JOURNAL OF MATERIALS SCIENCE 20 (1985) 32–36

On the formation of mullite from kandites

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Data are presented that support the explanation of the ~ 980° C differential thermal analysis (DTA) exotherm of kandites in terms of transitional mullite (premullite) formation. The evolution of this material towards final 3:2 mullite takes place with change in the tetrahedral aluminium/octahedral aluminium ratio, as evidenced by IR spectroscopy. The so-called mullite peak at 1250° C is shown to disappear when soaking experiments are carried out at lower temperatures, indicating that it is an effect of the dynamical character of DTA techniques.

1. Introduction

The equilibrium diagram for the SiO_2–Al_2O_3 system shows that the heating of kaolin at high temperatures yields a mixture of mullite and cristobalite. The intermediate steps through which this final state is achieved have been extensively studied and much controverted [1–11]. The main discrepancies refer to the interpretation of the sharp exothermic differential thermal analysis (DTA) peak at ~ 980° C. Brindley and Nakahira [6] attribute this peak to formation of a spinel phase with composition $Si_3Al_4O_{12}$ growing in a well defined orientation with respect to the metakaolin formed at ~ 550° C from the monocrystalline kaolin they used as starting material [5]. Nicholson and Fulrath [8] believe the peak at 980° C to be due to crystallization of silica, exsolved in the process of mullite formation, with the growth of β-quartz. Percival *et al.* [9] have studied the process by infrared (IR) spectroscopy, and they conclude that at 980° C a complete decomposition of metakaolin into amorphous silica and γ-Al_2O_3 takes place, and that subsequent reaction at temperatures higher than ~ 1100° C would give secondary mullite, the silica excess appearing as cristobalite. Chakraborty and Gosh [10] believe that the 980° C peak can be ascribed to the formation of a spinel phase with composition identical to that of mullite, and that this phase undergoes a transition to the mullite structure at ~ 1250° C, giving place to a smaller exothermic DTA peak frequently observed.

The observation by transmission electron microscopy (TEM) of the spinel phase at temperatures substantially lower than the exotherm led Roy *et al.* [3] and more recently Comer [7] to exclude the spinel formation as the cause of the exothermic effect. Recently, new evidence [11, 12] shows that the spinel is a metastable phase, and that mullite formation is responsible for the exotherm.

In this paper we present results that support the explanation of the exotherm in terms of transitional mullite (premullite) formation, and a study of the evolution of premullite with temperature towards crystalline mullite, in the hope of contributing to a better understanding of this technologically important process.

2. Experimental

A halloysite rock from Chihuahua (México) was used as starting material. Its chemical analysis gives the following oxide percentages: SiO_2, 44.01; Fe_2O_3, 0.15; Al_2O_3, 38.89; CaO, 0.42; MgO, 0.20; Na_2O, 0.07; K_2O, 0.27. Weight loss at 1600° C was 15.58%.

The material was crushed and ground to a particle size of $< 60\,\mu m$, and portions of the resulting powder were subjected to thermal treatment at temperatures between 900 and 1000° C; these were subsequently treated with aqueous dilute (10%) solutions of NaOH at 90° C with continuous stirring for periods between 5 and

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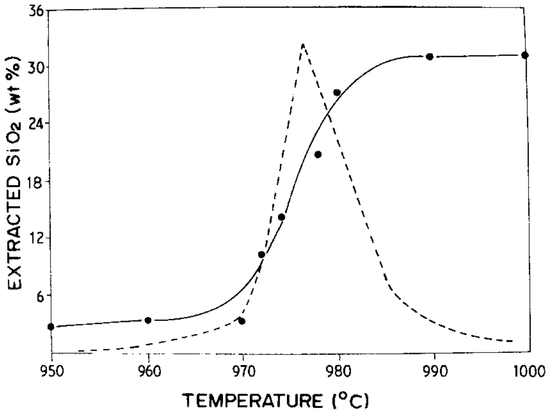

Figure 1 Extracted silica (wt% with respect to metakaolin) by alkaline attack. The dashed line represents the exotherm at 980° C.

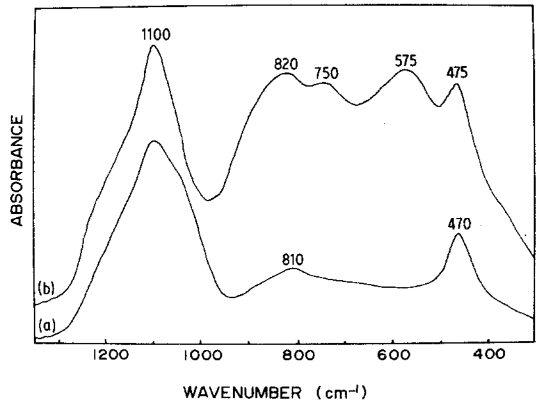

Figure 2 Infrared spectra of (a) halloysite heated at 925° C, 15 min (metakaolin), (b) premullite (see text).

