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Sintering of a clay from Burkina Faso by dilatometry Influence of the applied load and the pre-sintering heating rate

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Abstract

The sintering of a pottery clay from Burkina Faso was studied as a function of the heating rate, at 3 or 10°C/min. The experimental method used was loading dilatometry in isothermal conditions at 1120°C. In these conditions, we found that the densification rate of the material is low, but tend to a limiting value after 2 h at 1120°C, depending on the pre-sintering heating rate and the load used. The relationship between the pre-sintering heating rate and the densification rate indicated the existence of a weakly organised material at higher heating rates. Nevertheless, higher values of shrinkage were observed when the temperature increased continuously. It is, therefore, proposed that the material is subject to a preferential solid state diffusion mechanism at face to face of the remaining kaolinite layers at high temperatures. This mechanism is favoured by higher heating rates, mainly in the temperature range corresponding to the structural reorganisation of the metakaolin phase. © 2001 Elsevier Science Ltd and Techna S.r.l. All rights reserved.

Keywords: A. Sintering; D. Clay; Dilatometry; Burkina Faso

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1. Introduction

The raw material used is a natural clay for pottery (Poa), from a large deposit in Burkina Faso [1]. This clay is extensively used by thousands of potters, for which it is an essential activity. The technological methods are very traditional, especially in what concern the firing techniques in wood heated kilns. The maximum sintering temperatures used are below 1150°C and the heating rate could be rapid (up to 15°C/min).

The sintering behaviour of Poa clay was studied using similar conditions to the traditional techniques of local potters [2]. At the low 1000°C temperature, it was shown that favouring the nucleation and growth processes of recrystallised phases containing calcium results in a significant increase in the material strength. Nevertheless, the crystallisation kinetics decreased rapidly with time and the material microstructure remains porous and heterogeneous. In this study the Poa sintering behaviour was studied at a temperature close to the upper boundary of the generally used temperature range, at 1120°C. To optimise the product densification, we were interested in the influence of the firing process, with regard to the heating rate, 3 and 10°C/min, and the firing time, up to 2 h. To this end, dilatometry is a very convenient method but suffers from problems, which appear under the influence of load applied to the sample by the pushrod. In general, the load is between 0.1 and 1 N, but cannot be reduced more, to ensure a satisfying measurement.

2. Materials and methods

The Poa clay is a natural mix of a poorly crystallised kaolinite (Hinckley index: 0.32) and 21% by weight of quartz, the average size of which is about 5 μm. From a preliminary X-ray diffraction study, it appears that minor minerals, such as iron minerals, could not be detected over a significant quantity to influence the thermal comportment [2]. The global chemical composition is presented in Table 1.

All measurements were performed in a loading dilatometer (Adamel DI24), where the load was held constant at 0.1 N (3.15 kPa) or 0.2±0.01 N (6.3 kPa).

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Table 1
Chemical composition of Poa clay

Poa	Al_2O_3	Fe_2O_3	Na_2O	K_2O	SiO_2	CaO	MgO	TiO_2	Loss at 1000°C
Wt.%	28.2	4.48	0.06	0.72	54.3	0.01	0.33	1.37	11.1

These conditions were maintained for all experimental runs at the isothermal temperature, since the sample length and diameter variations are less than 2%. The diameter of the contact surface was larger than that of the sample, by using a small alumina cylinder between the pushrod and the sample.

The Poa clay was ball milled in an alumina jar with water, to remove agglomerated particles from the raw material. After drying the powder was granulated and die pressed (~10 MPa), to obtain well-shaped cylinders (Φ 5 mm; 10.5 mm height). The green density was maintained close to 1.45±0.01, corresponding to a relative density of 0.58. The sample weights were measured within 1 mg and the room temperature diameters within 10 μm. The diameter values were corrected using the corresponding material thermal dilatations. Lengths were obtained from dilatometric data. For complementary measurements [3], oriented samples were shaped by slip casting of a concentrated suspension (45 vol.%) in a plaster mould. A satisfactorily layered orientation was obtained by limiting the thickness of the cast sample to 3 mm. It was also checked by X-ray diffraction.

