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Influence of calcite on the microstructure and mechanical properties of pottery ceramics obtained from a kaolinite-rich clay from Burkina Faso

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Abstract

Addition of calcite to clay powders for the elaboration of ceramics lies in the fact that upon firing this mineral acts as a fluxing agent and a mineral promoter (formation of new mineral phases). In the case of a kaolinite-rich clay from Burkina Faso, a correlation of the mechanical properties and the microstructure characteristics determined by image analysis is proposed. The main influence of calcite on the material strength is a broader distribution of the flexural strengths. The key parameter relating the fracture toughness and the amount of calcite is the free mean path in the solid phase.

Keywords: Sintering; Calcite; Microstructure-final; Mechanical properties; Traditional ceramics

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1. Introduction

Pottery wares are commonly used as well for collecting and preserving drinking water, conservation of cereals as for cooking. That points out the importance of ceramic wares in the economic and social activities of villages in the Third World. However, poor quality products are often obtained due to the complex chemical and mineralogical nature of natural raw materials, and failing to control the starting powders and the different steps characterizing ceramic process engineering. So, calcite is often added to clay powders in the aim to master the dimensional variations of the products upon firing. Depending on the firing temperature, the concentration and the grains size distribution of the calcite, different mineral phases may form from its decomposition into calcium oxide.[1–6] Moreover, an excess of free calcium oxide induces an important porosity.[6]

The present work deals with the influence of calcite on the microstructure, the physical and mechanical properties of a kaolinite-rich clay exploited at present in a large pottery production area in Burkina Faso. Microstructural modifications were investigated, by using image analysis methods and three point bending tests were run to assess the fracture toughness and the flexural strength. The fracture behaviour of the materials is discussed in correlation with the morphological parameters.

2. Materials and experimental methods

The natural raw material under study was mined from alluvial deposits in the region of POA (Burkina Faso) known for centuries for intense pottery activities. The elementary chemical composition, detailed in Table 1, clearly reveals the aluminous-siliceous nature of that POA powder, with a predominance of silica. The high level of the ignition losses is ascribed to the natural character of POA and the important proportion of kaolinite in it. Further investigations of that power had shown the following main features:

- XRD analyses revealed that POA only contains kaolinite and quartz as minerals. The mineralogical composition of the powder, derived from these data and the elementary chemical analysis, is 71.3 wt.% of kaolinite and 21.1 wt.% of quartz.

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Table 1
Quantitative chemical analysis of the POA powder and a poorly crystallized reference kaolinite-rich clay Kg_2 from Georgia (USA)

	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SiO_2	CaO	MgO	TiO_2	Total	Ignition loss
POA (wt.%)	28.2	4.5	0.1	0.7	54.3	0.2	0.3	1.4	89.6	10.4
Kg_2 (wt.%)	38.5	1.1	–	<0.1	43.9	–	<0.1	2.4	85.9	13.8

Table 2
Composition of the different mixtures

Mixes	POA (wt.%)	Calcite (wt.%)
POA	100	0
MEL5	95	5
MEL10	90	10
MEL15	85	15
MEL20	80	20
MEL25	75	25

Moreover a comparison with Kg_2 proved that the kaolinite within POA is not much ordered.

- DTA data[7] showed a thermal decomposition in two steps: (i) a dehydroxylation of the clayey minerals in the 400–600 °C range; (ii) a structural reorganization for temperatures between 900 and 1000 °C. Extensive thermal expansion associated with these mechanisms gives evidence of the high content of the POA powder in clayey minerals.
- Analyses of the Mössbauer spectra showed that POA solely includes structural iron in octahedral site (in substitution for alumina) without any magnetic iron.

Different batches, obtained by replacement of 5, 10, 15, 20 and 25 wt.% of POA with calcite (Table 2), were mixed with water and ball milled using alumina as the grinding media. The resulting mixtures were dried in an oven (100 °C), ground again and formed into granulates prior to pressing (15 MPa) into samples with dimensions 12 cm × 5 cm × 1 cm. The compacts were dried for 24 h at 40 °C, and then fired at 1100 °C for 1 h under air by using a controlled heating rate of 3 °C/min.