60 min, washed with distilled water, chemically analysed, and the resulting products heated to 1000 to 1570° C during 1 to 30 days. Selected samples were analysed by X-ray diffraction (XRD), DTA and IR spectroscopy. A sample of the original halloysitic material was heated at 1000° C for 10 min, and after NaOH treatment was compacted in the shape of a prismatic bar 45 mm in length by isostatic pressing (200 MN m^{-2}). The velocity of densification of this sample was studied in a sintering furnace.

3. Results and discussion

3.1. DTA peak at 980° C

The curve representing the amount of silica extracted at each temperature is shown in Fig. 1. It is a monotonically increasing function, with an inflection point (maximum slope) at the temperature of the DTA peak, and approaches asymptotically the value corresponding to a final Al_2O_3/SiO_2 molar ratio of 1.5 in the solid phase, which corresponds to mullite composition. The final, low crystallinity (see Fig. 3) material thus obtained at 1000° C we call "premullite", for reasons which will become apparent below.

The IR spectra of a halloysite sample heated at 925° C (metakaolin) and that of premullite are in Fig. 2. In metakaolin, a typical spectrum of a disordered material is observed, with three broad bands at 1100 and 470 cm^{-1} (Si–O in tetrahedral coordination) and 810 cm^{-1} (Al–O in tetrahedral coordination). This is in agreement with Brindley and Nakahira's [5] contention that in metakaolin all aluminium is tetrahedrally coordinated. The spectrum of premullite shows, however, the presence of some aluminium in octahedral coordination, as evidenced by the absorption band at 575 cm^{-1} [13]. This spectrum has been analysed by Percival *et al.* [9] in terms of a possible γ-Al_2O_3 or an Al–Si spinel phase. The presence of γ-Al_2O_3 can be ruled out [14] on the basis of the existence of chemically bonded SiO_4, in agreement with our observations (Figs. 1 and 2). Besides, it is known [15] that γ-Al_2O_3 transforms into corundum at high temperatures, and this phase has not been detected in any sample heated at more than 980° C. Thermodynamic calculations [16] show, however, that γ-Al_2O_3 would be the favoured phase under equilibrium conditions. Our IR observations do not agree with a spinel phase with composition $3SiO_2 \cdot 2Al_2O_3$ ($SiAl_{1.33}O_4$) as proposed by Brindley and Nakahira [6] because this composition would not permit the existence of tetrahedral aluminium. Our silica extraction results (Fig. 1) are also in disagreement with that composition.

Our IR observations could be explained by either the presence of premullite (a mullite-like structure has been found in the study of some Si–Al glasses [17]), or a spinel phase of mullitic composition as postulated by Chakraborty [10, 14]. Very recently, Hornor *et al.* [12] have observed both mullite and spinel by TEM in samples heated dynamically to 975 and 1000° C, while only the spinel phase was detected at 925 and 950° C, in agreement with previously published results by Roy *et al.* [3] and Comer [7]. We also see many mullite broad peaks and the two strongest peaks of the cubic phase in a sample heated dynamically to 1000° C (data not shown). The fact that a spinel phase with a composition

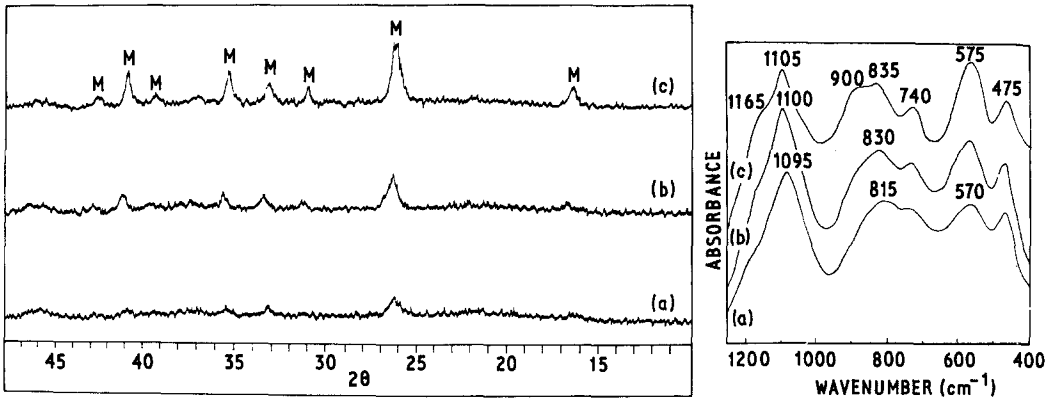

Figure 3 X-ray diffraction powder patterns and infrared spectra of premullite soaked at 1000° C, showing its evolution to mullite: (a) 2 h, (b) 4 days, (c) 30 days.