The dilatometric Poa comportment is plotted in Fig. 1, as a function of temperature, for the two different heating rates used, using a 0.1 N load. Here we observed large thermal transformations from a low crystallised kaolinite [4] that is — the dehydroxylation between 480 and 580°C — a structural reorganisation stage between 900 and 1000°C and a rapid densification above 1050°C. A higher heating rate shifts slightly the three phenomena toward a higher temperature, but reduces densification above 1050°C.

Our isothermal measurements at 1120°C were in a temperature range where a large densification takes place (Fig. 1). Consequently, we chose to sinter the samples at 1100°C without any load, using 3 and 10°C/min heating rates, and a subsequent quenching. In these conditions, the sintered densities remained within 1.98±0.01. This pre-firing operation ensured a reproducible and accurate starting point for isothermal experiments [5]. During dilatometric measurements, a preliminary rapid temperature ramp (20°C/min) up to 1120°C was used to limit a further densification before the isothermal stage. This heating rate is the highest value, which can be used with a loading dilatometer.

A series of isothermal runs was conducted during various times followed by a rapid cooling to obtain reproducible sample sizes and densities values.

From preliminary X-ray experiments, the material after firing at 1120°C is constituted of about 20% by weight of quartz particles, and about 5% by weight of mullite crystallites. The remaining material is an almost

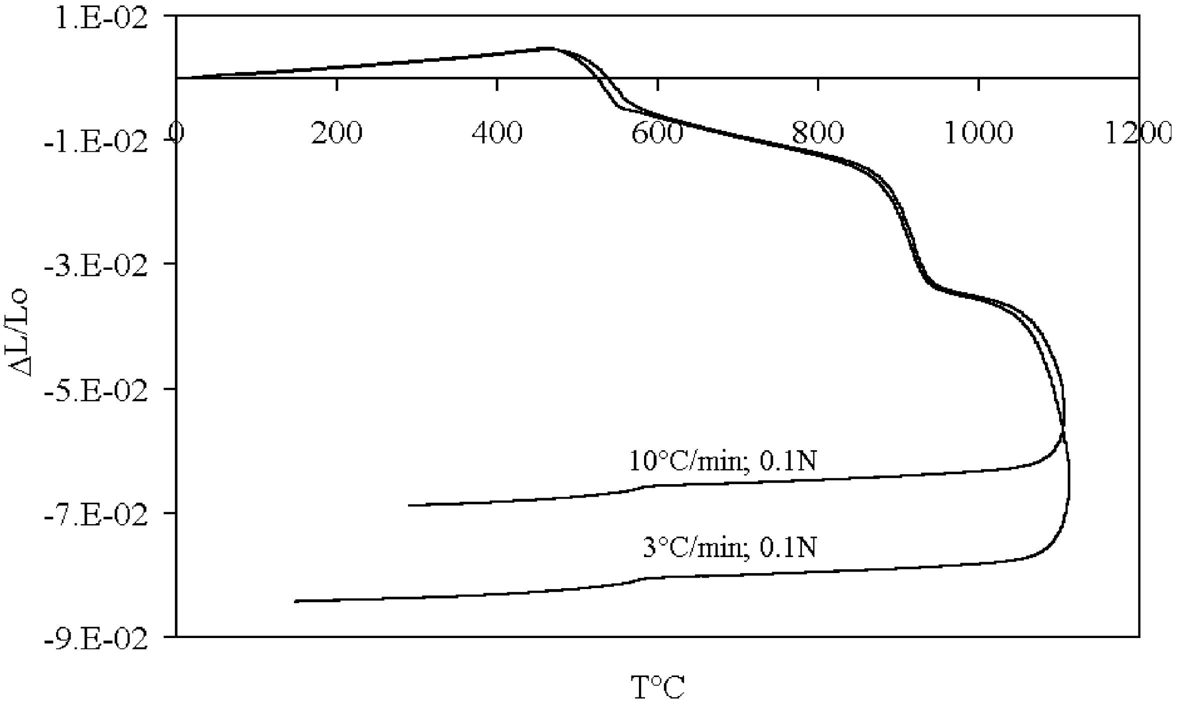

Fig. 1. Dilatometric characteristics of Poa clay fired up to 1100°C, using two heating rates (3 and 10°C/min).

