Journal of Thermal Analysis, Vol. 6 (1974) 513–519

SCANNING ELECTRON MICROSCOPIC INTERPRETATION OF THE THERMAL ANALYSIS OF KAOLINITE

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(Received December 21, 1972)

The morphology of kaolinite thermally processed to 1600° in a thermoanalyzer was studied and related to DTA/TG/DTG data. The results show that DTA/TG/DTG data refined with scanning electron microscopic information offers insight into some of the controversies concerning the kaolinite-mullite transformation. In particular, the study supports the hypothesis that a spinel phase forms in the 950 – 1000° region. Further, the study shows that during dehyroxylation in the 450 – 700° region, water escapes by a process opposite to that generally supposed.

The importance of kaolinite in ceramics and other industries is manifested in the vast amount of interest it has received by various experimental techniques. Despite this extensive study there is still considerable controversy as to the nature of the processes which occur as kaolinite transforms to mullite. In this study, the changes in the morphology of a kaolinite are related to the DTA/TG/DTG results and these data are then considered in light of the existing theories [1, 2].

Experimental procedure

The kaolinite studied was a water refined kaolin with a mean particle size of 4.2 μm.* The chemical analysis of the kaolin is given in Table 1.

Table 1

Chemical composition of kaolin

Component	Weight percent
SiO_2	45.42
Al_2O_3	38.92
Fe_2O_3	0.34
TiO_2	1.10
CaO	0.25
MgO	0.18
Na_2O	0.11
K_2O	Trace
Loss on ignition	13.81

* Georgia Kaolin Velvacast, Ga. Kaolin Co., Elizabeth, N. J., U.S.A.

The samples for thermal analysis and scanning electron microscopy (SEM) were prepared by dry pressing pellets at approximately 5000 psi. The pellet was then fractured in a fashion to achieve a piece which weighed approximately 0.3 g and had die face, die wall and fracture surface exposed. A separate sample was used for each heat treatment and was air quenched.

The Mettler Thermoanalyzer was used to prepare the SEM specimens and provide the DTA/TG/DTG data. Each sample was placed in an 8 mm diameter Pt macro crucible and covered with 60 mesh alumina. The reference material was minus 200 mesh alumina. The samples were heated in air at a rate of 8°/min. The air was passed through molecular sieve material to remove moisture prior to being passed over the sample at a rate of 5.7 1/hr.

The samples were prepared for examination in the scanning electron microscope by evaporating a 200 Å gold-platinum coating on the surface. The top die face surface was examined on each sample.

Results and discussion

The DTA and DTG data are shown in Figure 1. These data are consistent with those for kaolinite. Samples were quenched at 400°, 900°, 1150°, 1350° and 1600°. In addition the raw clay, an unheat treated pressed pellett, and a sample held isothermally at 1600° for 12 hours, were examined. These micrographs are shown in Figures 2–9.

The stacks or booklets of the laminated kaolin which was used as a raw material are seen in Fig. 2. Most significant is the presence of edge flocculation on the large stack. Figure 3 shows the pellet without heat treatment, the remnant structure

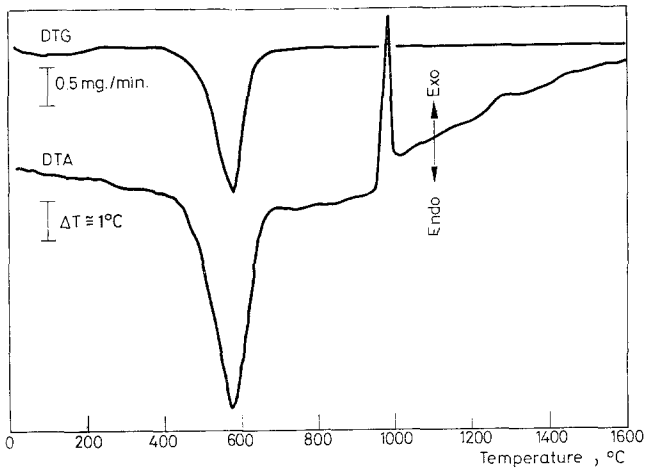

Fig. 1. Thermal analysis of Ga. Velvacast Kaolin

of the stacks of particles is clearly visible and has not been destroyed during the pressing operation. The pellet fired to 400° remains largely unchanged (Fig. 4). As noted in the TG results (Fig. 1) there was very little absorbed water in this

