JOURNAL OF MATERIALS SCIENCE 29 (1994) 1276–1283

Grinding effect on kaolinite–pyrophyllite–illite natural mixtures and its influence on mullite formation

P. J. SÁNCHEZ-SOTO*, A. JUSTO, J. L. PÉREZ-RODRÍGUEZ
Instituto de Ciencia de Materiales, Centro Mixto Consejo Superior de Investigaciones Científicas-Universidad de Sevilla, P.O. Box 1115, 41080-Sevilla, Spain

The effect of dry grinding (mechanochemical activation) on a natural mixture of aluminium silicates composed of kaolinite, pyrophyllite and potassium mica (illite) was studied. The evolution of the ground material was followed by X-ray diffraction, differential thermal analysis, thermogravimetric analysis, scanning electron microscopy and nitrogen adsorption methods. Grinding produces a strong structural alteration of the silicates that constitute the mixture, increasing the surface area and decreasing particle size, with progressive amorphization and formation of agglomerates as detected by X-ray diffraction and scanning electron microscopy. Marked changes were observed in the thermogravimetric analysis and differential thermal analysis curves as influenced by grinding, with weight losses at lower temperatures and the appearance of an exothermic differential thermal analysis effect at 985 °C, which increases in intensity and sharpness as grinding time proceeds. After grinding using the pure silicates, kaolinite, pyrophyllite and illite, it was found that the increase in intensity and sharpness of this exothermic effect was only associated with the presence of pyrophyllite in the natural mixture irrespective of the presence of kaolinite and/or illite, at least up to 325 min grinding. This effect is produced in the ground mixture by mullite formation mainly from pyrophyllite by combined mechanical (by grinding) and thermal treatments.

1. Introduction

Grinding is a common basic operation in the laboratory and in industry. Fine particles are obtained principally by grinding (wet or dry), the nature of which plays an important role in determining the physicochemical properties of the powdered material and ulterior processing steps [1–3]. In particular, grinding of clay minerals produces various effects on their structure and properties, often accompanied by polymorphic transformations and chemical reactions [4–11]. The significant grinding processes involved in the preparation of ceramic raw materials have been studied, especially those for kaolinite [4–7], montmorillonite or bentonite [8–10], and illite [11]. However, little is known about the effects of grinding on natural mixtures of layer silicates.

In previous papers [12–14], we have studied the effects of dry grinding on pyrophyllite and the formation of low-temperature mullite precursors from this ground activated material. In the present work, the effects caused by dry grinding in a ball mill on a pyrophyllite–kaolinite–potassium mica (illite) natural mixture have been studied. The evolution of the starting material was followed by X-ray diffraction (XRD), differential thermal analysis (DTA), thermogravimetric analysis (TGA), and surface area, showing how mullite is formed from the aluminium silicates that constitute the mixture. For this purpose, a comparative study was also performed using pure isolated aluminium silicates (mineral pyrophyllite, standard kaolinite and purified illite) with the aim of a better understanding of what is happening after grinding the pyrophyllite–kaolinite–illite natural mixtures. The results are of great interest in a broader systematic work on processing of silicates, especially their applications as raw materials in the synthesis of advanced ceramics.

2. Experimental procedure

2.1. Material

The pyrophyllite–kaolinite–illite natural mixture (ZS clay) was mined by one of the authors (J.L.P.R.) from a clay deposit near Badajoz (Spain), previously described in the literature [15, 16]. The geology of this deposit has also been previously reported [17]. This deposit is in pelitic rocks in the southwestern part of the Iberian massif (Iberian plateau), where similar deposits are commonly extended. Samples are mainly composed of pyrophyllite (range 5–50 wt %), kaolinite (5–30 wt %), and potassium mica or illite (30–60 wt %). Minor components, such as potassium feldspars,

---

* Author to whom all correspondence should be addressed.

0022-2461

calcium carbonate, rutile, iron oxides and possibly quartz, are sometimes found. A representative sample of this deposit was used in this study. The fraction under 63 μm of this sample was selected after dispersion, wet sieving and the obtention of free-agglomerated powders. The mineralogical composition of dried powder (110 °C) determined after X-ray diffraction analysis showed 40 wt % pyrophyllite, 30 wt % kaolinite and 30 wt % illite. Chemical analysis by atomic absorption (Perkin–Elmer model 703) of the raw material is shown in Table I, which is in accordance with the mineralogical composition. The K_2O content is due to the presence of illite (potassium mica). The TiO_2 content is associated with rutile, and the Fe_2O_3 content with iron oxides, which are in low proportions to be detected initially by X-ray diffraction (XRD).

Pyrophyllite from Hillsboro (NC, USA; Ward's N.S. Establishment Inc., Rochester, NY, USA) was also used in this study. The natural sample was crushed, lightly ground, sieved to pass 50 μm and used in that form. The mineralogical composition determined by XRD analysis showed pyrophyllite (~ 90 wt %), and minor quantities of kaolinite (~ 5 wt %) and mica (~ 5 wt %). The chemical analysis of this sample is also shown in Table I.

Pure well-ordered crystallized kaolinite (KGa-1, standard kaolinite from Georgia, USA; Source Clay Repository, Clay Minerals Society, MO, USA) was used. The chemical analysis of this sample is shown in Table I. The TiO_2 content is associated with anatase, as an impurity identified previously by XRD.

Illite was extracted from a raw material described previously [18] (sample J-24 containing originally illite, kaolinite, quartz and iron oxides) by wet sedimentation and separation of the 2–0.2 μm fraction after adequate dispersion in deionized water; this fraction, containing mainly illite, was purified of amorphous components and iron oxides according to standard methods [19]. After these treatments, the XRD pattern showed only illite (> 95 wt %), with kaolinite, quartz and interstratified illite–montmorillonite as minor components. Chemical analysis of this purified sample is also shown in Table I.