amorphous silico-aluminate phase and although this matrix phase underwent a progressive structural reorganisation above 900°C, the X-ray diffraction data does not indicate any related reflections. At this temperature, the presence of a liquid phase should be supposed, but it was not detected by usual technical means (DSC and EDS microanalysis). Furthermore, phase diagrams combining major and minor elements as oxides of the chemical composition (Table 1) are not decisive at all. Consequently, the matrix phase was considered to be characterised by a very reduced structural organisation and no detectable liquid phase.

3. Results

During the isothermal sintering under load at 1120°C, the relative axial densification against time for the two loads and pre-sintering heating rates are presented in Fig. 2. The curve shapes suggest a plastic deformation of samples under constant stress. When the pre-sintering heating rate increases, the load influence becomes more important.

In Fig. 3, the sample densities are plotted as a function of time. They all increase with time although they approach a limiting value after 100 min. The density limit is significantly linked to the load influence, mainly for a 10°C/min pre-sintering heating rate.

The load applied during dilatometry induces an anisotropic shrinkage, as shown in plots of $\Delta L/Lo$ versus $\Delta D/Do$ (Fig. 4). For the two loads and heating rates, $\Delta L/Lo$ remains almost proportional to $\Delta D/Do$, even up to 2 h sintering time. It is seen in Fig. 4 that the characteristic slope increases when the load and the pre-sintering heating rate increase, mainly for 10°C/min.

Fig. 5 presents a photo from scanning electron microscopy (SEM). For a sample sintered 1 h at 1120°C, the particular elongated shape of pores and densified agglomerates can be seen.

4. Discussion

Fig. 4 indicates a significant densification anisotropy, since the ratio between the axial and radial strain shrinkages differs from 1. The average ratio values are close to 0.82 for a 0.1 N load, independent of the heating rate. For a 0.2 N load, the slope attains 1.17 for 3°C/min and 1.41 for 10°C/min. It means that either sintering at 0.1 N load, or creep at 0.2 N load, predominates on the radial strain extent. This general behaviour is not very different from the behaviour of glass, a powder compact which presents values of strain ratios between 1 and 5, depending on the applied stress from the push rod [6–8] and on the characteristics of the glass used. However, for crystallised materials, similar values were measured even though the higher loads were used [9,10].

The material densification rate is given by:

$$\frac{\dot{\rho}}{\rho} = \frac{\mathrm{d}\rho}{\mathrm{d}t} \cdot \frac{1}{\rho} \tag{1}$$

