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APPLICATION OF TMA AND DTA FOR STUDY OF THE CRYSTALLIZATION BEHAVIOUR OF SiO_2 IN THE THERMAL TRANSFORMATION OF KAOLINITE

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TMA/DTMA with DTA studies on the thermal changes of kaolinite were performed with special emphasis on the crystallization behaviour of amorphous SiO_2. The results of four different physical techniques (semiquantitative XRD, DTA, TMA and DTMA) were clearly in good agreement with the fact that the 1420°C exotherm in DTA is due to silica crystallization.

Keywords: kaolinite, thermal transformation

Introduction

Kaolinite [1] liberates 35–37 wt% amorphous SiO_2 at 980°C and forms two intermediate phases: Si-Al spinel (cubic mullite) and amorphous aluminosilicate. The present investigation was undertaken to study the crystallization behaviour of this released silica on further heat treatment of kaolinite.

From theoretical calculations, Schieltz and Soliman [2] pointed out that the reaction

$$\text{metakaolinite} \rightarrow \tfrac{1}{3}\ \text{mullite} + \tfrac{4}{3}\ SiO_2\ \text{(crystalline)} \qquad (1)$$

showed a maximum decrease of free energy and calculated the energies of crystallization of mullite, γ-Al_2O_3 and SiO_2 as –336.180, –36.513 and –7.199 $kcal \cdot mole^{-1}$, respectively. The energy contribution of SiO_2 to the 980°C exotherm as in the above equation was –9.6 $kcal \cdot mole^{-1}$, in agreement with the value measured experimentally with a differential calorimeter [3]. However, neither β–quartz [3] nor cristobalite [4] has ever been reported in the XRD patterns of kaolinite heated at 980°C other than by Schieltz and Soliman [2]. This might be due to the presence of quartz as impurity in the original kaolinite. The apparent elimination of this exotherm on alkali treatment of metakaolinite with a view to extracting the free silica prior to DTA supported the β-quartz hypothesis. However, the actual reason behind the removal of the 980°C peak was the formation of a zeolitic phase [5] by the direct reaction between metakaolinite and NaOH solution, in contrast with the observation of Flank [6]. Furthermore, silica could not be extracted by NaOH due to the non-availability of free SiO_2 in the metakaolinite structure. The contentions of Roy *et al.* [7] and Blair and Chaklader [8] that neither spinel nor the spinel and mullite phases together were responsible for the 980°C exotherm because of their earlier development proved untenable. The phase transformations occurring either on equilibrium heating or under reactive heating conditions are entirely different from those taking place during non-equilibrium heating as in the case of DTA. Measured heats of formation of the first (980°C) and the second (1250°C) exothermic reactions were used to calculate the standard heat of formation of the Si–Al spinel phase [9] (ΔH_o=–1392.1 kcal·mole^{-1}) and its lattice energy was also found by using the Born-Haber cycle to be –14015.5 kcal·mole^{-1}, which is lower than that for γ-Al_2O_3 (–2963 kcal·mole^{-1}). Accordingly, the concept of a Si spinel with mullite-like composition gained ground and it was found to be a feasible 980°C phase in the K–M reaction series. Semiquantitative amounts of this spinel phase together with other phases that developed were estimated [10]. The formation of these phases from the sharp decomposition of metakaolinite is associated with an enthalpy change, and they should not be ignored, as was done by Blair and Chaklader [8]. In contrast, application of the Clausius–Clapeyron equation to the transformation of metakaolinite was found to be untenable [11]. On thermodynamic and experimental reasoning, the views of all earlier authors were re-examined so far as silica crystallization is concerned as the source of the 980°C exotherm in DTA. Ultimately, it was concluded that, as the formation of ~20 wt% Si–Al spinel and ~5 wt% mullite, together with ~40 wt% aluminosilicate phase and 35–37 wt% SiO_2 occurred very suddenly at 980°C, the most probable cause of the 980°C exotherm was formation of the latter phases. On further heating, the Si–Al spinel and aluminosilicate phase transformed to orthorhombic mullite with an exotherm at ~1250°C and at ~1330°C in the DTA curve [12]. Besides these two exothermic events, one more exothermic peak is noted at ~1430°C in the DTA trace of kaolinite (Fig. 1). The reason behind the occurrence of this peak is not yet known. X-ray analysis of heat-treated kaolinites from different origins generally showed an abundant formation of β-cristobalite in the temperature range 1300°–1400°C, besides the usual mullite formation. On the basis of these observation, Glass [13] and Johnson *et al.* [15] conjectured that the formation of cristobalite from amorphous silica liberated during the decomposition of metakaolinite might be the reason for this 1400°–1430°C exotherm in the DTA trace. During continuous X-ray diffraction studies on heated kaolinites, Wahl and Grim [14] noted the coincidence of β-cristobalite formation with the last exotherm in the DTA plot.