TABLE I Chemical analysis data of this samples (for further details, see Section 2)

	Content (wt %)			
	ZS	Pyrophyllite	Ordered kaolinite (KGa-1)	Illite
SiO_2	52.19	66.42	44.2	55.43
Al_2O_3	33.89	27.31	39.7	27.42
Fe_2O_3	1.77	0.20	0.13	0.23
TiO_2	1.38	0.10	1.39	1.30
CaO	0.45	0.09	ND[b]	0.52
MgO	0.22	0.01	0.03	0.73
K_2O	2.04	0.24	0.05	6.05
Na_2O	0.67	0.10	0.01	0.79
L.O.I.[a]	7.99	5.41	13.78	7.54
Total	100.6	99.88	99.29	100.01

[a] Loss on ignition = weight loss at 1000 °C during 1 h.
[b] ND, not detected.

2.2. Methods

Dry grinding of the samples was conducted in a ball mill (Model S-1 Retsch, Haan, Germany), at a rate of 250 r.p.m. from 5–325 min maximum, as described previously [12, 13].

Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) were obtained simultaneously in static air with a thermal analyser (Model PTC-10A Thermoflex, Rigaku Co, Tokyo, Japan), at a heating rate of 12 °C min^{-1}. Samples were gently packed each time in a platinum holder. Calcined alumina was used as a reference material. The areas under the experimental curves were determined by tracing them onto drawing paper of uniform weight and cutting out the inscribed area. The weights of the cut-outs were subsequently determined on an analytical balance in triplicate.

X-ray diffraction powder patterns were obtained using a diffractometer (Kristalloflex D-500 Siemens, Karlsruhe, Germany) with nickel-filtered CuK_α radiation, at a goniometer speed of $1° 2\theta\ min^{-1}$.

Specific surface areas (BET) were obtained with an automatic system (Model 2200 A Micromeritics, Norcross, GA, USA) using nitrogen gas as adsorbate at liquid nitrogen temperature.

Finally, original and ground samples dispersed in acetone were examined under a scanning electron microscope (ISI model SS-40).

3. Results and discussion

3.1. X-ray diffraction

XRD patterns of original and ground powdered samples are shown in Fig. 1. Grinding produces structural disorder in the silicates that constitute this natural

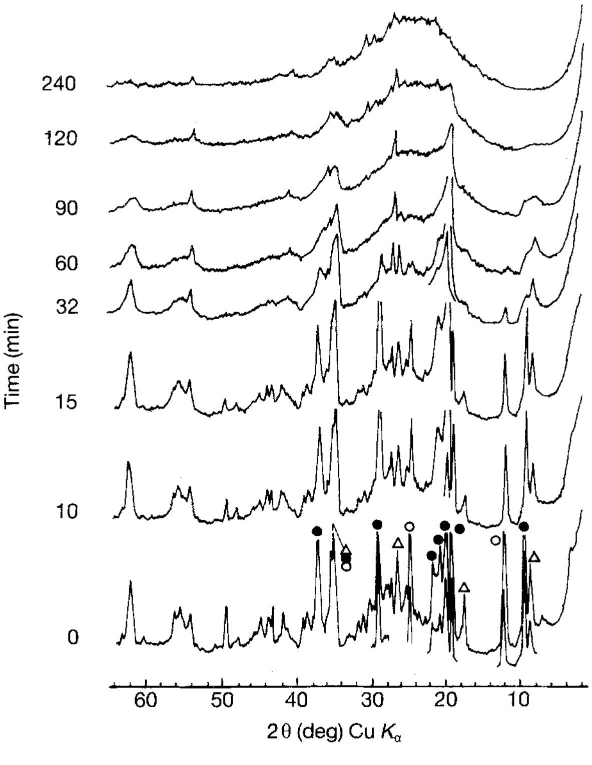

Figure 1 X-ray diffraction diagrams of original and ground pyrophyllite–kaolinite–illite natural mixtures. (○) Kaolinite, (●) pyrophyllite, (△) illite.

mixture, producing broadening of diffraction peaks and decreasing of X-ray intensities, originated mainly by particle size reduction, with total degradation of the crystal structure of kaolinite after 60 min of grinding; pyrophyllite and illite X-ray reflections disappear after 90 min, finally yielding a more amorphous material.

After detailed analysis of this set of XRD diagrams, we conclude that the general (*h k l*) reflections change to a lesser extent than the basal (0 0 *l*) reflections, because the alteration by grinding is greater along the *c*-axis of the silicate crystal structures, as occurs after grinding other silicates [4–11]. As a consequence, layer silicate minerals show a pronounced propensity towards cleavage perpendicular to one crystalline axis. This is more clearly illustrated in Fig. 2, where XRD diagrams of oriented original and ground samples (thin oriented films) are shown. After 32 min, (0 0 1) reflections of kaolinite, pyrophyllite and illite have almost disappeared, and the (1 1 0) reflection of pyrophyllite remained, but this is destroyed after 90 min. These facts are in accordance with those observed on grinding pure pyrophyllite under the same conditions [12]. At higher grinding times, only weak reflections corresponding to rutile in an amorphous matrix are detected.