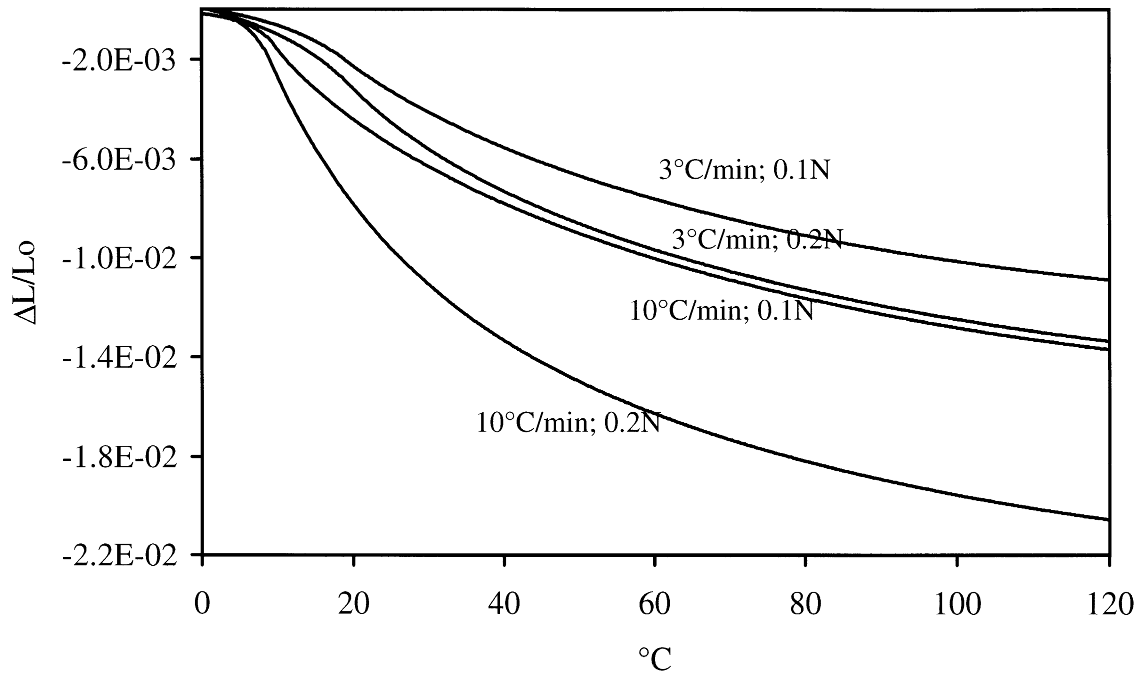

Fig. 2. Axial shrinkage against time, for the 0.1 N or the 0.2 N loads and the 3 or 10°C/min pre-sintering heating rates.

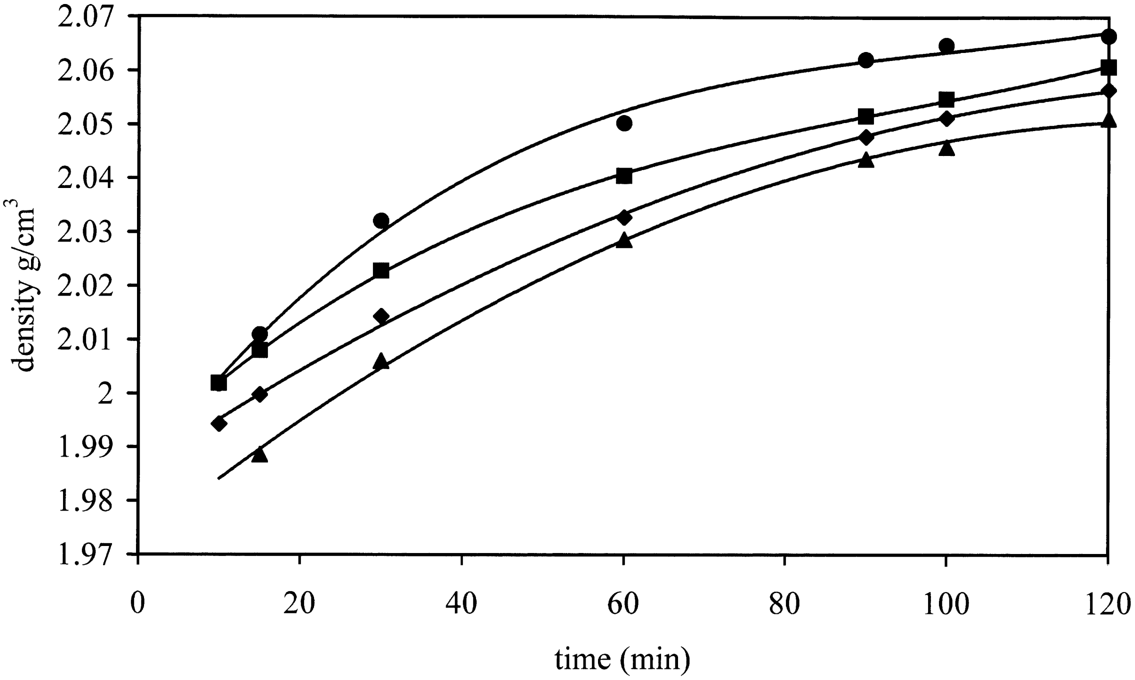

Fig. 3. Measured sample densities at 1120°C, against time and pre-sintering heating rates. (◆): 3°C/min, 0.1 N; (▲): 10°C/min, 0.1 N; (■): 3°C/min, 0.2 N; (●): 10°C/min, 0.2 N.

