mater. Sci., (1985) 32.

14 J. E. Comeforo, R. B. Fischer and W. F. Bradley, J. Am. Ceram. Soc., 31 (1948) 254.
15 W. D. John, Mineral Mag., 30 (1953) 86.
16 A. K. Chakraborty and D. K. Ghosh, J. Am. Ceram. Soc., 61 (1978) 170.
17 A. K. Chakraborty, J. Thermal Anal., 39 (1993) 289.