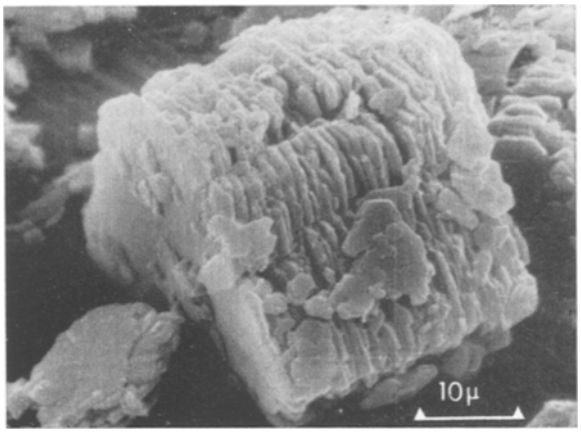

Fig. 2. Scanning electron micrograph of laminated clay

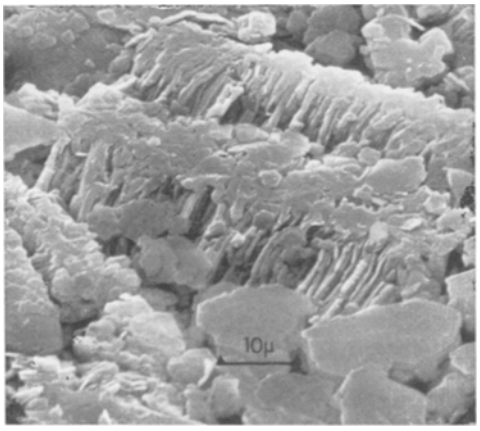

Fig. 3. Unfired pressed kaolin body — top die face surface

kaolin. The first major reaction is the endothermic dehydration of the kaolinite and the formation of the amphorous phase, metakaolin. This process occurs in the region 450–700°. MacKenzie [2] suggested, based on the fact that the thickness of individual particles markedly effects the DTA characteristics, that the water formed during dehydroxylation escapes at right angles to the planes of the layers. Figure 5 of a sample fired to 900° appears similar to the sample prior to dehydroxylation and offers little evidence for MacKenzie's theory and

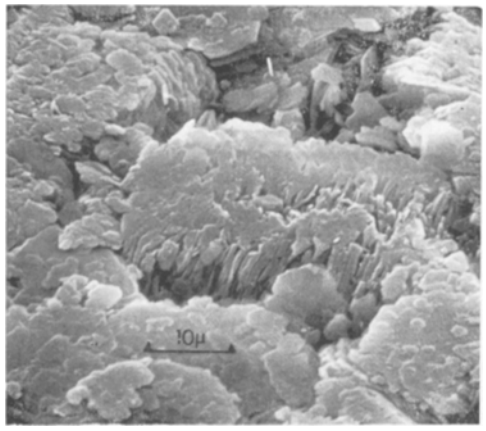

Fig. 4. Kaolinite fired to 400° and air quenched

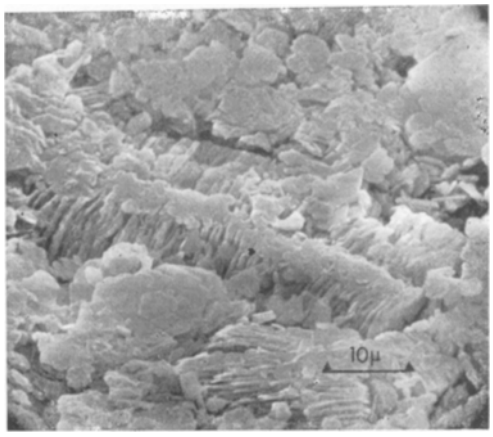

Fig. 5. Kaolinite fired to 900° and air quenched

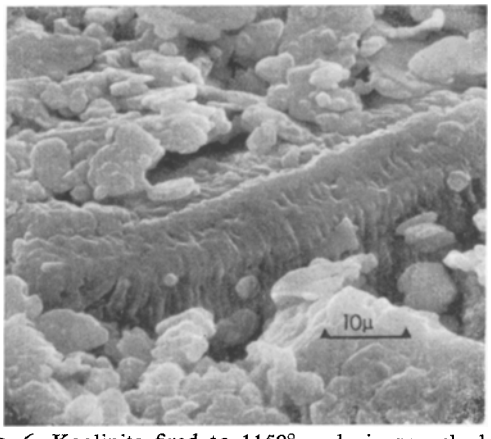

Fig. 6. Kaolinite fired to 1150° and air quenched

rather suggests a parallel mechanism of escape. This is contrary to the finding of Segnit and Anderson [3] who reported collapse of booklets at 900°.

