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Thermal phase sequences in gibbsite/kaolinite clay: electron microscopy studies

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Abstract

In Brazil, gibbsite/kaolinite clay is used extensively in the manufacture of refractory products. In this study, electron microscopy was used to characterize the phase sequences occurring during thermal transformation in this type of clay. The clay was powdered, heated on platinum foils to temperatures of 200–1550 °C and program cooled. The heated powders were characterized using transmission electron microscopy, selected area electron diffraction, elemental microanalysis and X-ray diffraction.

After heating the gibbsite/kaolinite clay to 200 °C or better at 300 °C, morphological characterization under a transmission electron microscope revealed that the chi-alumina from the gibbsite is identical in size and shape (hexagonal) to the undecomposed kaolinite crystals. The thermal transformations of gibbsite and well-crystallized kaolinite follow independent specific patterns up to 1100 or 1200 °C. Examining the organization of the internal granules formed from the dehydroxylation of gibbsite and kaolinite at increasing temperature (400–800 °C), a morphological difference was observed between the aluminas (chi and kappa) and the pseudomorphic metakaolin crystals. The two reaction sequences (a) metakaolin → spinel → mullite; (b) kappa-alumina → alpha-alumina occur in the 900–1100 °C range and characteristic morphological differences among the crystals are evident, especially in the spinel, which presents elongated particles. Mullite content increases between 1000 and 1550 °C, whereas alpha-alumina increases up to 1300 °C and decreases by 1550 °C, indicating interaction among the several high-temperature phases.

Keywords: B. Electron microscopy; D. Al_2O_3; D. Clays; D. Mullite

1. Introduction

Gibbsite $Al(OH)_3$ is a crystalline aluminum trihydroxide and is a very common component of high-alumina-kaolinite clays. There are various deposits of these clays in Brazil and they are extensively used in the manufacture of refractory products. Brazil is fifth-largest producer of refractory materials in the world.

Wefers and Misra [1] and Wefers [2] have presented two sequences and electron microscopy data from the thermal transformation of synthetic gibbsite into aluminas. Recent electron microscopy studies of the transition aluminas were conducted by Levin and Brandon [3] and by Souza Santos et al. [4].

Brindley [5,6] proposed a thermal transition sequence for kaolinite to mullite and cristobalite. However, his data are still being discussed, reviewed and investigated, using other physico-chemical methods [7–11].

Soluparnak et al. [12] reviewed the literature and concluded that the reaction mechanisms proposed for the “980 °C” exotherm of the kaolinite differential thermal analysis (DTA) can be classified into two general groups. In the first one, the common feature is the formation of a gamma-alumina type spinel phase and its association with the exothermic reaction. The differences reported for this group relate primarily to the composition of the spinel phase (especially the Si contents thereof) and whether the mullite

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phase (through a parallel reaction) also contributes to the exotherm. In contrast to these spinel-based models, the second group features the formation of mullite ($3Al_2O_3{\cdot}2SiO_2$) without a spinel phase.

Brindley [5] heated metakaolin to within the 850–925 °C range and observed the transformation into an Al–Si spinel and amorphous SiO_2. Sonuparlak et al. [12] used transmission electron microscopy (TEM) to show that the gamma-alumina type spinel phase is solely responsible for the "980 °C" exotherm and that spinel formation is preceded by phase separation in the dehydroxylated kaolinite (metakaolin) matrix at 850 °C.

Chabravorty and Gosh [13] suggested, based upon the hypothetical Si–Al spinel (composed of $2Al_2O_3{\cdot}3SiO_2$) proposed by Brindley [5], that there may exist a form of mullite having a 3:2 composition ($3Al_2O_3{\cdot}2SiO_2$) plus free amorphous silica. It was designated by the authors as the "cubic form of mullite", a polymorphic form of orthorhombic mullite which would be formed at the 980 °C exotherm of the DTA curve of kaolinite by the reaction: $1.5\,(2Al_2O_3{\cdot}3SiO_2) \Rightarrow 3Al_2O_3{\cdot}2SiO_2 + 2.5SiO_2$.

Using MAS/NMR, it has been shown that, at 980 °C, metakaolin crystallizes into gamma-alumina (spinel) [7] and that low "crystallinity" mullite nuclei with segregated amorphous silica may be generated [8]. According to the study of kaolinite thermal decomposition conducted by Sanz et al. [8], dehydroxylation is completed at 750 °C, partial separation of the tetrahedral sheet takes place at 850 °C and segregation of amorphous silica occurs at 980 °C.