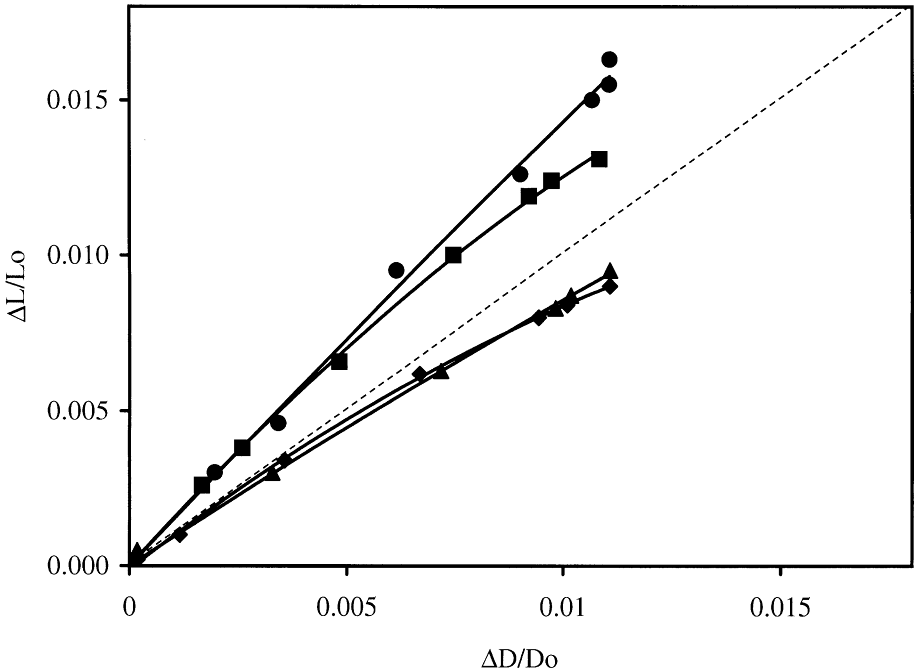

Fig. 4. Axial strain versus the radial strain during an isothermal cycle at 1120°C, 2 h. (◆): 3°C/min, 0.1 N; (▲): 10°C/min, 0.1 N; (■): 3°C/min, 0.2 N; (●): 10°C/min, 0.2 N.

Calculated values from measured strains are plotted in Fig. 6 against the measured material density. These densification rates in isothermal conditions are low although they are related to poorly crystallised materials. This result presents significantly reduced values in comparison with published values for CdO [10,11], zinc oxide [12] or glass [13,6,7] materials. The general trend is a progressive reduction of the densification rate when the isothermal sintering time increases, indicating a limiting value for the material density at each firing rate and applied load. In the course of the 2 h firing time, for a 3°C/min pre-sintering firing rate, the

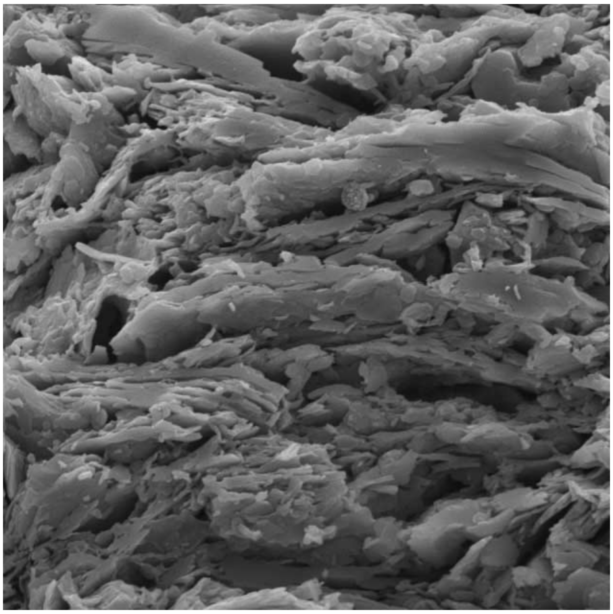

Fig. 5. SEM photograph of a sample sintered 1 h at 1120°C (bar = 100 μm).

shrinkage anisotropy is very weakly dependent from the load values (Fig. 4). It suggests that the load effect on densification is reduced. In the case of 10°C/min, the densification rate (Fig. 6), the material density (Fig. 3) and the shrinkage anisotropy (Fig. 4) are significantly influenced by a load increase. It appears, therefore, that the densification mechanisms are affected by the load, even for 2 h of isothermal sintering.