Specimens with dimensions $L = 80$ mm, $B = 8$ mm and $W = 5.5$ mm were loaded in three point bending (span over width $L/W = 4$) at a crosshead displacement rate of 3 mm/min, on a Schenck type testing machine equipped with a 10 kN load cell. For the smooth specimens, the maximum load to rupture, F_R, was used for the evaluation of the flexural strength, σ_R, [Eq. (1)]. Single edge notched specimens (SENB), with a notch length a_0 were loaded to rupture for fracture toughness measurement. That parameter, K_{Ic}, was calculated from the experimental fracture stress, σ_t, with a loading configuration $L/W = 4$, a notch over depth ratio $a_0/W = 0.35$ and Y a factor depending on both the configuration of the test and the specimen geometry [Eq. (2)]

$$\sigma_R = \frac{3}{2}\frac{LF_R}{BW^2} \tag{1}$$

$$K_{Ic} = \sigma_t Y \sqrt{a_0} \tag{2}$$

Microstructure observations were performed on a Philips FEG-type scanning electron microscope (SEM) after gold sputtering.

Morphological analyses were performed, for each type of material on a piece of sample embedded in a transparent epoxy resin under vacuum. After hardening of the resin, the obtained cylinders were finely polished by using absolute ethanol for SEM observations. The photomicrographs in grey levels, obtained at low magnification, were transformed in binary images where the solid phase appears in black colour and the pores in white. The following morphological parameters were determined on these binary pictures using an in-house software (the solid phase is denoted P and the porous phase S)[8]:

- The volume fraction of the pores, $V_V(P)$, which corresponds to the volume occupied by the porous phase by unit volume of the material. As the porous phase and the solid phase are complementary, $V_V(P) + V_V(S) = 1$.
- The specific surface of the pores, $S_V(P)$, which corresponds to the area occupied by the porous phase by unit area of the material.
- The mean free path through the porous phase, $L_m(P)$, or within the solid phase, $L_m(S)$, represents the mean length of the intersections between a line of analysis and the phase of interest.
- The mean free path through the solid phase weighted in measure, $L^*(S)$, and obtained from linear weighted size distributions.[9]

3. Results and discussion

Upon firing a mix of calcite and a kaolinite clay, a few chemical transformations may occur, among which the formation of: (i) different crystalline phases like gehlenite and wollastonite (intermediary phases) and anorthite[10–12]; (ii) pores as a result of CO_2 exhaust.

Table 3 summarizes the results of the mechanical tests. For each batch, the mean flexural strength was obtained from more

Table 3
Three point bending mechanical characteristics of the different batches

	POA	MEL5	MEL10	MEL15	MEL20	MEL25
σ_R (MPa)	26.57 ± 3.18	30.04 ± 4.48	23.77 ± 3.38	25.31 ± 3.32	26.16 ± 4.55	26.66 ± 4.17
K_{Ic} (MPa m$^{1/2}$)	0.78 ± 0.04	0.67 ± 0.3	0.66 ± 0.02	0.61 ± 0.04	0.62 ± 0.04	0.63 ± 0.05