The nature of the exothermic process in the region 950–1000° is the most disputed aspect of the kaolinite to mullite transformation. Brindley and Naka-

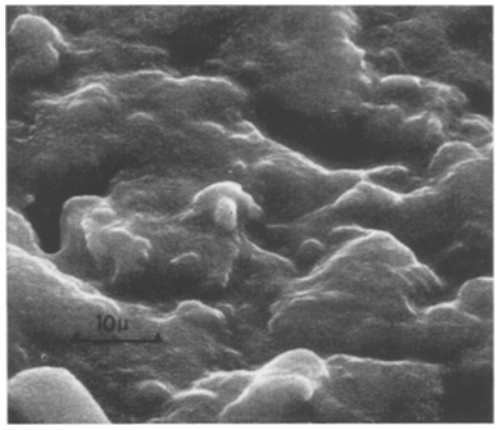

Fig. 7. Kaolinite fired to 1350° and air quenched

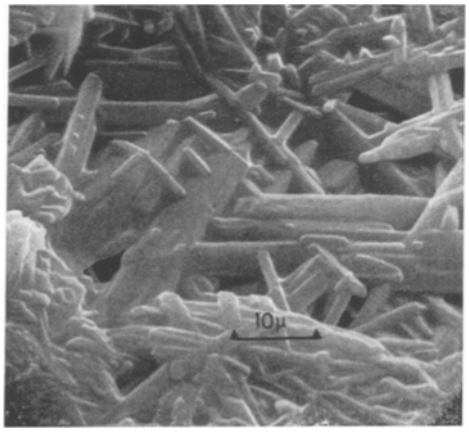

Fig. 8. Kaolinite fired to 1600° and air quenched

hira [4] suggested the metakaolin layers condense to form a spinel-type phase of approximate composition $2Al_2O_3 \cdot 3SiO_2$ with the discard of silica. Other researchers [5] have felt the peak was the result of the formation of mullite. Glass [5] reasoned that the formation of a dense hard phase more readily explains the exotherm than does a subcrystalline compound such as spinel.

The mullite theory has received support from electron microscopy and diffraction studies. Eital, Müller and Radczewski [6] and Bradley [8] showed that kao-

linite particles retain their hexagonal outline far above the dehydration temperature. Roy, et al. [9] detected a spinel phase at 850° in their electron diffraction work. Comer, Koenig and Lyons [10] identified both a spinel and mullite phase present in kaolinite flakes fired to 850°. At 950° they noted the disappearance of

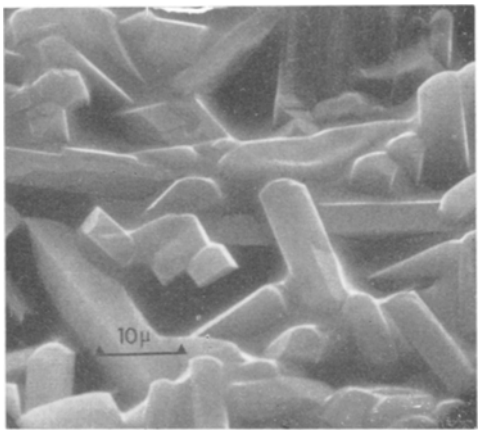

Fig. 9. Kaolinite fired to 1600°, held 12 hours isothermally and air quenched

the spinel and the strong presence of mullite. In the SEM work of Segnit and Anderson [3] the presence of mullite was not detected until 1200° in one sample and 1300° in a second kaolin. Fig. 6 from the sample quenched at 1150° does not resolve this dispute, but favors the spinel hypothesis. The crystalline morphology is less distinct and no mullite crystals are evident.

The second exotherm 1200–1300° is less distinct and has been attributed by Brindley and Nakahira [4] to the transformation of the spinel type of structure to mullite with further discard of silica. This thought is shared by Holdridge and Vaughan [11]. The micrograph, Fig. 7, of a sample quenched at 1350° shows the loss of the hexagonal morphology and the general lack of crystalline structure.