According to [14], the creep strain rate $\dot{\varepsilon}_c$ is related to the axial $\dot{\varepsilon}_z$ and the radial $\dot{\varepsilon}_d$ strain rates (Fig. 7):

$$\dot{\varepsilon}_c = \frac{2}{3}(\dot{\varepsilon}_z - \dot{\varepsilon}_d) \quad (2)$$

In which the axial and radial strain rates are defined as:

$$\dot{\varepsilon}_z = \frac{d}{dt}\left(\ln\frac{L}{Lo}\right) \quad (3)$$

$$\dot{\varepsilon}_d = \frac{d}{dt}\left(\ln\frac{D}{Do}\right) \quad (4)$$

Where the sample length L and diameter D are related to reference values Lo and Do measured after pre-sintering at 1100°C. The calculated values of $\dot{\varepsilon}_c$ for a 0.2 N load (Fig. 7) greatly exceed values of densification rates (Fig. 6), mainly during the first 30 min of sintering time. In general, creep appears to be the most important mechanism during the loading dilatometry measurement of the Poa clay. These creep values are high in comparison to published data [7,11] for glass materials, although it assumed the absence of a liquid phase in the Poa material.

This point is related to the particular nature of all clay-transformed materials at high temperatures, such as Poa clay. Above 650°C, they are amorphous material [15], which favour creep. A progressive structural reorganisation of the material took place as the temperature

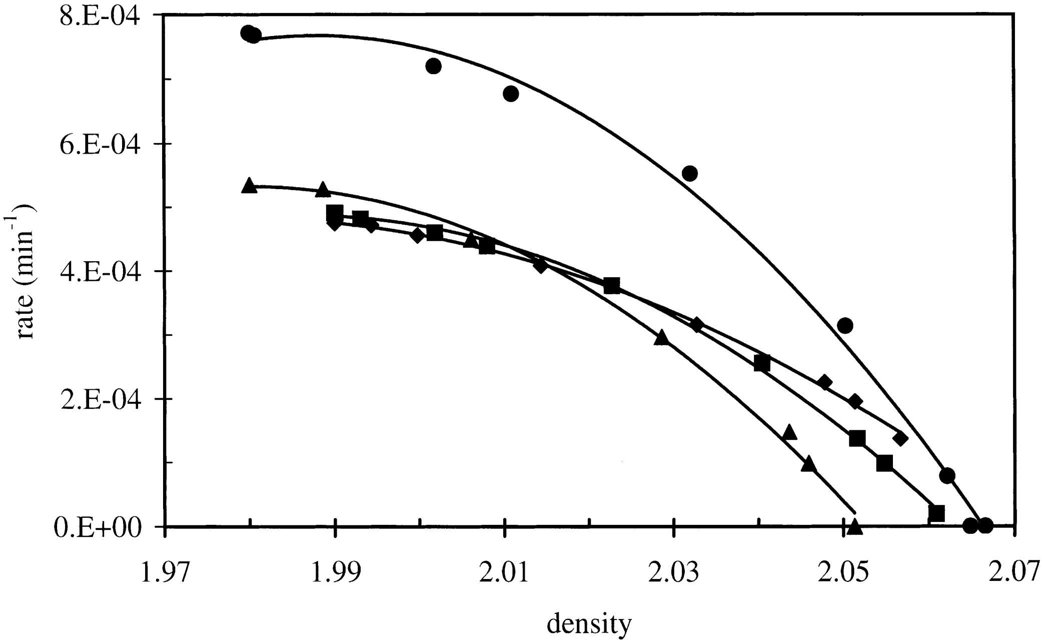

Fig. 6. Densification strain rates versus density for two pre-firing heating rates and for the two loads used. (◆): 3°C/min, 0.1 N; (▲): 10°C/min, 0.1 N; (■): 3°C/min, 0.2 N; (●): 10°C/min, 0.2 N.