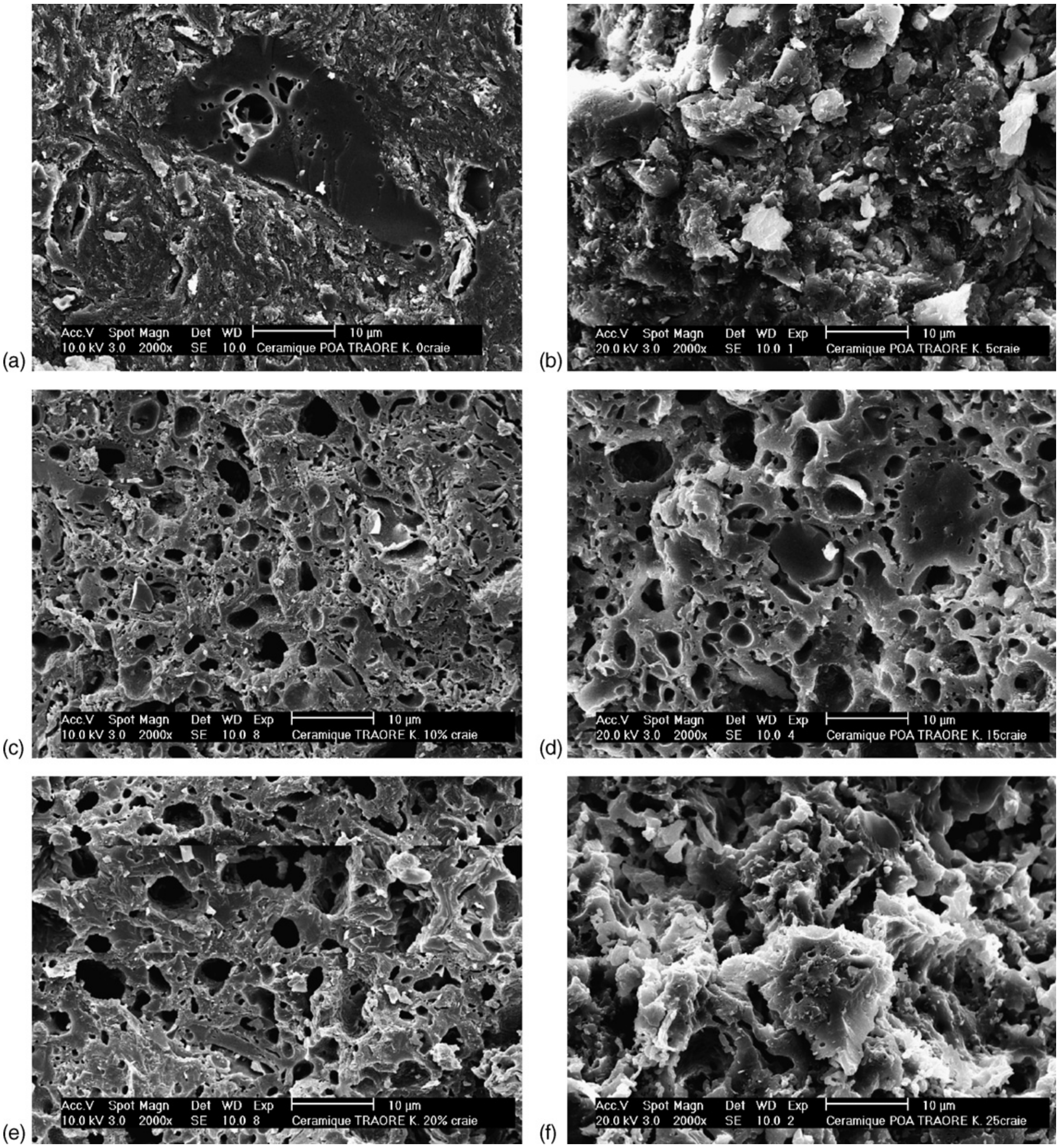

Fig. 1. SEM Microphotographs of the different POA and calcite mixes fired at 1100 °C.

than 71 samples. The flexural strength of POA appears relatively high in comparison with similar materials, and is not reduced further to the addition of calcite. On the contrary, an appreciable rise is noted when 5 wt.% of calcite is added to POA. The fracture toughness falls off drastically for calcite concentration below 15 wt.%, and then levels off at a plateau value comparable to the ones reported for soda glasses or bituminous schists.[13]

The influence of calcite on the structure of POA fired at 1100 °C is examplified on the microphotographs shown in Fig. 1. POA is characterized by a non-homogenous structure with pore sizes of 2–3 µm. Distinct quartz grains with distributed sizes are embedded in a likely amorphous bulk. Comparatively, in MEL5 a higher density of grains is noted while the density of large pores is noticeably reduced. That homogenous distribution of the grains and pores is probably responsible for its particularly high strength. For MEL10 the increased porosity is associated with a higher density of pores. With 15 wt.% of calcite, the grains are no more distinct and the porosity is higher. That may induce the pronounced brittleness of that mixture. In the mixes with 20 and 25 wt.% of calcite the porosity is very high.