In the present study, the differential thermomechanical analysis (DTMA) technique is applied with other physico-chemical techniques, e.g. alkali leaching,

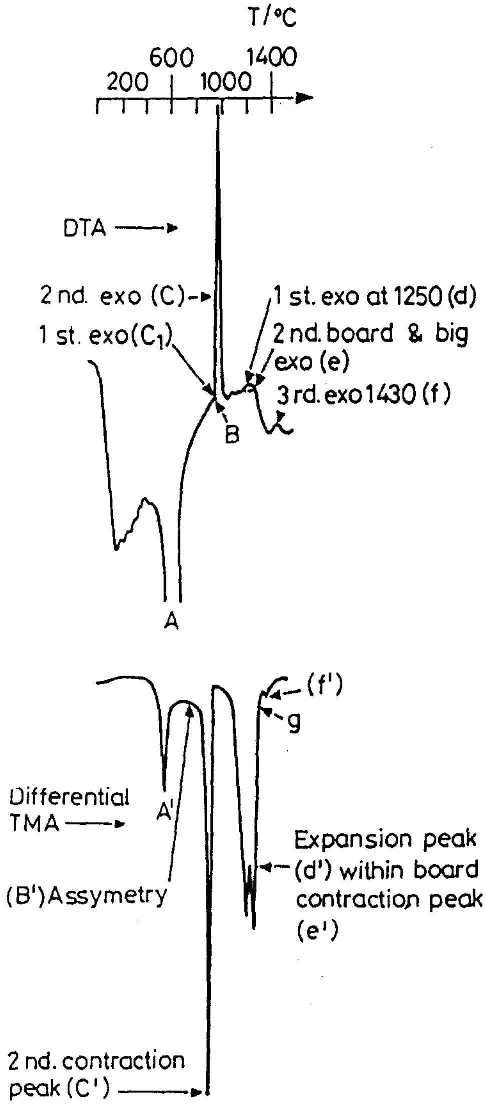

Fig. 1 Differential TMA curve of Rajmohol kaolinite compared with its DTA curve. Experimental conditions: In DTA: Rate of heating 20 deg·min^{-1}, sample weight 40 mg, sensitivity ± 50 μv and chart drive 1.25 mm/min. In DTMA: Rate of heating 20 deg·min^{-1}, sample size 2 mm height and 4 mm diameter. sensitivity ± 50 μm and chart drive 1.25 mm/min

XRD recordings, etc. and the results corroborate the fact that silica crystallization is the cause of the last exotherm.

Experimental

The following experiments were conducted sequentially.

a) Rajmohol kaolinite was run for DTA and DTMA analysis.*

Clay samples in the form of cylindrical rods were fabricated and analyzed under a constant load of 5 g at a linearly programmed rate of 20 deg·min^{-1} as for DTA analysis. DTA, DTMA and TMA traces are shown in Figs 1 and 2.