close to that of mullite is detected at and after the DTA peak at ~ 980° C in dynamic experiments (10 to 20° C min^{-1}) raises the possibility of a contribution to the exotherm due to metastable spinel formation, but we believe the main contribution comes from premullite formation.

3.2. Evolution of premullite

We have performed soaking experiments in order to study the transformation of premullite into mullite. Samples of premullite were soaked at 1000° C for 2 and 4 h, 4 and 30 days; at 1100° C for 3 and 46 h, and 5 days; and at 1200° C for 2 h. IR and XRD evidence (Figs. 3 and 4) indicate that the transformation of premullite into mullite is a continuous process. The IR spectrum undergoes the following changes in going from premullite to mullite (Fig. 3): (a) a portion of the Si–O stretching band (1100 cm^{-1}) shifts towards higher wavenumber (1160 cm^{-1}); (b) the band at 575 cm^{-1}, assigned to Al–O vibrations with Al octahedrally coordinated, increases in intensity. In agreement with Milkey's [18] result that there is a general trend for the Si–O band to shift to higher wavenumber with a decreasing fraction of tetrahedral aluminium, we conclude that some tetrahedral aluminium changes to octahedral coordination by a temperature controlled diffusive process in going from premullite to mullite.

The XRD powder patterns (Figs. 3 and 4) show a continuous increase in crystallinity and absence of the spinel phase in all samples soaked at 1000° C or above for more than 2 h, in agreement with the observation of Hornor *et al.* [12] that the spinel phase can be made to disappear at temperatures as low as 950° C by increasing the time of soaking.

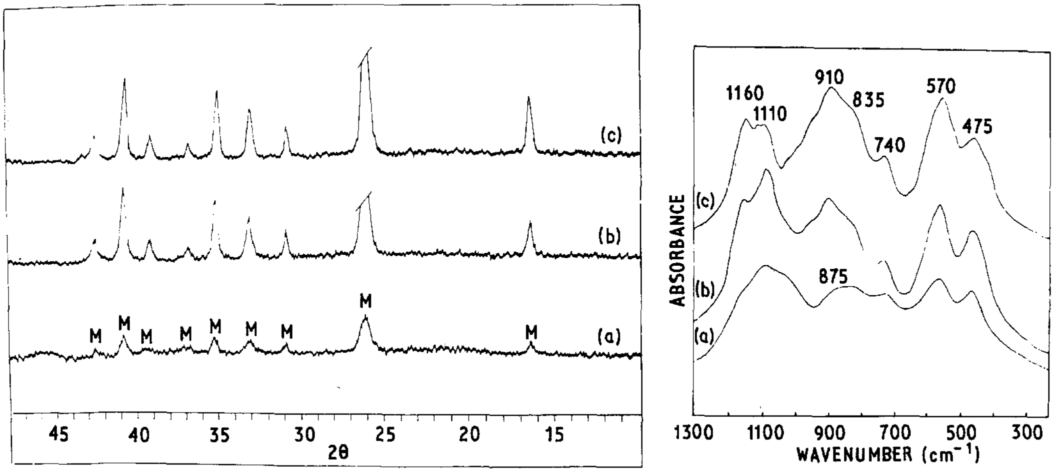

Figure 4 X-ray diffraction powder patterns and infrared spectra of premullite held at different temperatures: (a) 1000° C, 4 h, (b) 1100° C, 46 h, (c) 1200° C, 2 h.

