

IMAGE ANALYSIS OF SINTERED MOROCCAN CLAYS

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ABSTRACT

Sintering of Moroccan clays have been investigated by automatic image analysis. The knowledge of the classical morphological parameters determined from the $P(\ell)$ function allowed to follow the sintering process route of these materials and to assess clay quality.

Keywords : $P(\ell)$, linear granulometry, sintering, mathematical morphology, clays.

INTRODUCTION

Clays can be used to develop technical ceramics at low cost and, if the mineral is with low impurity content, ceramics obtained are of good quality for applications at low temperature ($\leq 1000^\circ\text{C}$). There are also some new applications in the field of porous catalysts based on pillared clays for petrochemistry industry (Figueras, 1988). These minerals are very common and without an overcost for part production. Moreover they can lead to materials based on mullite. Moroccan clays have been investigated for that purpose, in order to develop technical ceramics.

The scope of this paper is to investigate the morphology of clays and sintered materials by means of automatic image analysis methods. That gives access to the morphological and stereological parameters and allows to have information on the sintering mechanisms.

MATERIALS AND EXPERIMENTAL PROCEDURE

The clay investigated in this work is from Ben Ahmed country (Morocco) and is composed mainly of quartz, kaolinite, illite, and few talc and dolomite.

Clays are mainly a mixture of silicates, most often in layer form, called phyllosilicates and nearby minerals with fibrous and sometimes spherulitic features (Caillère & al., 1989), with different ratios and impurities. They are mainly hydrated aluminum silicates with a structure constituted of oxygen and hydroxyle ions. The association of the $(\text{SiO}_4)^{4-}$ tetrahedrons leads to many types of minerals and crystallographic structures (Wyart, 1965 ; Caillère & al, 1989).

The most common silicate phase in clays is the kaolinite : it is a stacking of a tetrahedral layer and an octohedral layer with a common plane of oxygen and hydroxyle (Fripiat & al., 1971); it corresponds to $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ and crystallizes in the triclinic system. The illite is derived from micas, with the stacking sequence tetrahedral-octahedral-tetrahedral layers. It crystallizes in the monoclinic system (Jouenne, 1980) and one of the structural formula can be $\text{KAl}_4(\text{Al}_x\text{Si}_{8-x}\text{O}_{10})(\text{OH})_4$ with $1 \leq x \leq 1.5$.

Sintering experiments were performed in a platinum crucible, in a crusilite furnace, under air. A specific thermal cycle has been chosen to avoid the so-called black coring defect (Nicholson & Ross, 1970; MacKenzie & Cardile, 1990) : $10^\circ\text{C}/\text{mn}$ until 400°C , then $1^\circ\text{C}/\text{mn}$ until the sintering temperature. The specimens were initially compacted in a cylinder chamber up to 40 MPa to obtain cylindrical rods of 20 mm in diameter and several centimeters in length. Specimens were annealed for time varying from 30 mn to 24 h in the $900 - 1300^\circ\text{C}$ temperature range.

After sintering the specimens were polished with diamond pastes according to the classical metallographic techniques. Figure 1 presents some micrographs of un-etched materials.

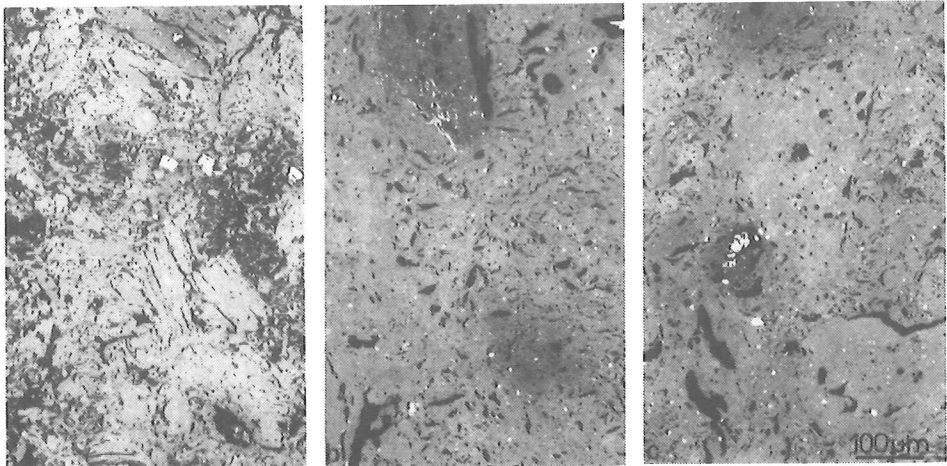


Fig. 1 : Microstructures of clays sintered during 2h at 1000°C (a), 1200°C (b) and 1300°C (c). Un-etched specimens.