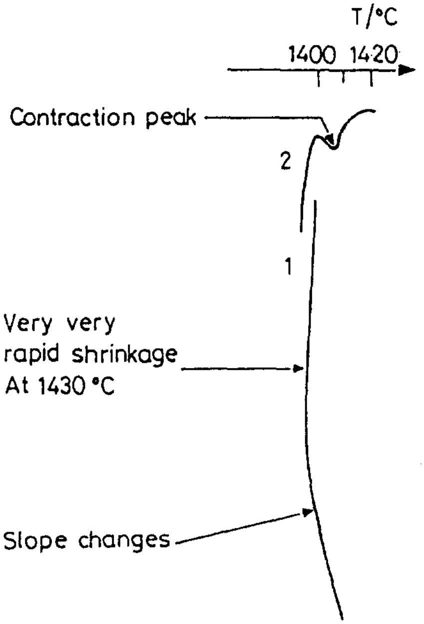

Fig. 2 TMA curve (1) and DTMA curve (2) of Rajmohol kaolinite in the vicinity of 1400°C

b) The amount of β-cristobalite formed in Rajmohol kaolinite heated to different temperatures with 2 h soaking was estimated semiquantitatively by the XRD technique (Fig. 3). The standard cristobalite used in this study was prepared

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* Shimadzu Thermomechanical Analyzer system fitted with a derivative attachment.

by heating pure quartz at 1650°C for 8 h, followed by leaching with 5% HF in an ice-bath for 5 minutes and lastly by X-ray analysis of the washed residue. This process was repeated till the height of the 0.404 nm XRD peak of β–cristobalite became nearly constant.

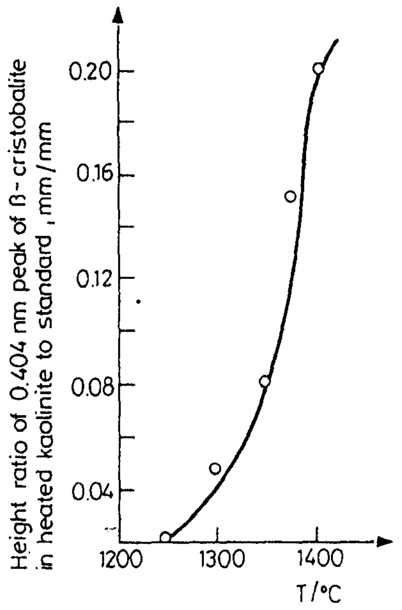

Fig. 3 Amount of β–cristobalite formed *vs.* temperature of heating of Rajmohol kaolinite under static heating conditions

c) Rajmohol kaolinite heated to 980°C was first freed from liberated SiO_2 by leaching with 10 wt% NaOH in a boiling water-bath as per the schedule described earlier [1], and then analyzed for DTMA (Fig. 4).

d) Different heat-treated kaolinite samples were collected from the DTA cell during heat treatment, by terminating the DTA run after attainment of the desired temperature. These samples were subsequently analyzed by XRD to record the 0.404 nm Bragg diffraction peak of β–cristobalite. The peak heights (in mm) are plotted against the temperature of heat treatment in Fig. 5.

e) Rajmohol kaolinite was run separately in the TMA instrument up to 1350°C and 1420°C respectively. After the desired temperatures had been attained both TMA and DTMA traces were recorded in the cooling cycle (Fig. 6).

Results and discussion

Figure 1 shows that the thermal events occurring in the DTA of Rajmohol kaolinite are in good agreement with the effects recorded in DTMA. For example:

i) Kaolinite forms metakaolinite at 500°–600°C by dehydroxylation. DTA shows an endothermic peak (*A*) and the DTMA records a differential contraction peak (*A*').

ii) Metakaolinite decomposes, followed by the removal of the final traces of –OH groups. DTA shows an endothermic dip (*B*), while the corresponding DTMA trace exhibits a contraction peak (*B*' asymmetric portion). During this period, amorphous SiO_2 to the extent of 35–37 wt% separates out of the decomposed metakaolinite structure and forms an amorphous aluminosilicate mass. This partially crystallizes to 20–25 wt% Si–Al spinel during the occurrence of the sharp exothermic peak at 980°C in the DTA plot (*C*) and the DTMA trace exhibits a very sharp differential contraction peak (*C*'). Just before the commencement of the 980°C peak, a portion of the aluminosilicate phase also crystallizes to ~4–6 wt% orthorhomic mullite, with the formation of a small exothermic DTA peak (C_1).