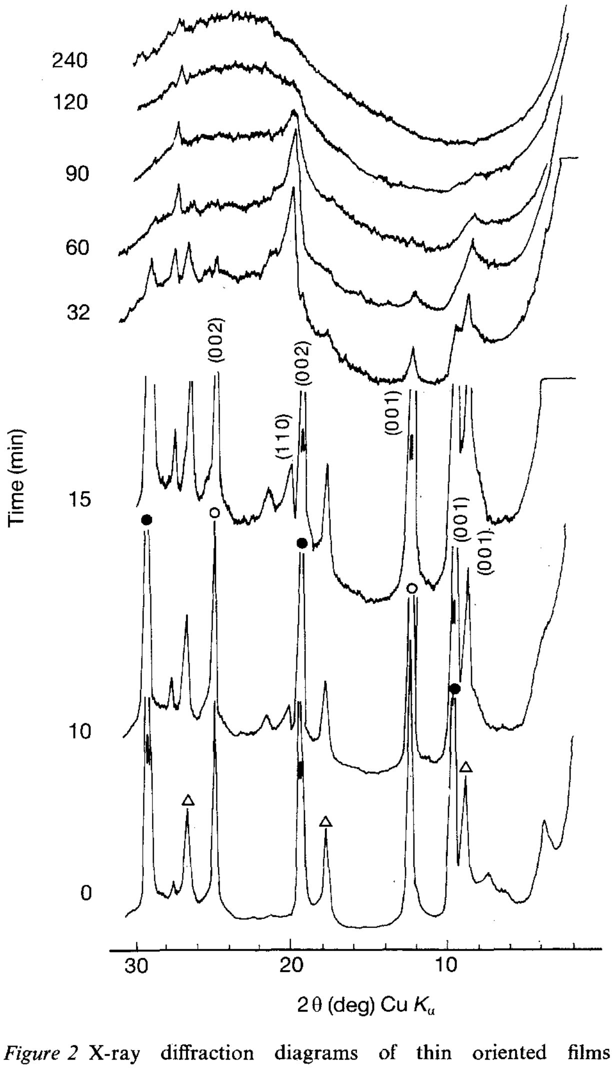

Figure 2 X-ray diffraction diagrams of thin oriented films corresponding to original and ground samples. (○) Kaolinite, (●) pyrophyllite, (△) illite.

3.2. Thermal analysis (DTA–TGA) and surface area

From TGA diagrams, weight losses as a function of temperature were calculated. These results are plotted in Fig. 3, and were assumed to be due entirely to water loss by dehydration (under 200 °C) and dehydroxylation. Important weight loss in unground sample begins at 400 °C at a low rate. The rate increases gradually with temperature, and dehydroxylation reactions of kaolinite to metakaolinite, pyrophyllite to dehydroxylated phase and illite to dehydroxylated phase, are finished at 1000 °C.

Grinding treatment produces an increased weight loss on heating under 200 °C, i.e. an increase in "free moisture" of the samples. This result suggests that some extremely weakly bound hydroxyl groups of an amorphous phase, as detected by XRD (Fig. 1), are being lost within this temperature range.

Surface area increases with grinding time (Table II). This increase may cause some rehydroxylation by adsorption of atmospheric water molecules. Both adsorbed water molecules and extremely weakly bound OH groups escape at lower temperatures than in unground samples. The formation of a broad endothermic DTA peak (Fig. 4) at low temperatures (< 200 °C) in ground samples is in accordance with the above interpretation. These results are similar to those reported for ground pure clay minerals [4–8].

Particle-size reduction by grinding (see Table II) also influences the thermal behaviour because the decrease in particle size causes the elimination of structural OH groups at lower temperatures in ground than in unground material, where a more

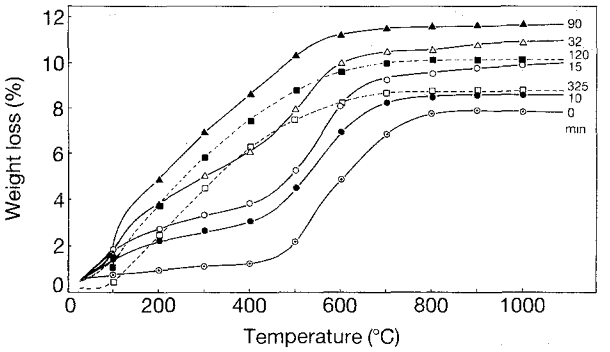

Figure 3 Weight loss in relation to grinding time.

TABLE II Powder characteristics of dry-ground pyrophyllite–kaolinite–illite natural mixture (ZS clay)

Grinding time (min)	BET surface area (m^2g^{-1})	Average particle size[a] (μm)
0	12.44	0.17
15	24.73	0.08
32	39.35	0.05
60	34.14	0.06
240	8.41	0.26

[a] Calculated from surface area data using the equation $S = 6/\rho D$, where S is the surface area (m^2g^{-1}), ρ the density of the sample (2.7 $g\,cm^{-3}$), and D the particle size (μm).

defective or stressed structure is also being produced by mechanical treatment. Thus, the endothermic DTA effect centred at ~ 700 °C associated with dehydroxylation of pyrophyllite present in the unground mixture is shifted to lower temperatures, reaching the endothermal effect of kaolinite dehydroxylation centred at 530 °C in this sample. After 32 min grinding, a single broader endothermic DTA effect centred at ~ 530 °C is detected. This effect decreases in intensity as grinding time proceeds and disappears after 90 min grinding. It is also illustrated in Fig. 5, where a plot of endothermic DTA peak areas of original and ground samples is shown. The first straight line in the logarithmic plot (Fig. 5b) is associated mainly with kaolinite structural OH loss, and the change in slope with the addition by shifting of the endothermic produced by pyrophyllite, and possibly illite, dehydroxylation reaction. These features are consistent with TGA data, as can be seen in Fig. 3. Single straight lines in the logarithmic plot similar to that shown in Fig. 5b have been found after grinding pure kaolinite and pyrophyllite [20].

