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The influence of heating rate on the thermal behaviour and mullite formation from a kaolin raw material

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Abstract

The thermal behaviour of a kaolin raw material (Bio) containing mainly well-crystallised kaolinite and muscovite minerals was studied in relation to heating rate, from 3 to 20°C min^{-1}. For comparison, reference raw materials, which were very rich in kaolinite or muscovite, were also analysed. The transformation heats during heating were quantified from DTA measurements and phase changes were followed by X-ray diffraction analyses. Results indicated that a fast heating rate increases the transformation heats associated with the endothermic dehydroxylation transformation of kaolinite and suggests the formation of a more disordered metakaolin. A similar trend was observed in the exothermic phenomenon. This suggests that Bio kaolin has a complex nature that changes the mechanisms involved in the structural transition. In Bio kaolin, mullite crystallises only from the kaolin-derived phase, which underlines the specific role of clay mineral interfaces in a natural mineral mix. In this case, the crystallisation of mullite occurs via a direct route without any spinel intermediate phase. The amount of mullite between 1050 and 1150°C increases with the heating rate and is comparatively higher than from a pure kaolinite phase. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

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1. Introduction

The present evolution in many ceramic processes aims to shorten the firing stage. Interactions between the raw materials present in the green body and between the constitutive minerals can be affected by any change in the thermal treatment. Furthermore, mutual interactions between minerals can be largely reduced when the firing rate increases.

Kaolin is commonly used to increase the refractoriness of traditional ceramic bodies. This raw material, from natural deposits formed during various, long, geological processes, is a complex mix of different mineralogical varieties. Commercial kaolins are selected by grinding, sieving, hydroclassification and high intensity magnetic separation. Unless treatments are applied, it is almost impossible to obtain a chemically and mineralogicaly pure raw material. As a result, commercial kaolins contain, besides kaolinite, small quantities of quartz, feldspar, smectite or mica. These minerals influence the thermal behaviour of the ceramic body to a certain extent.

This study is devoted to the thermal transformation of a commercial kaolin during fast firing (3 to 20°C min^{-1}). Particular attention was paid to the influence of heating rate on phase transformation and mullite formation.

2. Raw materials characterisation

The chemical composition of the studied kaolin, known as Bio (Echassière, France), is detailed in Table 1. The identified minerals are kaolinite, mica and quartz. To determine the crystallinity of the kaolinite, Bio was compared with two reference minerals, Kga1 (well crystallised) and Kga2 (poorly crystallised) [1, 2]. Similarly, the mica mineral in Bio was compared with a muscovite known as Mu (ordered phase) and an illite [3] (low ordered phase). The mineralogical composition of each reference material is given in Table 2.

Analysis by X-ray diffraction peak profiles is commonly used to determine the crystallinity of a material. In the case of kaolinite and mica group minerals, it was

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shown that the comparison of the broadening of the [001] and [002] peaks, respectively, is a satisfactory crystallinity criterion [4, 5]. For kaolinite, it has been shown that this analysis is well correlated with the usual Hinckley index, which is the ratio of peak heights [6]: $(\mathbf{I}^{[1\bar{1}0]}+\mathbf{I}^{[11\bar{1}]}/\mathbf{I}^{[02,11]})$ The [001] and [002] X-ray diffraction peaks of the different kaolinites and micas are reported in Fig. 1a and b and respectively. These X-ray diffraction analyses were performed on powder using a Debye Scherrer apparatus equipped with an Inel CPS 120 detector. The width at half height of the [001] peaks of the kaolinite in Bio and Kga1 and the [002] peaks of mica phases present in Bio and Mu respectively, are very similar. The Hinckley indexes calculated for Bio and Kga1 are 0.98 and 1.03 respectively. This confirms the high crystallinity degree of the kaolinite phase present in Bio. It is possible, therefore, to consider that kaolinite in Bio is rather well crystallised and that the mica phase is similar to muscovite. From the chemical composition presented in Table 1, the mineralogical composition of Bio can be estimated (Table 2) as ~79 wt.% of well-crystallised kaolinite, ~17 wt.% of muscovite and ~4% of quartz.