In conclusion, these findings suggest that, in kaolinite, the reaction Al–Si spinel ⇨ 3:2 mullite + non-crystalline SiO_2 begins within the 850–900 °C range. Although several authors have investigated prepared mixtures of kaolinite with synthetic aluminas or with diaspore and boehmite [11,14–20], few report the changes in morphological features of, or interactions between, mullite and alpha-alumina crystals when exposed to the elevated temperatures used in production of high alumina refractory materials. To date, there have been no studies of the transformation sequences that occur when clays containing a natural mixture of gibbsite and kaolinite are fired at high temperatures.

2. Aim

The aim of the present paper is to apply electron microscopy methods to study the thermal transformation of a natural mixture of gibbsite and kaolinite crystals at temperatures of up to 1550 °C.

3. Experimental

3.1. Clay

The sedimentary gibbsite/kaolinite clay from the locality of Suzano, near the city of São Paulo in Brazil, is a refractory clay and is used in ceramics. The clay is predominantly composed of gibbsite, kaolinite and a small amount of quartz. The ground clay is gray in color. From among 12 gibbsitic clays, this clay was chosen for its thin hexagonal crystals, which allow more precise TEM examination of the thermal changes along the c direction, and for its high relative ratio of gibbsite to kaolinite (0.76 gibbsite; 0.24 kaolinite). The chemical analysis is shown in Table 1. The Al_2O_3/SiO_2 molar ratio is 3.17, which is higher than in $3Al_2O_3{\cdot}2SiO_2$ mullite (1.50) or in $2Al_2O_3{\cdot}SiO_2$ mullite (2.00). Therefore, the clay selected may produce mullite and alpha-alumina when fired to appropriate temperatures. The kaolinite is low-defect, presenting good resolution of the two triplets in the 0.0228–0.0256 nm range.

Table 1
Chemical analysis of suzano high alumina clay[a]

Clay	Suzano	Kaolinite (theoretical)	Gibbsite (theoretical)
L.O.I. (%)	29.1	14.0	34.6
SiO_2 (%)	11.0	46.5	–
Al_2O_3 (%)	59.2	39.5	65.4
TiO_2 (%)	–	–	–
In Fe_2O_3 (%)	0.54	–	–
MgO (%)	–	–	–
CaO (%)	–	–	–
Na_2O (%)	0.02	–	–
K_2O (%)	0.04	–	–
Total	99.90	100.0	100.0

[a] Clay dried at 105–110 °C.

According to Tertian and Papée [21] and Brindley and Choe [22], gibbsite crystals finer than about 1 μm begin the transformation into chi-alumina at 270 °C. Therefore, 200 °C was chosen as the first heating temperature. A programmable electric furnace was used to heat powdered clay samples on platinum foils in an oxidizing atmosphere. Samples were heated from 200 to 1550 °C (maximum temperature) over a period of 4 h and then program cooled.

3.2. Characterization

X-ray diffraction (XRD), selected area electron diffraction (SAD) and elemental microanalysis (MA/TEM) were used in the analysis of all phases.

The heated dry material was sprinkled onto a microscope grid, as described by Souza Santos and Yada [23], for characterization by electron microscopy. The samples were observed in a Philips CM200 transmission electron microscope at 200 kV. The same microscope was used as a diffraction camera for obtaining the SAD identification of the crystalline structures in the various phases. Both gibbsite and kaolinite thermal sequence particles were collected and MA/TEM was performed. The structural characterization was also performed using XRD in a Philips PW 3050 X'PERT MPD diffractometer operating at 40 kV and 40 mA, between $2\theta = 1°$ and $2\theta = 90°$, using copper K-alpha radiation.

4. Results and discussion

4.1. XRD analysis

The XRD curve of undecomposed Suzano clay presents reflections from kaolinite at 0.716 nm, gibbsite at 0.485 nm and quartz at 0.334 nm, as well as other reflections from those minerals. The relative intensity of the basal kaolinite reflection is lower than that of the gibbsite.

At 200 °C, no change was observed in d values, but the reflection intensity of the gibbsite was found to be lower than that of kaolinite or quartz. At temperatures above 300 °C, gibbsite reflections disappeared and the 0.139 nm chi-alumina reflection appeared, although no changes in kaolinite were seen. At 400 °C, chi-alumina and kaolinite diagrams were observed.

Above 500 °C, all kaolinite reflections disappeared and formation of metakaolin occurred. The metakaolin reflections were diffuse and weak, so its diagram does not appear in the X-ray powder diffraction curve of the heated clay. However, single metakaolin crystals can be characterized by SAD, as was shown by Clinard et al. [24]. From 600 to 800 °C, the chi-alumina pattern was present, but no metakaolin was detected.