At longer grinding times (240 min and higher), as a consequence of the enhanced surface energy of the comminuted and activated particles provided by the grinding treatment, the particles become more agglomerated, and the specific surface area begins to decrease (Table II), as occurs on grinding other solids [1–3]. The agglomeration processes probably impede the water elimination caused by thermal treatment and water diffusion is hindered. These facts are revealed by the weight-loss curves showing a decreasing weight loss as grinding time increases (Fig. 3). The water loss in the remaining zones of structural OH groups also decreases and occurs at lower temperatures. Finally,

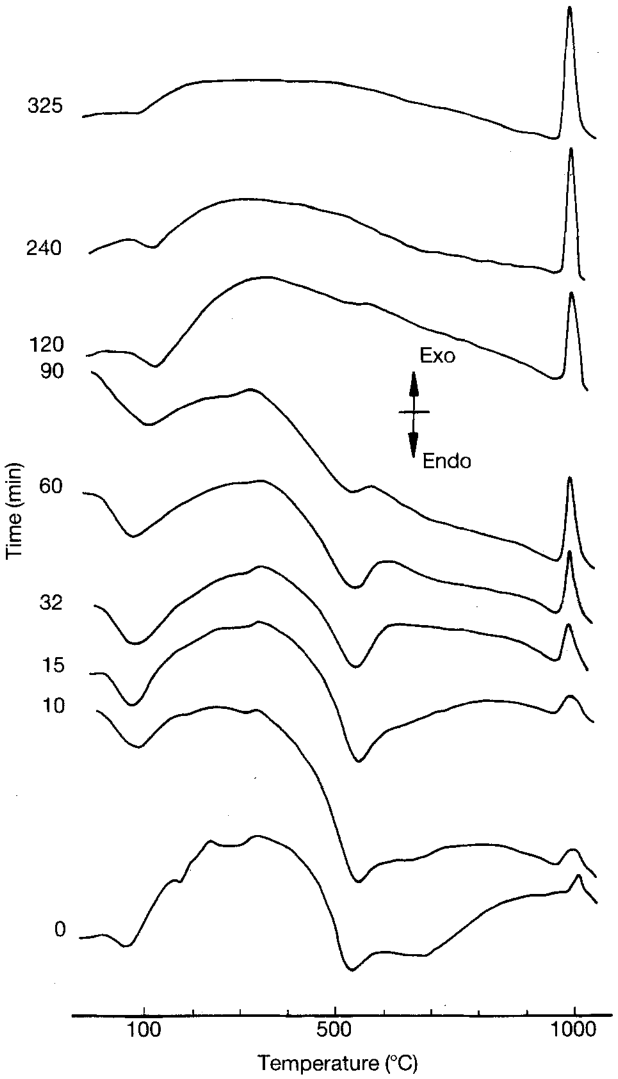

Figure 4 DTA diagrams in relation to grinding time.

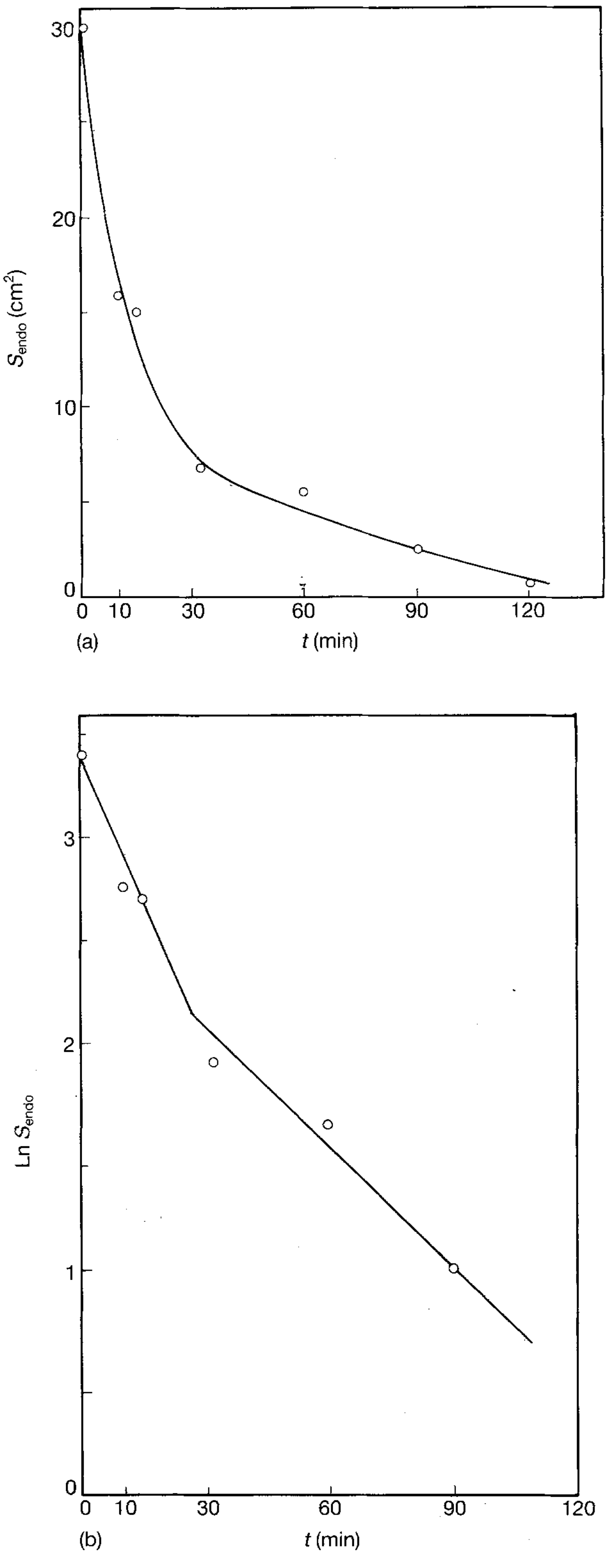

Figure 5 (a) Evolution of the endothermic DTA peak areas as a function of grinding time, and (b) logarithmic plot from the above data.

after 120 min grinding, the slopes of the curves change gradually to positive values as a result of the agglomeration processes, and reduced diffusion of water molecules by heating. All these effects are due to the mechanochemical activation of the ground powder, and coincide with those observed in our earlier studies on grinding of pure pyrophyllite [12–15].

3.3. SEM study

The gradual size reduction and associated morphological changes which occur during grinding of this kaolinite–pyrophyllite–illite natural mixture were also revealed by SEM. Some selected micrographs are shown in Fig. 6. At the beginning of the grinding treatment (10 min), the original stacking layers (Fig. 6a) are delaminated, and the lamellar phyllosilicate mineral particles are broken by mechanical impact, producing a decrease in particle size (Fig. 6b), and an increase in surface area (Table II). After 32 min, agglomeration by cold welding of comminuted and activated particles begins to be detected by SEM (Fig. 6c). This occurs when structure disruption is greater, according to our XRD results (see Figs 1 and 2).