Table 1
Chemical composition of Bio, Kga1 and Kga2 kaolins (wt.%)

	Bio	Kg1	Kg2
SiO_2	47.10	44.20	43.9
Al_2O_3	36.70	39.70	38.5
Fe_2O_3	1.16	0.21	1.13
TiO_2	0.07	1.39	2.08
CaO	0.11	–	–
MgO	0.21	0.03	0.03
Na_2O	0.11	0.01	–
K_2O	2.17	0.05	0.06
Li_2O	0.11	–	–
P_2O_5	–	0.03	0.04
Loss on ignition	12.26	14.38	14.36

Table 2
Principal mineral phases for Bio kaolin and reference materials (wt.%)

	Kg1	Kg2	Mu	Illite	BIO
Kaolinite	96±1	97±1	7	0.7	79±2
Muscovite	–	–	79.4±1	89±1	17±2
Quartz	<	<	10.4	< 1	4±1
Rutile	1.4	2.3	0.8	1.6	–
Gibbsite	2.5	–	–	–	–
Orthose	–	–	–	1	–

3. Experimental

The influence of the heating rate on water loss was determined by thermogravimetric analysis (TGA) using a Linseis apparatus (L81). The study was performed on 80 mg samples of Bio, previously treated for 1 h at 200°C. The weight losses were recorded during heating at 5, 10 and 15°C min^{-1} up to 1000°C in flowing air.

Differential thermal analysis (DTA) was performed in static air during heating from 25 to 1050°C at 3, 8, 10, 12, 15 and 20°C min^{-1}, using a Linseis apparatus (L70). The powder was previously dried for 1 h at 200°C. To evaluate the heat exchanged during the different transformations, a preliminary set of experiments was carried out on reference materials, i.e. K_2SO_4 and $SrCO_3$, at each heating rate. Q values were calculated using the peak surface ratios and published data [7]. Similar experiments were also performed on Kga1, Kga2 and Mu powders.

X-ray diffraction analyses were performed on ground ceramics in a B4C mortar. The ceramics were prepared from an homogeneous suspension obtained by mixing 46.5 wt.% of Bio, 53.35% of water and 0.15% of

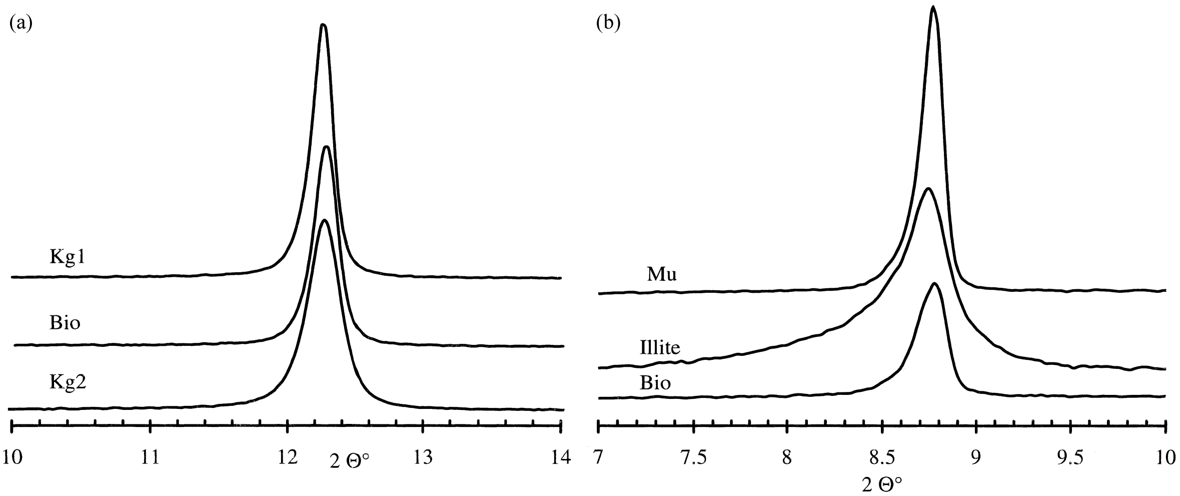

Fig. 1. (a) [001] kaolinite and (b) [002] mica X-ray diffraction peaks of Bio and reference materials.