Within the 800–900 °C range, only the kappa-alumina pattern was observed, even though Brindley [6] has reported that metakaolin persists up into the 925–950 °C range.

At 1000 °C, kappa-alumina and Al–Si spinel reflections, as well as five intense alpha-alumina reflections, were characterized. As predicted by Brindley [5], no mullite reflection was detected. At 1100 °C, only spinel and alpha-alumina reflections were observed. Sharp 3:2 mullite and alpha-alumina reflections were noted at 1200 °C, and the intensity of these reflections increased within the 1300–1400 °C range.

At temperatures from 1400 to 1500 °C, the mullite and alpha-alumina patterns displayed very sharp peaks and the relative intensity of the 0.334 nm quartz reflection had decreased significantly (to 60%). Considering the 0.339 nm mullite reflection as 100%, the most intense cristobalite reflection (0.404 nm) was observed to have a low (2.7%) relative intensity. The other reflections (0.3138, 0.2845 and 0.2489 nm) were not detected.

At 1500 °C, very intense mullite and alpha-alumina reflections were observed. The 0.404 nm cristobalite reflection decreased to 0.6% relative intensity in relation to the 0.339 nm mullite reflection. At 1550 °C, no cristobalite reflection was observed, but the intense and sharply peaked reflections from 3:2 mullite and alpha-alumina were still present. The observations on mullite formation are in agreement with Bratton and Brindley [16] on high temperatures reactions of diaspore-boehmite-kaolinite clays.

4.2. TEM/SAED analysis of untreated clay

In the electron micrographs, the original clay sample consists of an intimate mixture of platy particles of gibbsite and kaolinite. However, the morphological aspects of the gibbsite and the kaolinite monocrystals, as well as their particle sizes, are quite similar, both being micrometric pseudohexagonal plates (Fig. 1). These facts make it very difficult, and sometimes even impossible, to distinguish between gibbsite and kaolinite by crystal shape alone. Therefore, direct characterization through SAD is essential.

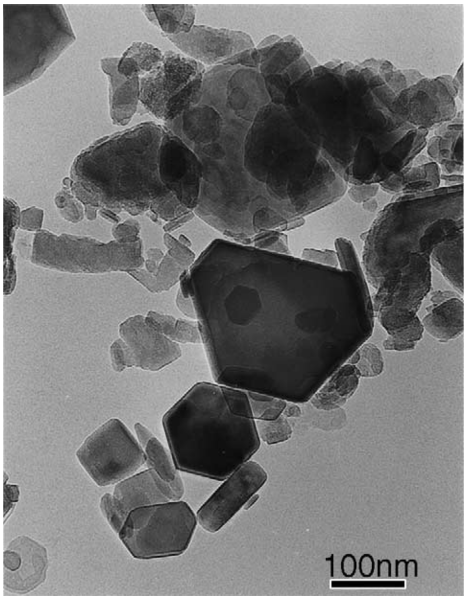

Fig. 1. Undecomposed Suzano clay, consisting of pseudohexagonal platy crystals of kaolinite and gibbsite.

4.3. TEM/SAED analysis of heat-treated clay

At 200 °C, the SAD diagrams displayed three kinds of crystalline structures: gibbsite, kaolinite and chi-alumina, depending on the chosen particle. In sequences presented by Wefers and Misra [1] and by Wefers [2], chi-alumina was the first transition alumina. This leads us to assume that, in our sequence, some gibbsite crystals dehydroxylated into chi-alumina, while other crystals in the same sample did not. In the Suzano clay sample, that transformation occurred at a temperature 70 °C lower than what has been reported in the literature [1,2,5]. It is not detected by XRD because the most intense chi-alumina reflection (0.139 nm) is masked by the sharp gibbsite reflections in the 200 °C heated clay. Morphologically, the crystals characterized as chi-alumina by SAD display a fine granularity, which is distributed at random inside the pseudomorphs. At 300 °C, the same phases were detected by SAD. However, the morphological organization of chi-alumina granules is seen much more clearly in some of the crystals, where a definite parallel alignment of the granule strings is observed (Fig. 2A). The SAD characterization of the chi-alumina is shown in Fig. 2B. At this temperature, the chi-alumina crystals (gibbsite pseudomorphs) are easily distinguished from the undecomposed gibbsite and kaolinite crystals. In Fig. 2A, an intimate association between chi-alumina and kappa-