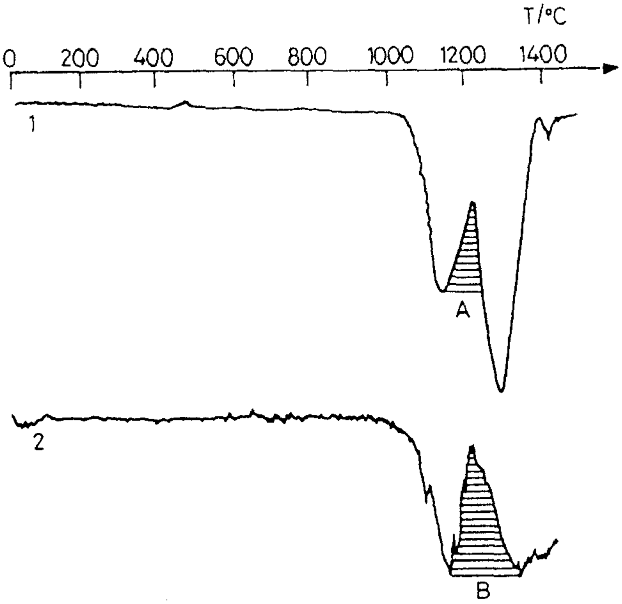

Fig. 4 Differential dilatometric curve (1) of 980°C — heated Rajmohol kaolinite and (2) of 980°C-heated Rajmohol kaolinite leached with alkali. Sample size 2 mm/4 mm dia, rate of heating 10 deg·min^{-1}, sensitivity ± 50 μm and chart drive 1.25 mm/min in both cases

iii) Transformation of the Si–Al spinel (cubic mullite) to orthorhombic mullite occurs at ~1250°C, with a DTA exotherm (*d*) and a differential expansion peak (*d*') in the DTMA at the same temperature trace.

iv) Nucleation followed by crystallization of orthorhombic mullite takes place over the temperature range 1100°–1400°C from the residual amorphous aluminosilicate phase left to an extent of 30–40 wt% after crystallization of the two mullite polymorphs in the first exothermic region of metakaolinite transformation. DTA shows an exothermic peak at ~1330°C (*e*). During this mullitization reaction, a large differential contraction peak (*e*') is observed.

(v) DTA exhibits an exothermic peak (*f*) in the temperature range 1410°–1440°C. This peak coincides with the differential contraction peak (*f*') in the same temperature range in the DTMA record for Rajmohol kaolinite. Also in the above temperature range, the predominant crystallization of β-cristobalite (20–21 wt%, determined via the height of the 0.404 nm XRD peak of 1400°C heated Rajmohol kaolinite relative to that of standard cristobalite) takes place (Fig. 3), which confirms the earlier observation. The contraction profile, i.e. TMA trace (1) as shown in Fig. 2, is very steep around 1400°C and it tallies with the theoretically expected rapid contraction which may take place during the crystallization of amorphous SiO_2 as in the equation

$$\begin{tikzcd}
\text{SiO}_2\text{ (amorphous)} \arrow[r, "1420^{\circ}\text{C}", "\text{contraction}"'] & \alpha\text{–cristobalite} \\
\text{Density }-2.20 & 2.22 \arrow[d, "\text{cooling}"] \\
 & \beta\text{–cristobalite} \\
 & 2.38\text{–}2.34
\end{tikzcd} \tag{2}$$

The above results support the concept of SiO_2 crystallization as the cause of the last exotherm in the DTA trace of a kaolinitic clay.

The corroborative evidences are outlined below.