dispersant. This slurry, with a relative density of 1.7, was cast into a plaster mould and dried at 120°C for 2 h. The parallelepipedal samples (50 × 30 × 8mm^3) were heated in air at 3 and 20°C min^{-1}, up to a temperature in the 1000–1250°C range. After holding for 3 min, the ceramics were quenched in air down to room temperature. To determine the influence of heat treatment on the amount of formed mullite, NiO was used as an internal reference [8, 9]. 25 mg of NiO was added to 0.5 g of ground powder before being subjected to X-rays. An abacus was made using the ratio between the peak surfaces of the [220] mullite reflection and the [003] NiO reflection.

The mullite formation was observed by transmission electron microscopy (TEM), using JEOL equipment (200 kV). The Bio derived sample was observed after a previous heating and quenching at 1050°C, using a 3 and 20°C min^{-1} temperature rates and a subsequent Ar ion beam etching.

4. Results

The weight losses observed during heating of dried Bio powder at 5, 10 and 15°C min^{-1} are reported in Fig. 2. An increase of the heating rate led to a slight shift of the curve variations towards high temperature, but at 700°C and above for the three temperature rates, the same amount of water was released. For a kaolinite mineral, the larger dehydroxylation phenomenon (metakaolin formation) is limited to the 450–700°C temperature range, even if a continuous loss of the OH$^-$ groups trapped in metakaolin can be observed up to 900°C [10]. At 700°C, the weight loss associated with the metakaolin formation is independent of the heating rate. The metakaolin stoechiometry, therefore, must be the same for all the monitored heating rates. Between 700 and 1000°C, the dehydroxylation of muscovite mineral must also contribute to the weight loss [11, 12].

DTA curves recorded during heating of Bio at three different heating rates are presented in Fig. 3. The characteristics of the endo and exothermic peaks are reported in Table 3 for each treatment rate. Some data relative to Kga1 and Kga2 are also indicated. The obtained values show that a fast heating rate enhances the heat exchanged during each phenomenon and a similar trend is observed for Kga1. For Bio, between 3 and 20°C min^{-1}, the total increase of exchanged heat is 21.9% for the main water loss (endothermic phenomenon) and 12.5% for the exothermic phenomenon. The influence of heating rate is appreciably larger for Bio than for Kg1.

The influence of the firing temperature on the amount of mullite formed from Bio after a 3 min hold time is presented in Fig. 3 for 4 and 20°C min^{-1} heating rates. The mullite reference quantity was obtained from a sample maintained at 1400°C for 2 h. At temperatures higher than 1150°C, the mullite quantity is the same for the two very different heating rates. Between 1050 and 1150°C, mullite formation is favoured by fast heat treatment.

The X-ray spectrum of Bio fired at 20°C min^{-1} showed specific reflections of Mu at temperatures up to 1050°C. This suggests that Bio minerals transforms individually when firing at high heating rates.

A TEM photo (Fig. 5) of a sample fired at 1050°C, 20°C min^{-1}, reveals the presence of small needle-like crystals of mullite (about 50×15×8 nm^3), located inside platelets caused by the decomposition of the kaolinite crystals.

5. Discussion

The ratio between transformation heats during the main endothermic phenomenon, Qp, by Bio and by well-crystallised Kga1 (Table 3) during a heating at 3°C min^{-1} is 0.78. This value, which is similar to the ratio of

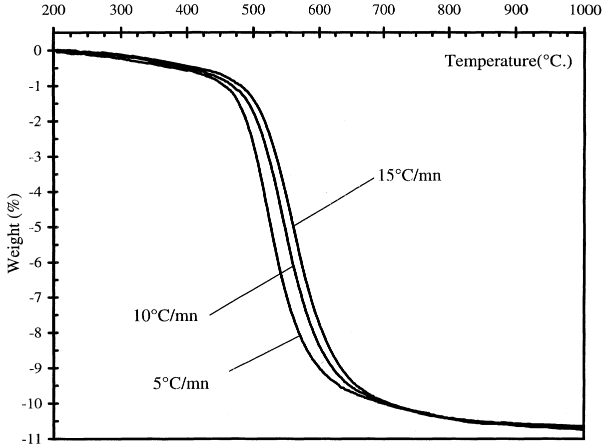

Fig. 2. The influence of heating rate on the weight loss of a Bio powder.