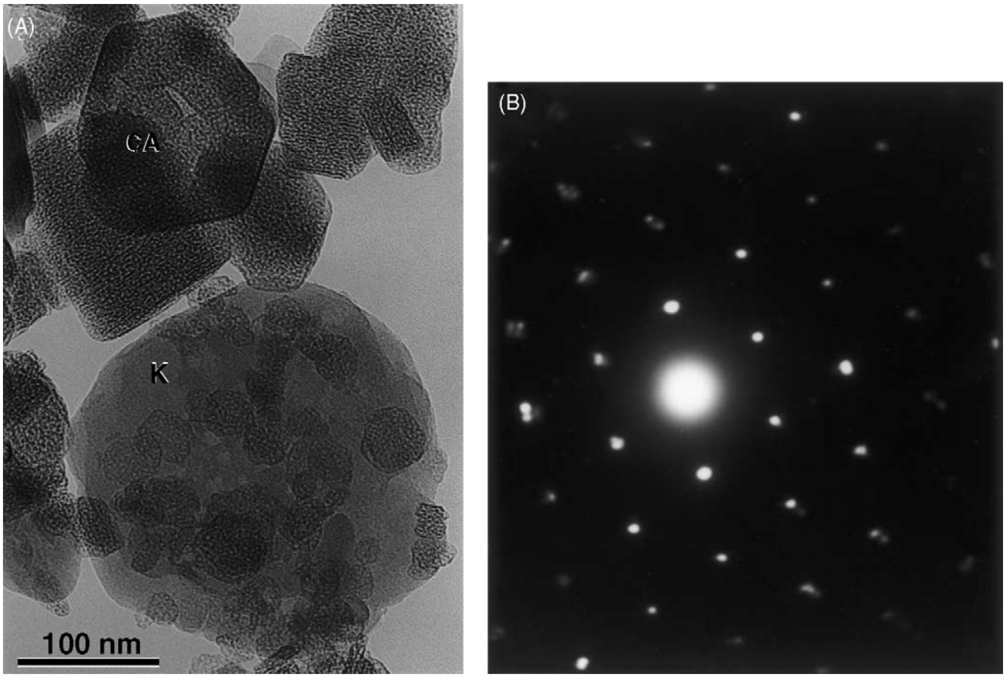

Fig. 2. (300 °C)—(A) TEM of chi-alumina (CA) pseudomorphs from gibbsite, showing the internal organization of the alumina granules and undecomposed kaolinite crystals (K) and (B) SAD characterization of CA.

alumina crystals on or inside a larger undecomposed kaolinite crystal can be seen. This same association was also found at higher temperatures.

The parallel orientation of the strings may be the origin of the ''lamellae'' that have been previously observed in TEM images of chi-alumina in exfoliated gibbsite prisms [25] and in acicular gibbsite crystals [1]. The gibbsite/boehmite/alumina thermal sequence described by Wefers and Misra [1] was not detected in any crystal examined under SAD. This was probably due to the smaller size of the gibbsite crystals, as compared with the typically larger crystals of the synthetic Bayer gibbsite, which were reported by Misra [25] to be between 73 and 143 μm. At 400 °C, gibbsite was no longer detected by SAD, but chi-alumina and kaolinite were still present.

At 500 °C, chi-alumina was still present in some crystals. However, kappa-alumina was the most frequently detected during SAD. This is an interesting finding because, according to Wefers and Misra [1], chi-alumina in Bayer gibbsite crystals begins to transform into kappa-alumina only at 750 °C. This discrepancy could also be attributed to the smaller size (and, in particular, the thinness) of the chi-alumina crystals in Suzano clay. Fig. 3 shows the well-developed granules and their orientation inside the pseudomorphs. An undecomposed kaolinite crystal is also presented in Fig. 3. Since no difference in their internal arrangements could be observed by TEM, the only way to differentiate between the remaining chi-alumina and kappa-alumina crystals was through SAD.

At temperatures between 600 and 700 °C, SAD revealed chi-alumina, kappa-alumina and metakaolin. The morphology points to a second dehydroxylation of the kaolinite crystals. The kaolinite crystals maintained their hexagonal platy shape, but their upper surface was no longer smooth. Fig. 4 shows the transformation in the heated kaolinite crystals. Surrounding the metakaolin crystals (kaolinite pseudomorphs), the progressive increase in the internal organization of the striated chi-alumina and kappa-alumina crystals

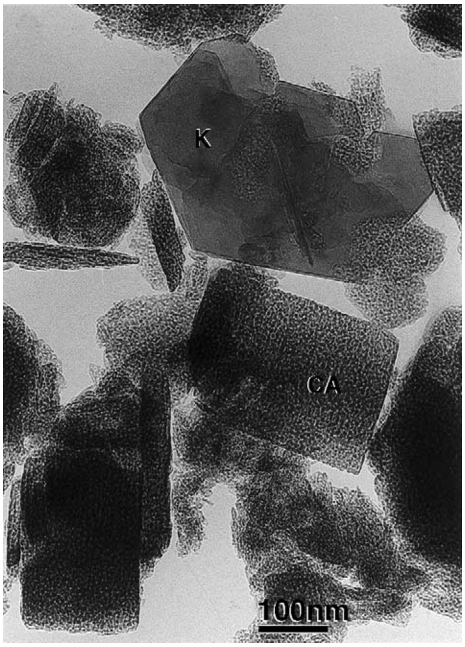

Fig. 3. (500 °C)—Well-developed granules inside chi-alumina (CA) crystals. Undecomposed kaolinite (K) crystals can also be seen.