1) Effect of alkali treatment on DTMA. When the free SiO_2 liberated during the 980°C reaction of metakaolinite had been removed by alkali leaching, the DTMA run of the leached sample showed an increment in the area (shaded portion of the differential expansion peak at ~1250°C (*B*') in comparison to the area for the unleached sample (a) (Fig. 4). Secondly, the large differential contraction peak (*e*') decreases on leaching. These two observations confirm the effectiveness of silica removal by NaOH leaching. Thirdly, due to silica removal, the dif-

ferential contraction peak at ~1430°C is completely eliminated and the XRD recording of the DTMA run sample shows only mullite and the absence of β–cristobalite. This test definitely proves that cristobalite formation is responsible for the occurrence of the last differential contraction peak in the DTMA plots.

2) Mode of cristobalite formation. In the XRD analysis of dynamic heat-treated Rajmohol kaolinite, the growth pattern of β–cristobalite occurs as a faint 0.404 nm Bragg diffraction peak at ~1300°C. The intensity of this peak increases slightly at ~1320°C, but at ~1420°C a marked increase in its intensity is noted. This observation indicates that cristobalite crystallizes slowly before the occurrence of the differential contraction peak at ~1420°C. It may crystallize partially during the DTMA run, in the portion marked (*g*) (Fig. 1), and at or around the peak temperature, i.e. at 1420°C, a considerable amount of cristobalite formation takes place. This observation is corroborated by recording the cooling curves during TMA and DTMA runs of Rajmohol kaolinite (Fig. 6). In the cooling cycle, kaolinite run previously up to 1420°C shows a contraction in the TMA trace (A_1) and correspondingly a differential contraction peak in the DTMA record (*A*). This phenomenon is due to the reversible transformation of α-cristobalite formed

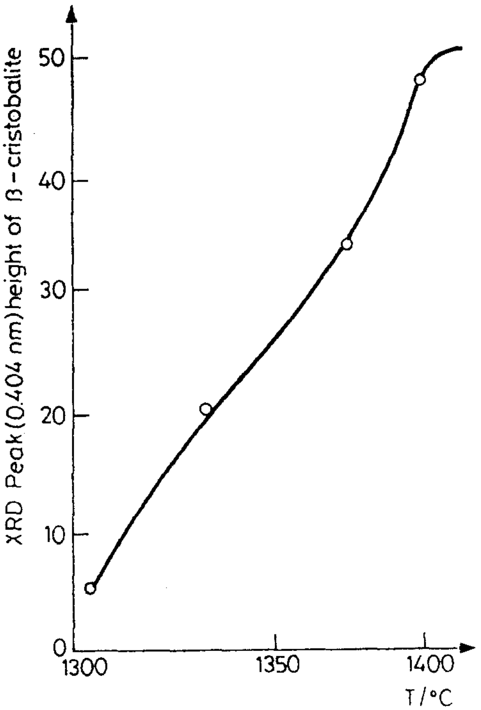

Fig. 5 XRD intensity (peak height) of β-cristobalite *vs.* temperature of heating of Rajmohol kaolinite under dynamic heating conditions (rate of heating 20 deg·min^{-1}) with no soaking time

during the heating cycle of kaolinite run to its β–modification at ~240°C during the normal cooling run, as shown in Eq. (2). This inversion is also recorded in kaolinite heated to 1350°C, i.e. a temperature less than the peak temperature of cristobalite formation, usually at 1420°C. However, in this run (*B*, B_1)the deflection of the peak (*B*) and the amount of contraction are less than in the previous case. The amount of contraction and the geometry of the DTMA peak are related to the quantity of α–cristobalite formed during the heating cycle in the kaolinite sample. This contraction behaviour indicates that a fraction of the α-cristobalite is formed prior to the differential contraction peak at ~1420°C in DTMA. This is also evident from the semiquantitative XRD estimations of cristobalite out of kaolinite heated to 1350°C to 1420°C (Fig. 5). At ~1420°C, the heat liberated due to the transformation of residual amorphous SiO_2 (Eq. 2) to a major amount of α–cristobalite is enough for the exhibition of a marked contraction in the TMA plot and a corresponding exothermic peak in the DTA record.