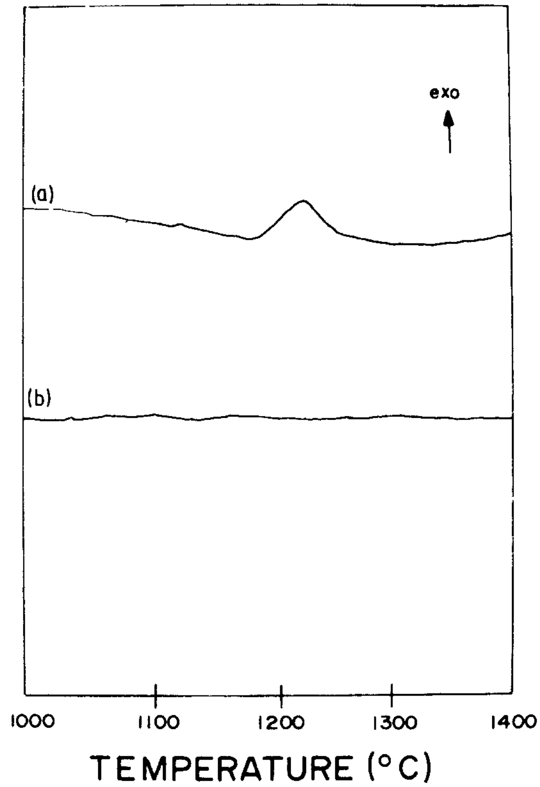

Figure 5 Differential thermal analysis of premullite (a) untreated, (b) soaked at 1100° C, 48 h.

3.3. DTA peak at 1250° C

The exothermic peak at ~ 1250° C (known in the literature as the mullite peak) has been attributed by Chakraborty and Gosh [10] to the reaction Al–Si spinel → mullite. In order to contribute to the understanding of this thermal effect we have carried out the following experiments.

(a) A premullite sample was heated at 1100° C for 48 h, and subsequently its DTA was recorded up to $T = 1400°$ C. The DTA trace is shown in Fig. 5, together with the trace obtained from untreated premullite.

(b) A premullite sample was compacted by isostatic pressing, and the shrinkage curve recorded as shown in Fig. 6. In order to ascertain which phases were present at the step the curve shows between 1195 and 1460° C, different premullite samples were heated at the same rate as in the sintering furnace (10° C min^{-1}) up to 1195, 1350 and 1468° C, following with a quench from these temperatures. The XRD powder traces show a progressive development of mullite crystallinity, similar to that exhibited in Fig. 4.

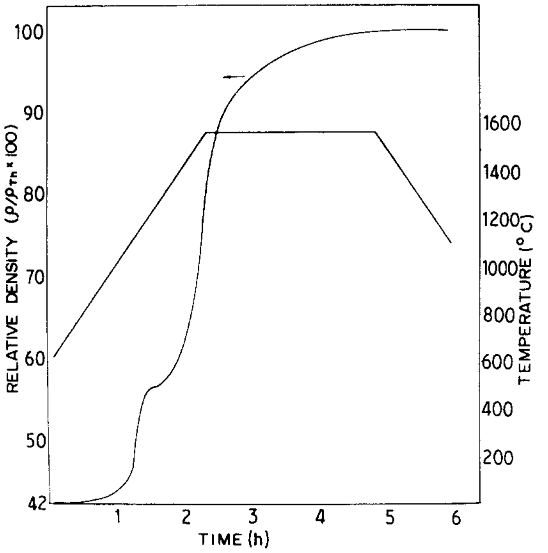

Figure 6 Shrinkage data of premullite powder.

From DTA data (Fig. 5) it is clear that the exothermic peak at ~ 1250° C is no longer observed in samples heated at 1100° C for 48 h. On the other hand, the plateau of the sintering curve occurs at the temperature interval where the exothermic peak is observed in untreated samples. We conclude that in the far from equilibrium conditions of these dynamical tests the transition from tetrahedral to octahedral aluminium and the ordering of the new mullitic phase occurs suddenly when the temperature is sufficiently high, perhaps, by the formation of a liquid phase [19], but a similar effect can be achieved by prolonged heating at a lower temperature.

4. Conclusions

(a) The exothermic peak at ~ 980° C is mainly due to the formation of a phase we call premullite, with the same chamical composition as 3 : 2 mullite, a different tetrahedral aluminium/octahedral aluminium ratio and low crystallinity.

(b) The exothermic DTA peak at ~ 1250° C is due to an abrupt ordering of the premullite structure, with some tetrahedral aluminium shifting to octahedral positions and formation of 3 : 2 crystalline mullite. The rate of this transformation is temperature dependent, and the process can be made to occur to completion at 1100° C, although probably it would also take place at temperatures just slightly above the 980° C exotherm, maintained for very long periods of time.

Acknowledgements

We thank Prof. J. A. Pask and Prof. S. de Aza for several enlightening observations and comments on the results reported in this paper. Financial support from CAICYT (projects 3171/79 and 0079/81) is gratefully acknowledged.

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Received 22 December 1983
and accepted 8 February 1984