At 1450° there is a change in the baseline slope and a sample at 1600° shows a distinct mullite phase (Fig. 8). This shift in the baseline appears to mark the point where a clearly defined mullite phase emerges. A sample held for twelve hours at 1600° showed substantial grain growth (Fig. 9). The lack of distinct crystalline interfaces suggests that this grain growth is in the presence of a liquid phase (silica).

Conclusions

The scanning electron microscope has provided some additional insight into the processes which occur during the thermal analysis of kaolinite. The results do not resolve much of the controversy, but provide additional information. This approach is likewise important to the technologist as he uses the mineral in ceramic applications.

References

1. R. F. DAVIS and J. A. PASK, High Temperature Oxides, ed. A. Alper, 3 (1972) 48–49.
2. R. C. MACKENZIE, Differential Thermal Analysis, Academic Press, New York, 1970. pp. 524–527.
3. E. R. SEGNIT and C. A. ANDERSON, J. Am. Ceramic Soc., 50, 5 (1971) 480.
4. G. W. BRINDLEY and M. NAKAHIRA, J. Am. Ceram. Soc,. 42, 7 (1959) 311.
5. H. D. GLASS, Am. Mineralogist, 39 (1954) 193.
6. W. EITEL, H. O. MÜLLER and O. E. RADCZEWSKI, Ber. Deut. Keram. Ges., 20 (1939) 249.
7. W. EITEL and H. KEDESDY, Abhandl. preuss. Akad. Wiss. Math-Natur W. Kl., 5 (1943) 37
8. J. E. COMEFORD, R. B. FISHER, W. F. BRADLEY, J. Am. Ceram. Soc., 31 (1948) 254.
9. R. ROY, D. M. ROY and E. E. FRANCIS, J. Am. Ceram. Soc., 39 (1955) 198.
10. J. J. COMER, J. H. KOENIG and S. C. LYONS, Ceram. Ind., 67 (1956) 125, 148 150.
11. D. A. HOLDRIDGE and F. VAUGHAN, The Differential Thermal Investigation of Clays, ed. R. C. MACKENZIE, Mineralogical Society, London (1957) 98–139.

RÉSUMÉ — On a étudié la morphologie de la kaolinite après un traitement thermique à 1600° et rapproché ces observations des données obtenues par ATD–TG–TGD. Les résultats montrent que les données de l'ATD, de la TG et de la TGD, complétées par les renseignements fournis par le microscope électronique à balayage, permettent de mieux comprendre les controverses sur la transformation kaolinite-mullite. En particulier, cette étude vient à l'appui de l'hypothèse de la formation d'une phase spinelle entre 950 et 1000 °C. De plus, elle montre que l'eau s'échappe suivant un mécanisme contraire à celui généralement supposé lors de la déshydroxylation entre 450 et 700°.

ZUSAMMENFASSUNG — Die Morphologie des in einem Thermoanalysator bis zu 1600 °C bearbeiteten Kaolinits wurde untersucht und mit DTA/TG/DTG-Daten in Verbindung gebracht. Die Ergebnisse zeigen, daß durch SEM-Information verfeinerte DTA/TG/DTG Angaben Einsicht in einige Streitfragen bezüglich der Kaolinit-Mullit-Veränderung gegeben werden. Besonders wird durch diese Studie die Annahme unterstützt, daß sich im Gebiet von 950–1000 °C eine Spinell-Phase bildet. Ferner wird durch diese Studie gezeigt, daß im Laufe der Dehydroxylierung im Bereich von 450–700 °C das Wasser durch einen Vorgang entweicht, welcher dem allgemein vermuteten entgegengesetzt verläuft.

Резюме — Изучена морфология каолина при термическом процессе до 1600° С в термоанализере и получены данные ДТА, ТГ, ДТГ. Результаты показывают, что эти данные, уточненные информацией, полученной на сканирующем электронном микроскопе (СЭМ), представляют возможность проникновения в некоторые спорные проблемы, касающиеся перехода каолинит-муллит. В частности, изучение подтверждает гипотезу, что фаза шпинеля образуется в области 950—1000° С. Далее, изучение показало, что при дегидроксилировании в области 450—700° С вода удаляется в результате процесса противоположного обычно предполагаемому.