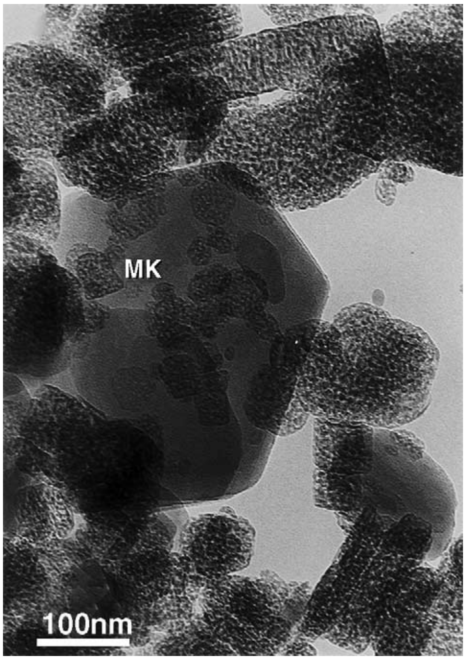

Fig. 4. (600 °C)—Metakaolin (MK), chi-alumina and kappa-alumina crystals presenting granular textures.

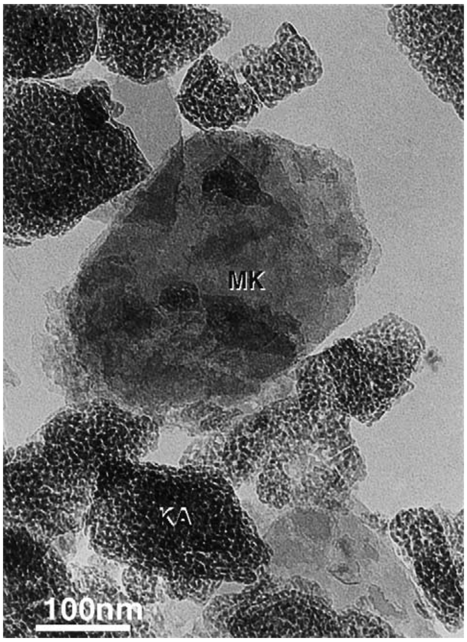

Fig. 5. (700 °C)—Micrograph highlighting the difference between the striated aspect of kappa-alumina (KA) crystals and the exfoliated and ragged texture of the metakaolin (MK) crystals.

can be followed. Thus, it was possible to distinguish the two aluminas from metakaolin crystals.

At 700 °C, SAD detected kappa-alumina and metakaolin, as well as trace chi-alumina. Fig. 5 shows the difference between the striated aspect of kappa-alumina crystals and the exfoliated and ragged texture of the metakaolin crystals. At this point, it is evident that the two kinds of crystals, one from the gibbsite series and one from the kaolinite series, present morphological temperature alterations that are completely independent, each following its own specific sequence. Hyatt and Bansal [26] made a similar observation when heating a synthetic mixture of colloidal silica and boehmite crystals.

Between 800 and 900 °C, SAD analysis revealed kappa-alumina, as well as metakaolin, in the majority of the crystals examined. However, chi-alumina was no longer detected, supporting the findings of Wefer and Misra [1], who designated 750 °C as the temperature at which sharp transition of chi-alumina into kappa-alumina occurs. The morphology only emphasizes the same features present at 700 °C; the kappa-alumina granules showed their individuality and striated organization, although in a markedly sharper way. Therefore, at 700 °C (and more so at 800 °C), it is possible to distinguish between kappa-alumina and metakaolin crystals.

Within the 900–1000 °C range, SAD detected kappa-alumina and Al–Si spinel. The kappa-alumina crystals were thicker and electronically denser. In Fig. 6A, SAD characterization of the spinel crystals (metakaolin pseudomorphs) can be seen. Within the metakaolin pseudomorphs, one can observe a structure consisting of small, elongated particles of a cilindrical shape (Fig. 6B). These particles probably represent the sites where spinel ⇨ mullite + silica reactions originate and mullite laths begin to nucleate. The MA/TEM analysis of the spinel pseudomorphs confirms the presence of Al + Si (Fig. 6C).