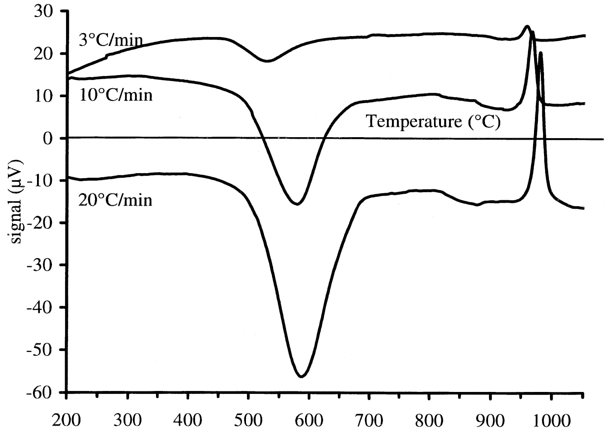

Fig.3. DTA curves of Bio recorded during heating at 3, 10 and 20°C min^{-1}.

Table 3
Characteristics of the endothermic and exothermic phenomena observed for Bio, Kga1 and Kga2 heated at different rates (heat data are given per kg of kaolin)

		Endothermic phenomenon		Exothermic phenomenon	
Material	Heating rate (°C/min)	Starting temperature (°C)	*Qp* (kJ/kg)	Starting temperature (°C)	*Q′p* (kJ/kg)
Bio	3	470	539±5	945	64±1
	8	480	548±5	955	64±1
	10	490	567±5	960	64±1
	12	490	583±5	965	67±1
	15	495	610±5	965	69±1
	20	500	657±5	970	72±1
Kg1	3	–	690±5	–	62±1
	20	495	770±5	985	64±1
Kg2	20	495	–	985	64±1

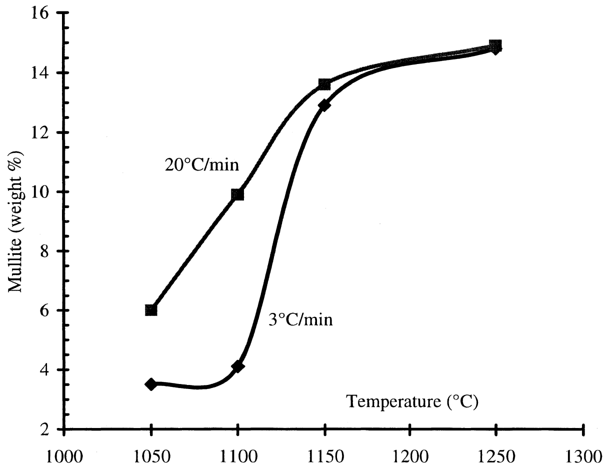

Fig. 4. The influence of firing temperature on the quantity of mullite formed after a 3 and a 20C min^{-1} heating rates followed by a 3 min hold.

kaolinite amounts present in these two materials, suggests that Qp is mainly due to metakaolin formation. Comparison with data from literature (Table 4) shows that the results of the present study corresponds to the lowest values of the published data range [13–16]. In this case, it can be supposed that the discrepancy results from the very high sensitivity of that transition to the surrounding atmosphere.

Assuming that the following reaction:

$$2SiO_2, Al_2O_3, 2H_2O(s) \rightarrow 2SiO_2, Al_2O_3(s) + 2H_2O(g) \tag{1}$$

occurs at constant Gibbs free energy at $T \approx 490°C$ in open air, we have:

$$\Delta G = \Delta H - T\Delta S = 0 \tag{2}$$

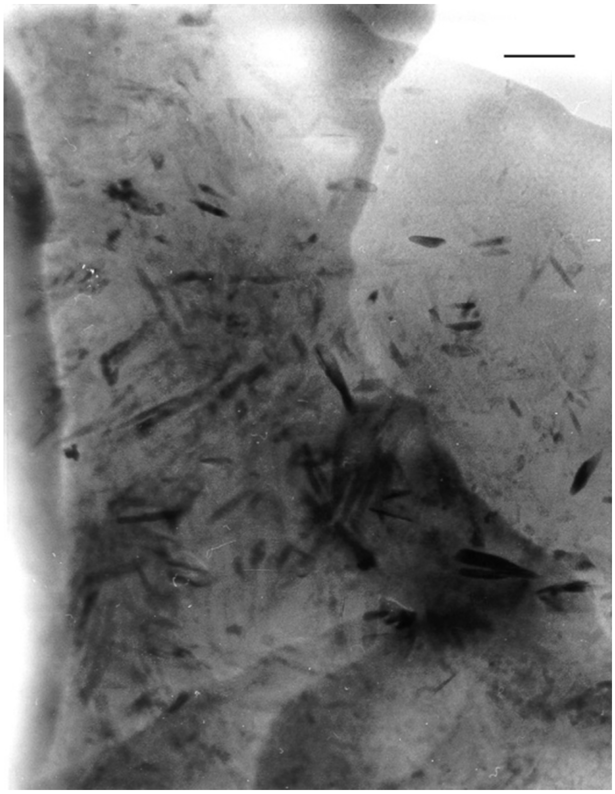

Fig. 5. TEM image of needle like mullite crystals formed in Bio after heating up to 1050°C at 20°C min^{-1}. Bar = 100 nm.

where ΔG, ΔH and ΔS are, respectively, the variations of Gibbs free energy, enthalpy and entropy of reaction (1) at $T \approx 490°C$, $P = 1$ bar and pH2O = 0.21 bar. At constant pressure:

$$Qp = \Delta H \tag{3}$$

Therefore, the change in *Qp* at the heating rate observed (Table 3) corresponds to an increase of both enthalpy and entropy variations with different firing rates.

Table 4
Tabulated data of transformation energy for kaolinite (heat data are given per kg of kaolinite)

Mineral	Metakaolin formation Heat (kJ/kg)	Heat reference	Experimental conditions
Kaolinite	860	19	Isotherm under N2
	825	20	At 10^{-3} mm. Hg.
	1813	20	At 47 mm. Hg.
	542 to 1162	21	Isotherm, various pH_2O
	542	22	Controlled transformation rate
Bio	700–850		Air
Kga1	720–810		Air

As the amount of water exchanged during this phenomenon is independent of the heating rate (Fig. 2), the increase of ΔS must be related to a change in metakaolin entropy. This suggests that a faster dehydroxylation rate favours a more disordered metakaolin phase.

The *Q'p* values reported in Table 3 show that the heat exchanged during the exothermic phase, just below 1000°C, is always more important for Bio, with its 79 wt.%, kaolinite amount than for reference materials Kga1 and Kga2, which contain respectively 96 and 97 wt.% of kaolinite. Such an excess of exchanged heat cannot be explained only by a variation of disorder in the Bio derived metakaolin, as *Q'p* for poorly (Kga2) and well (Kga1) crystallised kaolins are very similar, about -44 kJ kg^{-1} for both Kga1 and Kga2, at a 20°C min^{-1} heating rate.

From X-ray diffraction patterns of Bio and Kga1 samples heated at 1000°C (Fig. 6), it was observed that heating Bio at 3 and 20°C min^{-1} leads to a direct formation of mullite from metakaolin. This particular behaviour differs from that of the Kga1 derived sample, where the mullite quantity was weak. Such change, including the possible presence of an intermediate γ-alumina derived spinel, has been observed elsewhere [17]. It suggests that the metakaolinite decomposition of Bio and Kga1 has a very different mechanism. The significant difference of *Q'p* values must be related to a difference in the nature of the phase formed during the structural transition.