An automatic image analyzer, Nacet NS 1500 (Microcontrôle, France) has been utilized to investigate, in a first step, the porous phase (P) on un-etched specimens. We have measured the volume fraction of pores, $V_v(P)$,

and performed linear granulometry methods via the $P(\ell)$ function, erosion by linear structuring element ℓ , (Haas & al., 1967; Serra, 1982; Coster & Chermant, 1985; 1989), as it has already been shown that this function is very well suited for the investigation of sintered materials (Jernot, 1982).

RESULTS AND DISCUSSION

For a given temperature, if we plot the volume fraction of pores, $V_v(P)$, as a function of time, t , (figure 2), one observes an important decrease at

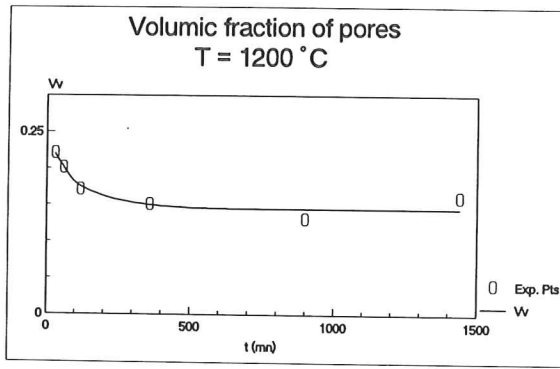


Figure 2 : Change in the volumic fraction of pores, $V_v(P)$, as a function of the sintering time, t , for clays sintered at 1200°C.

the beginning of the sintering process, and then a stabilization: only a very small change can be considered after 2 hours of sintering. It confirms the results of Saadi (Saadi, 1992; Saadi & al., 1992), indicating a weak influence of the sintering time above 2h on one hand on the ratio of the main crystalline phases up to 1200°C and on the other hand on measured

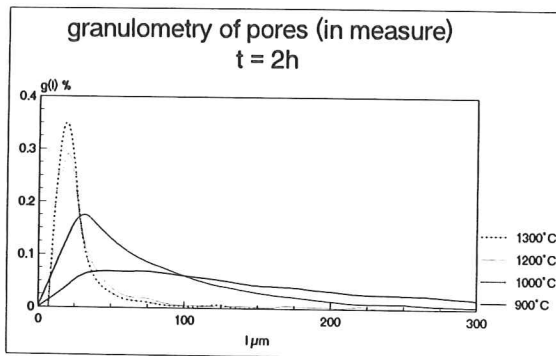


Fig.3 : Pores size distribution densities for clays sintered 2h at different temperatures.

physico-chemical parameters (specific surface area, apparent density, mechanical characteristics, ...)

Size distribution of pores has been obtained from the $P(\ell)$ function: size distribution densities for clays sintered for 2h at temperature in the range from 900°C to 1300°C are presented in figure 3. The mean size of pores decreases rapidly with increasing the temperature in the range from 900 to 1200°C, where it seems to be stabilized. A rapid change in the size distributions arises above 1000-1100°C due to the fact that the large pores are eliminated most rapidly. That is confirmed by the plot of the mean

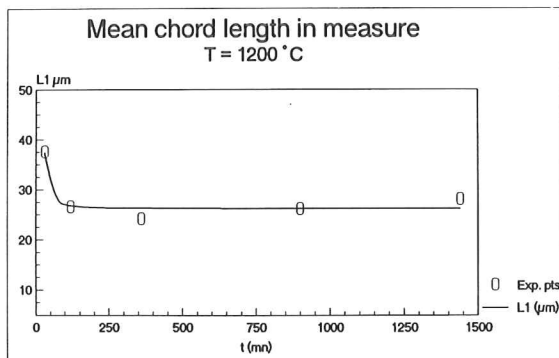


Fig. 4 : Change of the mean chord length in measure as a function of time, t , for clays sintered 2h at 1200°C.

chord length, $L_1(P)$, as a function of the sintering time at 1200°C (figure 4), where the same stabilization is observed after 2 hours. When we plot the same mean chord length as a function of the sintering temperature for sintering periods of 2h, there is an important decrease in $L_1(P)$ until 1200-1250°C.