Agglomeration processes increase with grinding time, as shown in Fig. 6d after 60 min, although the porous agglomerates are constituted by smaller particles. Thus, the particles gradually lose their original layered shape due to the grinding, and become round-edged particles with a rugged surface. At longer grinding times, the agglomerates are constituted by a greater number of welded particles, and the surface area strongly decreases (see Table II).

These SEM features were also found on grinding pure pyrophyllite [12] and kaolinite [5–7].

3.4. Analysis of the exothermic DTA peak after grinding

The unground sample (Fig. 4) shows a small exothermic effect at ~ 1000 °C associated with the kaolinite present in the mixture, because this is not found in pure pyrophyllite [21, 22]. The cause of this exothermic DTA peak is controversial in the literature [23–26]. In short, it has been attributed to the formation of either mullite nuclei and spinel (γ-Al_2O_3) or both, because at DTA heating rates, it is possible for both mullite and spinel to form concurrently [26]. On the other hand, the presence of impurities incorporated with kaolinite influences the size and temperature of the exothermic DTA effects at high temperatures [27, 28].

Recent work has indicated that the formation of this exothermic peak is most likely due to the release of energy associated with the aluminium ions transforming to a more stable six-fold coordination, facilitating the formation of mullite, as proposed by Sanz *et al.* [29].

As shown in Fig. 4, at the beginning of grinding (10, 15 min), this exothermic DTA effect becomes broader, but increases markedly in sharpness and height as grinding proceeds, especially from 32 min to longer grinding times, when structural breakdown is very important (see Figs 1 and 2).

After 240 and 325 min, the intensities (as peak areas) of the exothermic effects remain practically constant. Fig. 7 shows the linear relationship found between

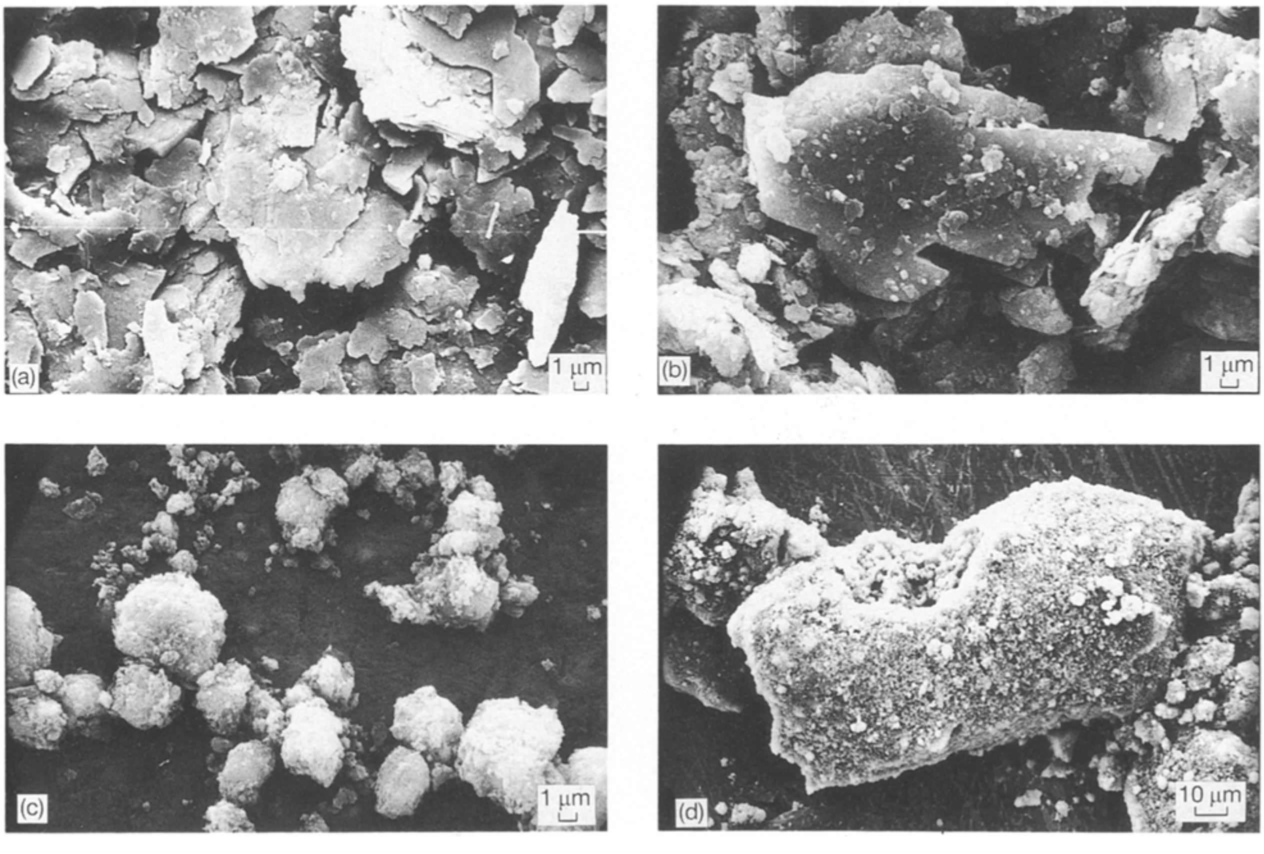

Figure 6 Scanning electron micrographs of (a) original sample, and after grinding for (b) 10 min, (c) 32 min and (d) 60 min.

peak areas, S_{exo}, and grinding time, ln *t*, deduced quantitatively from the above DTA curves. First, it is clear from this plot that increasing the grinding time leads to an increase in the intensity of this thermal effect. However, it is not clear which of the aluminium silicates present in the natural mixture (kaolinite, pyrophyllite and illite) contributes to or is mainly responsible for the increase observed in this thermal effect as grinding proceeds.