Between 1000 and 1100 °C, it was possible to detect kappa-alumina, spinel and alpha-alumina by SAD. This is in agreement with sequences shown by Wefers and Misra [1] and by Wefers [2], in which 1030 °C was established as the temperature at which kappa-alumina becomes alpha-alumina. In the electron micrographs, the kappa-alumina crystals are much thicker and electronically denser, which makes visualization of their internal organization problematic, especially since the spinel phase is scarce. One can see fields completely dominated by 120°-oriented laths (Fig. 7), which were characterized by SAD as a mullite phase. No micrographic evidence was found for amorphous free-SiO_2 particles resulting from the decomposition of the spinel phase.

At 1100 °C, SAD analysis detected alpha-alumina, some Al–Si spinel, 3:2 mullite and no more kappa-alumina. Fig. 8 displays round alpha-alumina of high electron density and enlarged lath-like 120°-oriented mullite crystals. It has been reported that amorphous silica begins to crystallize into cristobalite at temperatures from 1100 to 1200 °C [6]. However, in this study, no cristobalite was detected within this temperature range.

Within the 1200–1400 °C range, SAD and XRD identified mullite and alpha-alumina. Quartz was present up to 1400 °C, when a small amount of cristobalite was characterized. Therefore, probably by 1100 °C, but certainly by 1200 °C, alpha-alumina from gibbsite begins to react

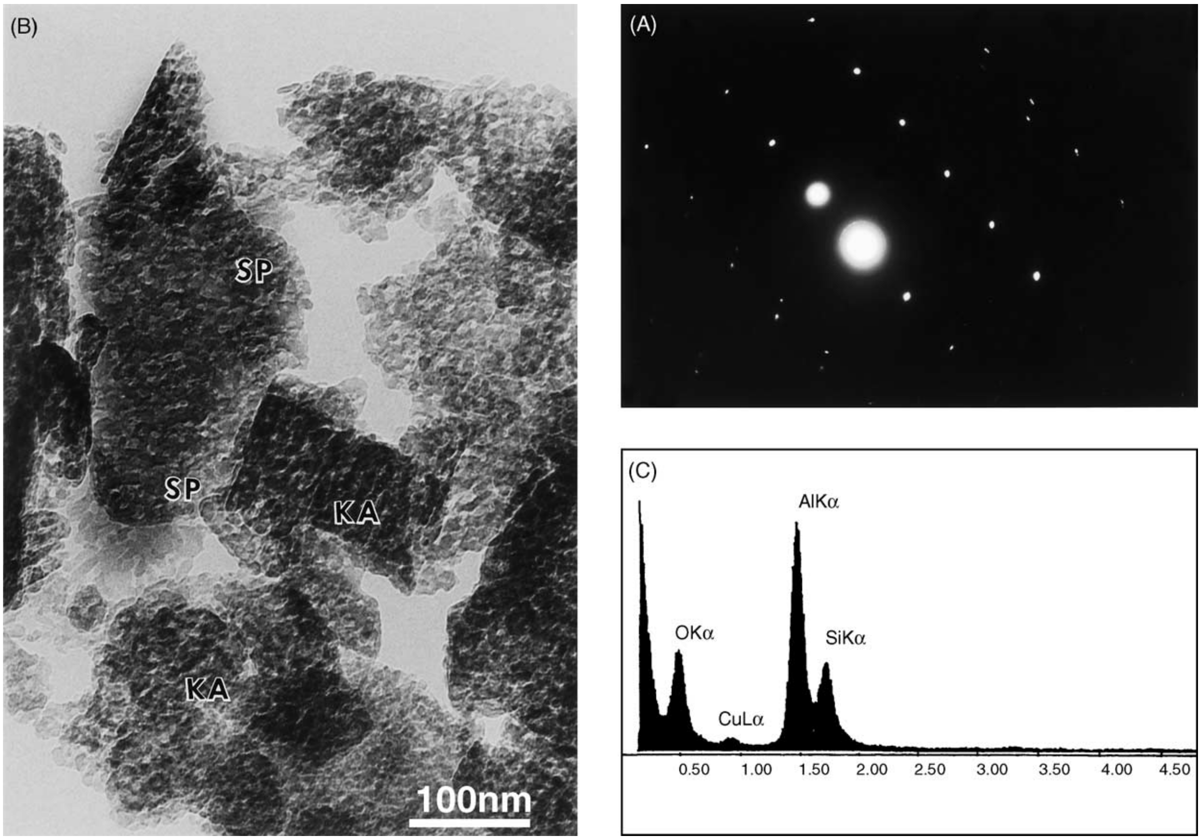

Fig. 6. (900 °C)—TEM of Al-Si spinel (SP) and kappa-alumina (KA) crystals. (A) SAD characterization of the spinel region (SP); (B) The of Al-Si spinel is seen to consist of elongated cylindrical particles in close alignment; and (C) MA/MET analysis of the spinel chemical composition.