Fig. 2 shows an example of a SEM microphotograph in grey levels and the corresponding binary image used for morphological measurements. The main parameters obtained for the different batches are collected in Table 4. It appears a weak dependence of the free mean path within the porous phase on the concentration of calcite and the main contribution at the total porosity is provided by the small pores. These results indicate that the increase of porosity linked to the formation of new phases does not correlate with a morphological change of the pores: their density rises with the amount of calcite but not their

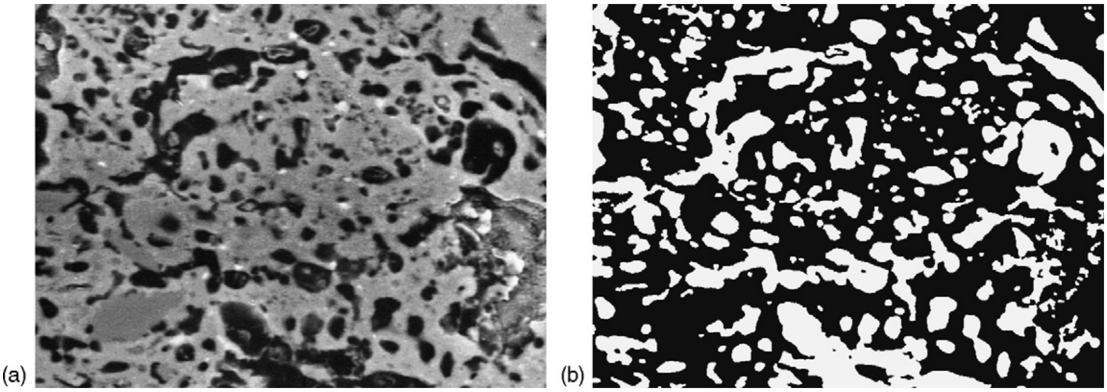

Fig. 2. Image of a mix in grey levels (a) and the corresponding binary image (b).

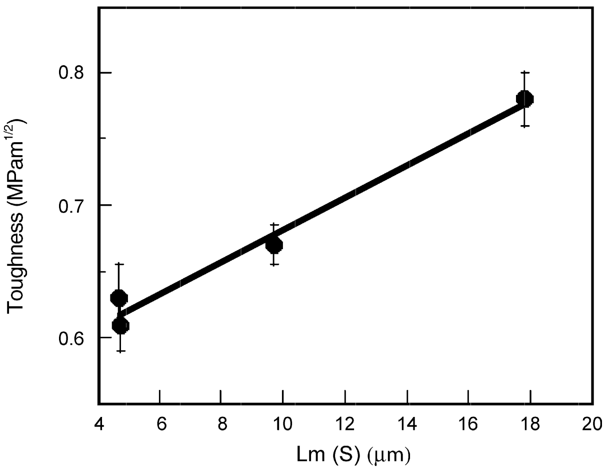

Fig. 3. Relationship between the fracture toughness and the mean free path within the solid phase for the different batches.

mean size. Hence the increase of the specific surface area of the solid/pore interface is not a consequence of the presence of new and finer structures, but simply means a higher density of pores. That increase of the pores density with the amount of calcite combines with a thinning of the walls between neighbouring pores, i.e. a reduction of the mean free path within the solid phase.

For a porous body it can be expected that the fracture toughness should depend on the thickness of the walls between the pores. To validate that hypothesis we have plotted in Fig. 3 the fracture toughness of the different materials as a function of the mean free path within the solid phase. The line of regression fitted in Fig. 3 describes a linear relationship between the fracture toughness (a mechanical parameter) and the mean free path $L_m(S)$ (a morphological parameter). Hence, the mean free path within the solid phase is a pertinent morphological parameter for investigating the influence of calcite on the microstructure of POA-based ceramics.

Table 4
Main morphological parameters measured on the different batches

	$V_V(P)$	$S_V(S/P)$	$L_m(P)$ (μm)	$L_m(S)$ (μm)	$L^*(S)$ (μm)
POA	0.092	204	1.81	17.79	3.69
MEL5	0.167	344	1.94	9.68	3.66
MEL15	0.294	598	1.96	4.72	3.87
MEL25	0.318	582	2.18	4.68	3.77

4. Conclusion

The microstructure of ceramics obtained by mixing a kaolinite-rich clay with different concentrations of calcite was investigated by using image analysis, and correlated with mechanical properties. Although the presence of calcite reduces the shrinkage upon firing, the formation of crystalline intermediary phases generates a multimode distributed porosity, which strongly reduces the mechanical properties for calcite content above 5 wt.%. A linear dependence of the fracture toughness on the mean free path in the solid phase characterizes the porous bodies.

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