For that purpose, experiments were performed under the same grinding conditions using pure silicates (kaolinite, pyrophyllite and illite) described in Section 2. It was assumed that the crystallinity of the aluminium silicates used in these experiments was the same as that present in the mixture. Johnson *et al.* [28] reported, for kaolinite, that the size and temperature of the high-temperature exothermic peaks are related to the presence of impurity phases (both type and amount), and thus only indirectly to the state of order (crystallinity) of the silicate.

Figs 8 and 9 show the plots obtained for pure pyrophyllite (Fig. 8) and pure kaolinite (Fig. 9) in a similar way to that shown in Fig. 7; DTA experiments with pure illite were also performed, and exothermic DTA effects were not observed after 325 min grinding (Fig. 10). Clearly, the exothermic DTA peak areas of pure pyrophyllite increase with increasing grinding time (Fig. 8), irrespective of the low proportion of kaolinite present in this sample as an impurity. This is not the case with pure kaolinite (Fig. 9), and illite (Fig. 10).

For kaolinite, contradictory results on the evolution of the exothermic DTA effect after grinding have been reported [5–7, 30]. The different results might have arisen due to differences in starting materials and compositions. In this work, we selected a standard well-ordered and perfectly characterized sample of kaolinite for grinding experiments. Under our experimental conditions using this pure sample, no increases in exothermic DTA peak areas were observed, at least up to 325 min grinding.

It can thus be deduced that the main contribution to the increased exothermic DTA peak (Figs 4 and 7) in the kaolinite–pyrophyllite illite natural mixture after grinding is due to pyrophyllite, irrespective of the other aluminium silicates present in the sample. In other words, in the studied mixture, pyrophyllite is the

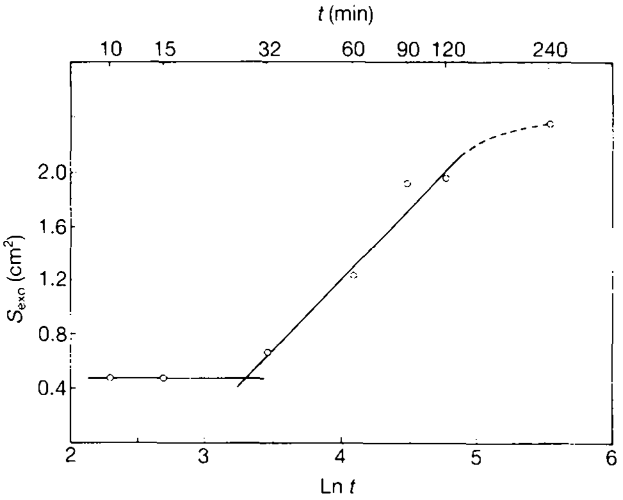

Figure 7 Plot of the variation of exothermic DTA peak areas as a function of grinding time for the pyrophyllite–kaolinite–illite natural mixture, as deduced from Fig. 4.

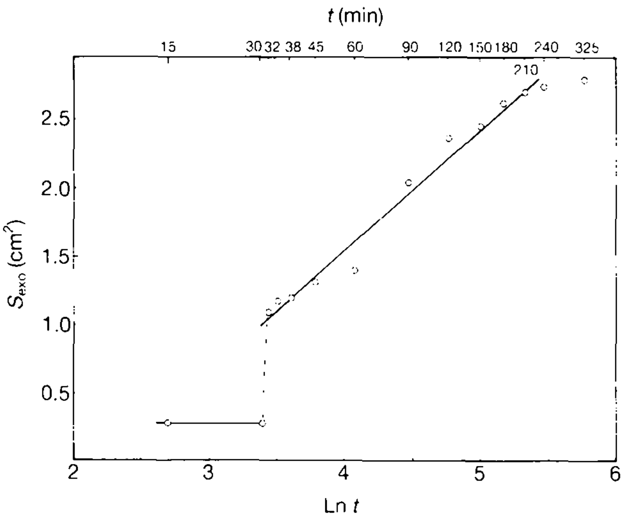

Figure 8 As Fig. 7 for pure pyrophyllite (see text).

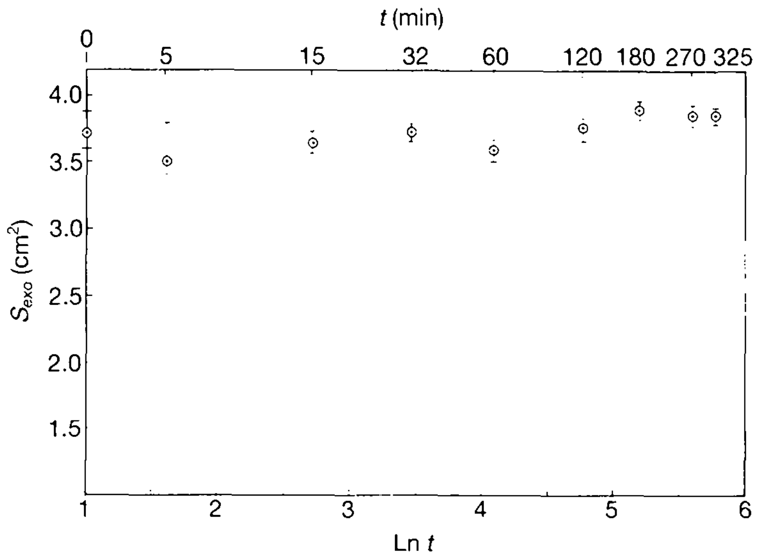

Figure 9 As Fig. 7 for pure kaolinite (see text).