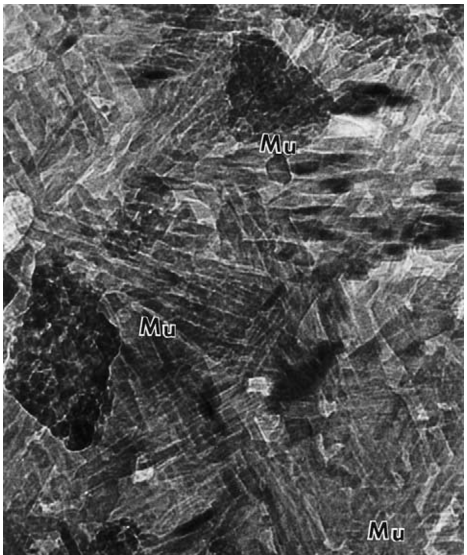

Fig. 7. (1000 °C)—Field dominated by 120°-oriented mullite (Mu) laths.

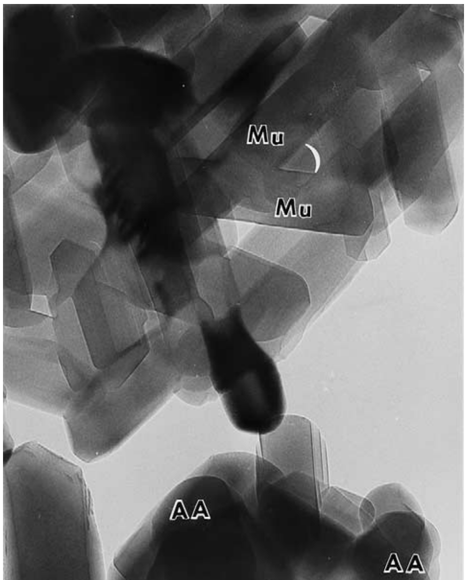

Fig. 8. (1100 °C)—Rounded alpha-alumina (AA) crystals. Mullite (Mu) laths and thick rods, many oriented to 120°, are also evident.

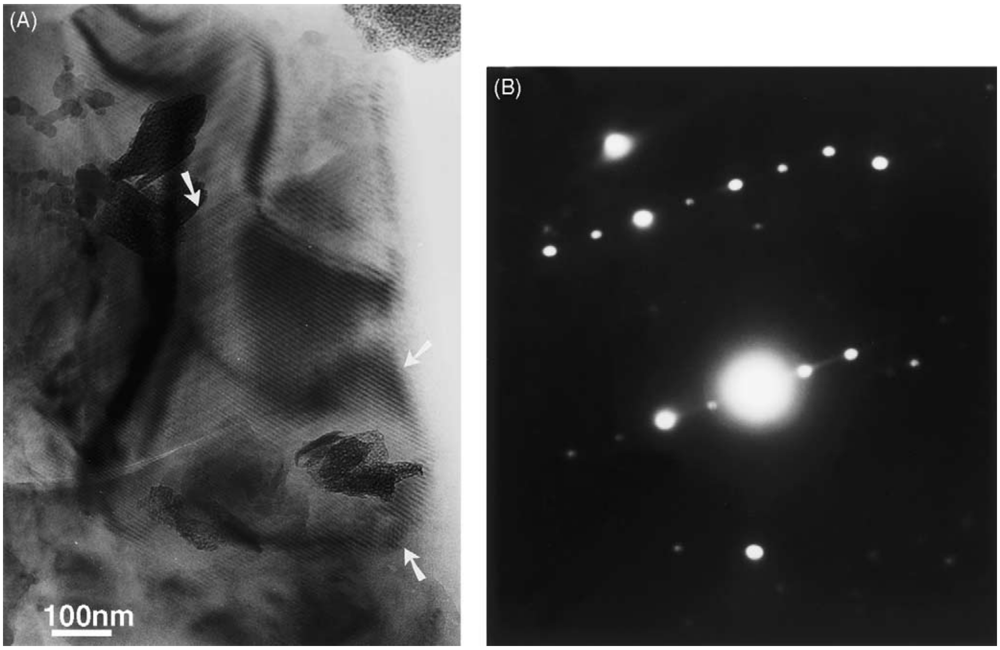

Fig. 9. (1400 °C)—(A) cristobalite as very fine overlapping lamellar crystals. (B) SAD analysis of the cristobalite region.

with free-SiO_2 and with the spinel, forming 3:2 mullite laths and rods. Therefore, the transformation sequences of kaolinite and gibbsite are independent up to the 1100–1200 °C range. However, above this range, interaction among the reaction products begins, resulting in the production of mullite.