Figure 5 presents the evolution of the porosity as a function of the sin-

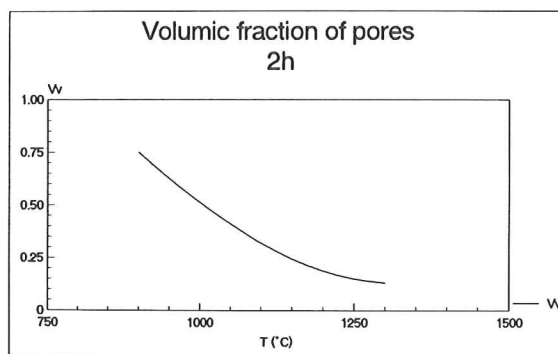


Fig.5 : Change in the volume fraction of pores, $V_v(P)$, as a function of the temperature, T , for clays sintered 2h at different temperatures.

tering temperature, T , for clays sintered 2h. One notes, as for the evolution of the mean chord length with the sintering temperature, a regular decrease with an asymptotic tendency above 1200-1250°C. This result confirms these of Saadi (1992) obtained by measurements by mercury porosimetry.

The beginning of the stabilization of the curves from 1200-1250°C (Fig. 5) can be attributed to the phenomenon of swelling which compensates for the loss of porosity, as Saadi (1992) has already shown from the change in the shrinkage with temperature.

During the sintering, many chemical reactions arise : loss of water (100°C) and then of organic matters by burning (from 300 to 700°C); from 450°C there is the dehydroxylation of the kaolinite in metakaolinite, and from 900°C disappearance of the illitic phase and apparition of sapphirine and then mullite. Finally from 1100°C there is the dissolution of the cristoballite (Cambier & al., 1981). These sequence of reactions explains the complexity of these materials from the chemical and microstructural points of view. It is the reason why experiments performed at temperatures higher than 1200°C during long periods can lead to other structures.

The densification of these ceramics based on clays with silicate phases occurs according to a viscous flow process. If we draw the Arrhenius plot - $\ln V_V(P)$ as a function of $1/T$ - (Fig. 6) a straight line is obtained. The slope gives estimation of the apparent activation energy of sintering, which is 75 kJ. mol⁻¹. That is the order of magnitude of an activation energy for pore elimination in solids.

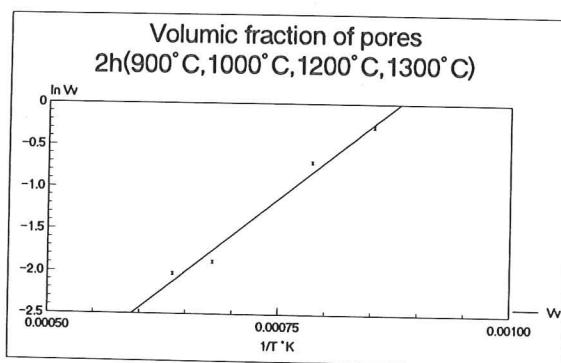


Fig. 6 : Change in the volumic fraction of pores, $\ln V_V(P)$, as a function of the sintering temperature, $1/T$, for clays sintered during 2h.

CONCLUSION

Pore elimination during the sintering of Moroccan clays in the 900-1300°C temperature range have been investigated by image analysis methods, and more specifically from the linear granulometry via the $P(\ell)$ function.

The mean size of pores decreases rapidly if the temperature is increased in the range from 900 to 1200°C and seems to be stabilized after 2h, leading to ceramic materials of good quality. An apparent activation energy of about 75 kJ.mol⁻¹ have been found for the pore elimination.

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