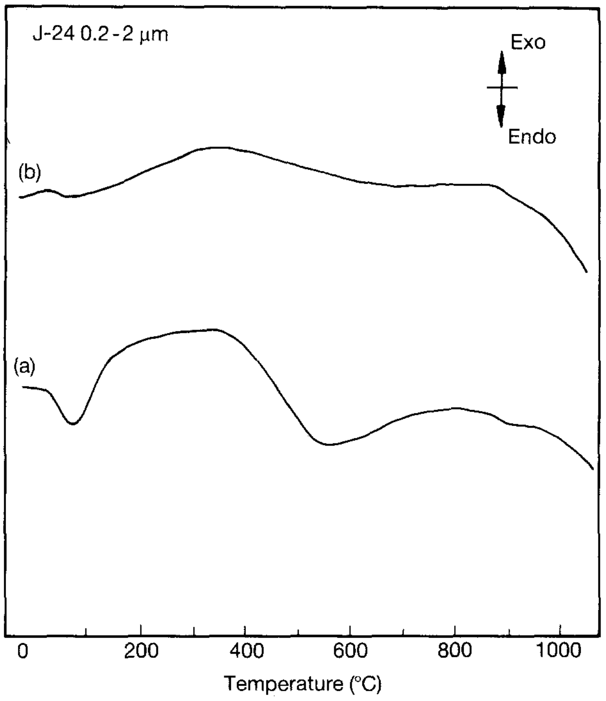

Figure 10 DTA diagrams of (a) pure illite, and (b) after grinding for 325 min.

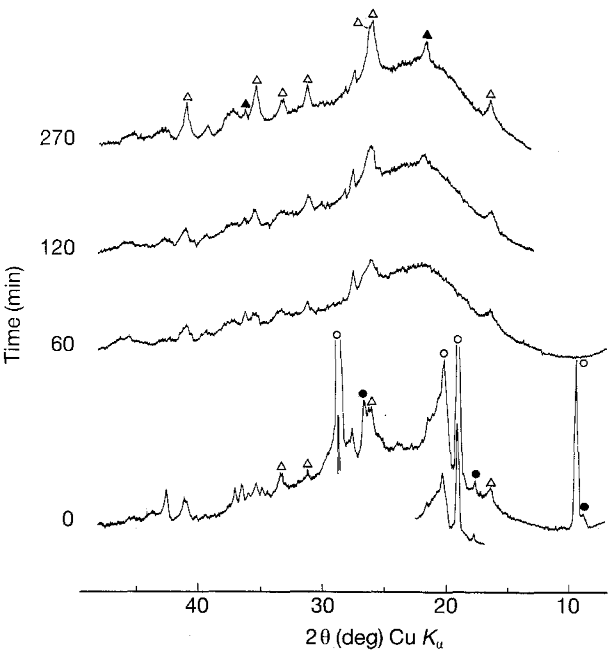

Figure 11 X-ray diffraction diagrams of original and ground pyrophyllite–kaolinite–illite natural mixture after heating at 1050 °C. (●) Dehydroxylated illite, (○) dehydroxylated pyrophyllite, (△) mullite, (▲) cristobalite.

only silicate responsible for the increase in intensity of the exothermic DTA peak after grinding.

It should be noted that the crystallization sequence in kaolinite is dependent on the crystallinity and the impurities that are present [27, 28]. However, no such effect is observed in our pyrophyllite–kaolinite–illite natural mixture, although further experimental work on the role of different impurities in the high-temperature crystallization sequence would be interesting to carry out.

3.5. Nature of the exothermic DTA peak produced by grinding

For a more detailed analysis, X-ray diffraction was used to identify the phases originated in the original mixture of silicates after combined mechanical (by grinding) and thermal treatments. It has been suggested that high-temperature exothermic DTA peaks can be considered as an indication of presence of Si–O–Al linkages in non-crystalline aluminosilicate materials [31], such as in the case of ground samples.

Fig. 11 shows the XRD diagrams of pyrophyllite–kaolinite–illite ground samples after heating at 1050 °C. Mullite is always detected after heating. The intensities of the X-ray peaks of this phase increase with increasing grinding time, with subsequent destruction of dehydroxylated pyrophyllite X-ray patterns detected in the unground mixture.

Cristobalite as a disordered phase [32] is also detected as grinding proceeds, possibly from amorphous silica crystallization, as well as from silica segregated when mullite formation takes place.

Although low-crystalline mullite is originally detected by XRD in unground samples from decomposed metakaolinite, it is clear that the mechanical treatment by grinding produced a structural breakdown of the silicates that constitute the natural mixture, with rupture between silica and alumina layers. This will produce Si–O–Al linkages (mullite) by reaction after adequate thermal treatment, in accordance with that proposed in the literature [31]. Note that kaolinite is a 1:1 aluminium silicate with OH groups, whereas illite and pyrophyllite are 2:1 containing originally aluminium octahedra bonded with OH groups perfectly sandwiched between silica tetrahedra. Structural breakdown is facilitated a priori in kaolinite after thermal [22–29] and/or mechanical treatment by grinding, but does not in the others. On the other hand, mullite formation is facilitated in pyrophyllite after grinding, but not after thermal treatment only [21, 22].

The above discussion leads us to conclude that the presence of pyrophyllite in our mixture contributes strongly to the detection and increase in intensity of mullite in the XRD patterns, in accordance with the DTA results (Fig. 4) and those obtained after the grinding of pure silicates (Figs 8–10).

In fact, it was demonstrated in a previous paper [13] that the formation of high-temperature phases from ground pyrophyllite at lower temperatures than in unground samples is associated with the exothermic DTA effect. Recent evidence obtained by MAS-NMR [20] supports the formation of an exothermic DTA peak after grinding pyrophyllite, associated with a change in coordination of the aluminium ions with a release of energy, as occurs analogously in kaolinite after heating [29].