From 1400 to 1500 °C, alpha-alumina, mullite and cristobalite were very clearly seen in both SAD and XRD analyses. Fig. 9A presents cristobalite as very fine lamellar overlapping crystals presenting irregular profiles, Bragg contours and Moiré fringes. Fig. 9B shows a SAD analysis of the cristobalite region.

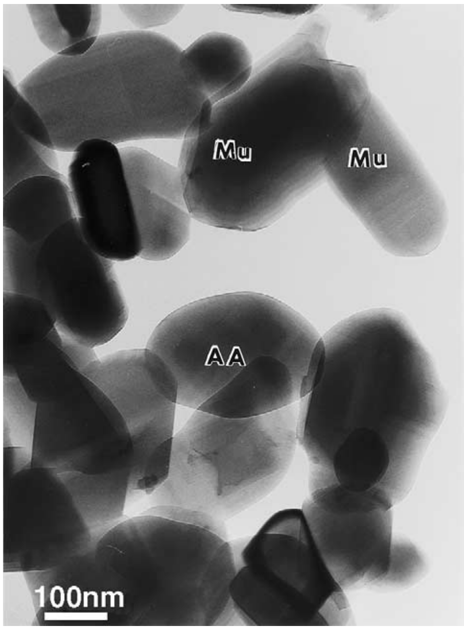

Fig. 10. (1500 °C)—Thick mullite (Mu) rods and rounded alpha-alumina (AA) crystals.

At 1500 and 1550 °C, SAD characterized alpha-alumina and mullite. Their morphologies can be seen in Fig. 10, where alpha-alumina appears as thick, clearly outlined, somewhat round particles and platelets and mullite appears as thick elongate mullite rods.

5. Conclusions

Conclusions drawn from the TEM, SAD and XRD data follow:

1. The transformation temperature intervals of gibbsite and of some transition aluminas in the gibbsite/kaolinite clay from Suzano, Brazil confirm data from Wefers and Misra [1]. However, SAD examination of single alumina crystals suggests that some crystals exist outside these ranges, such as chi-alumina at 200 °C and kappa-alumina at 500 °C.
2. The thermal transformations of the gibbsite and the low-defect kaolinite crystals in the gibbsite/kaolinite clay follow independent specific sequences up to the 1100–1200 °C range.
3. The organization of the internal granules formed from the dehydroxylation of gibbsite and kaolinite crystals at increasing temperature gradients (200 °C/800 °C) are morphologically different between the aluminas (chi-alumina and kappa-alumina) and the pseudomorphic metakaolin crystals.
4. By heating gibbsite/kaolinite clay to 200 °C or (preferably) 300 °C, it is possible to morphologically

distinguish chi-alumina from gibbsite and from undecomposed kaolinite crystals.

5. By heating to within the 600–800 °C range, it is possible to morphologically distinguish chi-alumina and kappa-alumina from metakaolin crystals.
6. Electron microscopy indicated that the metakaolin ➔ spinel plus silica reaction, forming single elongated spinel particles inside the metakaolin pseudomorphs, begins to occur within the 900–1000 °C range.
7. The elongated spinel particles are the sites where the reaction mullite plus silica occurs and mullite nuclei are formed within the 1000–1100 °C range.
8. From 200 to 1550 °C, the independent thermal transformations of natural gibbsite and kaolinite crystals follow the sequences:
    (a) gibbsite ➔ chi-alumina (200–700 °C) ➔ chi-alumina ➔ kappa-alumina (500–1000 °C) ➔ kappa-alumina ➔ alpha-alumina (900–1550 °C);
    (b) kaolinite ➔ metakaolin (500–900 °C) + non-crystalline silica (NC-SiO_2) ➔ metakaolin ➔ Al–Si spinel (900–1100 °C) + (NC-SiO_2) ➔ Al–Si spinel ➔ 3:2 mullite (1000–1100 °C) + (NC-SiO_2).
9. Within the 1000–1550 °C range, mullite XRD reflections increase dramatically. Relative intensities of alpha-alumina XRD reflections also increase from 1200 to 1300 °C, but decrease between 1300 and 1550 °C. Within the 1000–1550 °C range, alpha-alumina reacts with the several types of silica present in the system and forms 3:2 mullite crystals. Within the same temperature range, the remaining alpha-alumina particles recrystallize into thick anhedral platelets.

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