Between 1050 and 1150°C, the amount of mullite formed when Bio was heated up to a given temperature is strongly dependent on the heating rate: faster heating rates increase the amount of mullite (Fig. 4). Such a trend, already described [18], was supposed to be the result of an evolution in the mullite nucleation mechanism [19]. However, it could also be the result of chemical interactions between mineral impurities and kaolinite derived phases. Nevertheless, X-ray energy dispersion microanalysis during TEM experiments indicated that potassium and iron were never detected in the mullite crystals or in their vicinity. This suggests that mullite formation is only slightly dependent on interactions between minerals.

The mullite formation from muscovite is questionable, as both the presence [20] and the absence [21] of mullite after firing was observed. For Bio, the simultaneity between the muscovite breakdown at about 1050°C (Fig. 6), and the rapid increase of the mullite amount during fast firing could suggests that a significant part of mullite may be a muscovite derived phase. However, TEM experiments revealed there is a

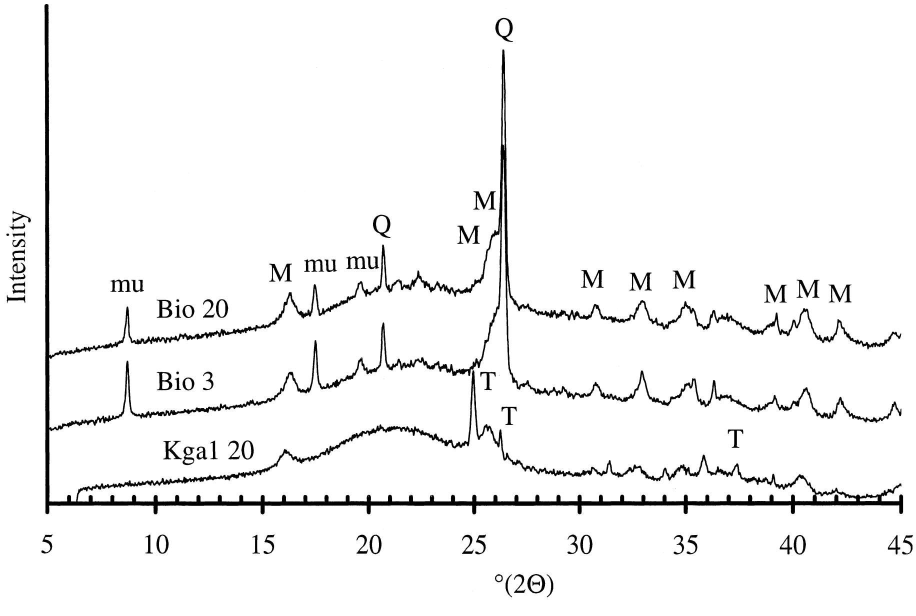

Fig. 6. X-ray diffraction pattern of kaolins heated until 1000°C: (a) Bio at 20°C min^{-1} ; (b) Bio at 3°C min^{-1} ; (c) Kga1 at 20°C min^{-1}. Holding time at 1000°C : 3 min. X-ray exposure time : 8 h. M = mullite; mu = muscovite; Q = quartz; T = rutile.

lack of potassium in the vicinity of mullite crystals after heating at 1050°C. It can therefore be considered that mullite forms in Bio from the kaolinite derived phase.

It has already been reported that mullite formation is very sensitive to chemical homogeneity. The nucleation temperature can be as high as 1300°C when very good homogeneity is observed at atomic level in a mullite precursor [22]. For Bio, the influence of the heating rate on the mullite development derived phase supports the idea of a mechanism controlled by the cationic distribution at atomic level. A fast heating rate which favours disorder, should enhance inhomogeneous cation distribution in silicon and aluminium rich domains.

6. Conclusion

The influence of the firing rate on the thermal changes to a commercial Bio kaolin was studied. Kaolinite dehydroxylation, metakaolinite structure change, exothermic structural organisation and mullite formation are very sensitive to the heating temperature rate. The main effect concerns mullite development below 1100°C, which is enhanced by an increase in firing rate, from 3 to 20°C min^{-1}. The whole behaviour reflects an increase of the cationic disorder in the kaolinite derived phases. Results described in this paper suggest that a correlation exists between the heat exchanged during the metakaolin decomposition and the ability of the kaolinite to form mullite at low temperature through a more direct formation route. High *Q'p* values correlate with low temperatures of mullite formation.

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