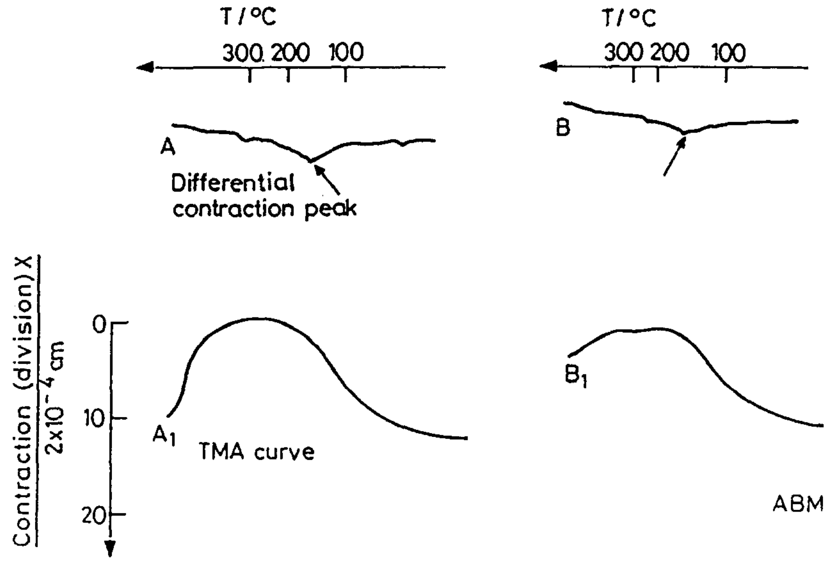

Fig. 6 Cooling curves (A_1) TMA and (*A*) DTMA of Rajmohol kaolinite run up to 1420°C in the region of $\alpha \rightleftarrows \beta$–cristobalite inversion compared with the same *B* and B_1 of the same kaolinite run up to 1350°C. Sample size 15 mm, sensitivity 100 ± μm, cooling rate: normal cooling in ordinary atmosphere

The formation of cristobalite before the commencement of this exotherm was also noted by Wahl and Grim [14] and Johnson *et al.* [15] in their poorly crystallized kaolinite and impurity-mixed kaolinite, respectively. Therefore, the earlier explanation put forward by Chakravorty and Ghosh [5] that amorphous SiO_2

liberated at 980°C did not crystallize at the same temperature, and that the 980°C exothermic peak was not due to the crystallization of either β–quartz or β–cristobalite, holds good. At the same time, the corroborative evidence presented in this paper definitely suggests that the transformation of ~37 wt% amorphous SiO_2 to 20% β-cristobalite is responsible for the 1420°C exotherm in the DTA trace and the contraction peak in the DTMA record.

Conclusions

The thermal effects observed during a DTA study of kaolinite corroborate well with the dimensional changes noted in DTMA.

Crystallization of amorphous silica to β–cristobalite, as noted from the semi-quantitative XRD data, accounts for the 1420°C exotherm in the DTA plot and a sharp contraction or a differential contraction peak at the same temperature in the DTMA trace.

Removal of free SiO_2 by prior alkali leaching eliminates the 1420°C contraction peak, which confirms that cristobalite formation is the cause of the last exotherm.

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Zusammenfassung — Unter besonderer Beachtung des Kristallisierungsverhaltens von amorphem SiO_2 wurden TMA-, DTMA- und DTA-Untersuchungen des thermischen Verhaltens von Kaolinit durchgeführt. Die Ergebnisse von vier verschiedenen physikalischen Methoden (semiquantitative Röntgendiffraktion, DTA, TMA und DTMA) stehen in recht guter Übereinstimmung mit dem Umstand, daß der exotherme Effekt bei 1420°C in der DTA der Kristallisierung von Siliziumdioxid zuzuschreiben ist.