4. Conclusion

The effects of dry grinding (mechanochemical activation) on a natural mixture of aluminium silicates composed by kaolinite, pyrophyllite and illite was studied. Grinding produces structural alteration of these silicates, and a decrease in particle size of the original material, producing weight losses (water dehydration and dehydroxylation) at lower temperatures than in unground samples. DTA endothermic effects also are shifted to lower temperatures. Further grinding produces a breakdown of the crystal structure of the silicates, and also an agglomeration of the amorphous and activated material, accompanied by a decrease in surface area and a strong increase (in intensity and sharpness) of the exothermic DTA effect at 985 °C.

From experiments with pure pyrophyllite, kaolinite and illite under the same grinding conditions, it has been clearly demonstrated that the increase in intensity of the characteristic exothermic effect at 985 °C in the natural mixture of silicates studied in this work is only associated with the presence of pyrophyllite, being uninfluenced by the presence of kaolinite and illite, at least up to 325 min grinding. This effect is produced by mullite formation mainly from pyrophyllite by combined mechanical (by grinding) and thermal treatments, starting from 32 min. Kaolinite also contributes to mullite formation, but is not increased after grinding.

Disordered cristobalite is also detected after longer grinding times than 120 min, possibly from amorphous silica crystallization upon heating.

The results presented above are of great value to a better understanding of the mechanism of silicate disruption when intensive grinding of natural mixtures of silicates (clays) is being performed in the laboratory and in industry, to use the ground products as ceramic raw materials.

Acknowledgements

The authors thank CICYT for financial support through research project number GE090-0060. The technical assistance of Mr E. Gomez during SEM work, and helpful discussions with Dr Jesús Sanz, head of MAS-NMR Laboratory, Institute of Materials Science, Madrid, are acknowledged. The authors thank Mr J. C. Rivero for typing the manuscript and Mrs A. Garcia for drawing the figures.

References

1. I. J. LIN and S. NADIV, *Mater. Sci. Eng.* **39** (1979) 193.
2. M. SOMASUNDARAN, in "Ceramic Processing before Firing", edited by G. Onoda and L. L. Hench (Wiley, New York, 1978) p. 105.
3. V. V. BOLDYREV, in "Reactivity of Solids", edited by K. Dyrek, J. Haber and J. Nowotny (Elsevier, Amsterdam, 1982) p. 519.
4. J. G. MILLER and T. D. OULTON, *Clays Clay Miner.* **18** (1970) 313.
5. E.F. AGLIETTI, J. M. PORTO and E. PEREIRA, *Int. J. Miner. Proc.* **16** (1986) 125.
6. *Idem, ibid.* **16** (1986) 135.
7. F. GONZALEZ, M.T. RUIZ and M. GONZALEZ, *Clay Miner.* **26** (1991) 549.
8. B. CICEL and G. KRANZ, *ibid.* **16** (1981) 151.
9. U. MINGELGRIN, L. KLIGER, M. GAL and S. SALTZMAN, *Clays Clay Miner.* **26** (1978) 299.
10. C. VOLZONE, E. F. AGLIETTI, A. N. SCIAN and J. M. PORTO, *Appl. Clay Sci.* **2** (1987) 97.
11. Z. A. JUHASZ and I. SOMOGYI, *Keram. Z.* **36** (1984) 659.
12. J. L. PEREZ-RODRIGUEZ, L. MADRID and P. J. SANCHEZ-SOTO, *Clay Miner.* **23** (1988) 399.
13. P. J. SANCHEZ-SOTO and J. L. PEREZ-RODRIGUEZ, *J. Am. Ceram. Soc.* **72** (1989) 154.
14. J. L. PEREZ-RODRIGUEZ and P. J. SANCHEZ-SOTO, *J. Thermal Anal.* **37** (1991) 1401.
15. J. L. PEREZ-RODRIGUEZ, C. MAQUEDA and A. JUSTO, *Clays Clay Miner.* **33** (1985) 563.
16. *Idem, Soil Sci.* **150** (1990) 671.
17. J. M. MESA, PhD Thesis, University of Seville, Spain (1986).
18. A. BERNAL, G. GARCIA, F. GONZALEZ, A. JUSTO and J. L. PEREZ-RODRIGUEZ, *Bol. Soc. Esp. Ceram. Vidr.* **17** (1978) 17.
19. M. L. JACKSON, "Soil Chemical Analysis. Advanced Course," 2nd Edn (published by the author, Madison, Wisconsin, USA, 1975) p. 537.
20. P. J. SANCHEZ-SOTO, PhD Thesis, University of Seville, Spain (1990).
21. R. C. MACKENZIE, in "Differential Thermal Analysis", Vol. 1, Chap. 18, ed. R. C. Mackenzie (Academic Press, London, 1970) p. 497.
22. P. J. SANCHEZ-SOTO and J. L. PEREZ-RODRIGUEZ, *Thermochim. Acta* **138** (1989) 267.
23. G. W. BRINDLEY and M. NAKAHIRA, *J. Am. Ceram. Soc.* **42** (1959) 311.
24. A. K. CHAKRABORTY and D. K. GHOSH, *ibid.* **61** (1978) 170.
25. J. S. MOYA, C. J. SERNA and J. E. IGLESIAS, *J. Mater. Sci.* **20** (1985) 32.
26. J. A. PASK and A. P. TOMSIA, *J. Am. Ceram. Soc.* **74** (1991) 2367.
27. M. BULLENS and B. DELMON, *Clays Clay Miner.* **25** (1977) 271.
28. S. M. JOHNSON, J. A. PASK and J. S. MOYA, *J. Am. Ceram. Soc.* **65** (1982) 31.
29. J. SANZ, A. MADANI, J. M. SERRATOSA, J. S. MOYA and S. AZA, *ibid.* **71** (1988) C418.
30. T. A. KORNEVA and T. S. YUSUPOV, in "Proceedings of 1st European Symposium on Thermal Analysis" (Heyden, 1976) p. 336.
31. T. HENMI and N. YOSHINAGA, *Clay Miner.* **16** (1981) 139.
32. J. JAMES and M. S. RAO, *Am. Ceram. Soc. Bull.* **65** (1986) 1177.

Received 12 October 1992
and accepted 24 August 1993