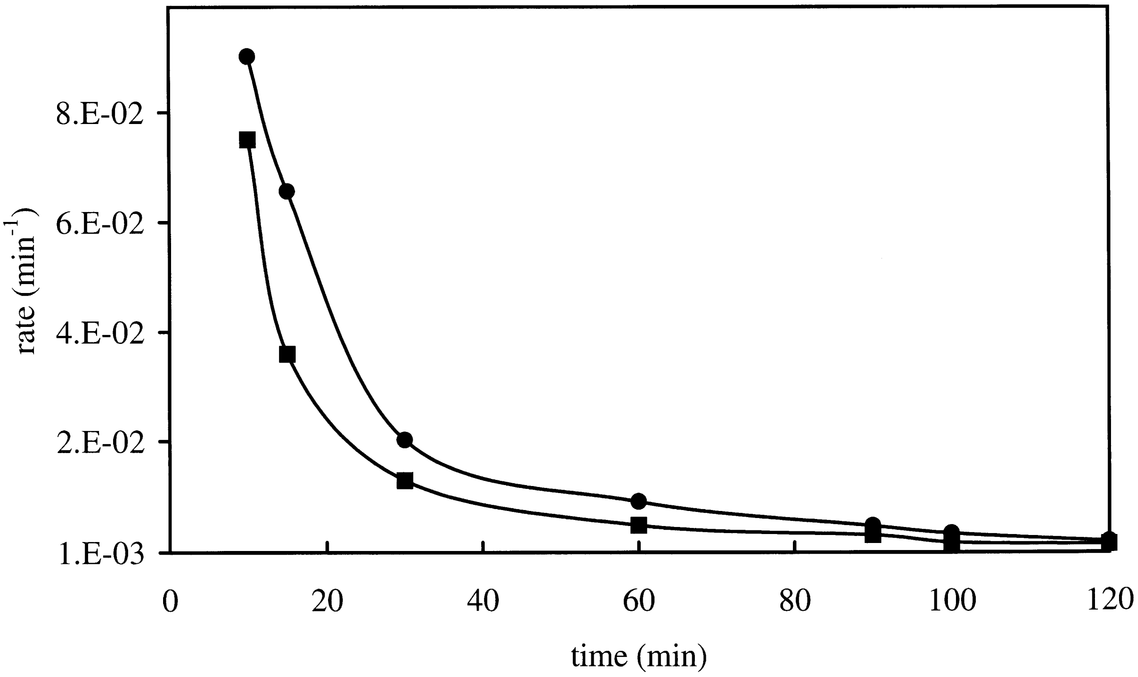

Fig. 7. Creep strain versus time when the load and the pre-firing heating rate varies. (■): 3°C/min, 0.2 N; (●): 10°C/min, 0.2 N.

increases. The extent of this latter phenomenon is limited by a rapid heating [16,17] which should favour the large creep comportment of materials preheated at high firing rates.

As in many studies, we pointed out the complex sintering mechanism of a clay material. These behaviours can be related to intrinsically material behaviour at high temperatures, but also to microstructural effects related to the preferential shrinkage of clay agglomerates and the role of large pores. It is too soon to propose a specific sintering mechanism, but some interesting features should support future discussion.

In that way, it has been shown in Fig. 1 that the Poa clay densification against temperature is significant when the temperature varies continuously above 1050°C. In this temperature range, the very large densification is not associated with the presence of a liquid phase but rather to mullite formation, the quantity of which is low. Even though this crystallisation induces a local volume densification, its extent should not be sufficient to generate the observed densification. But during an isothermal sintering at 1120°C, we showed that the shrinkage is very limited. The density characteristics tend to limit values after 2 h and the strain rate curves tend to zero.

It appears that the sintering process is activated mainly by the temperature but not by the firing time. Therefore, mechanisms associated with solid state diffusion should be proposed.

This is supported by the high specific surface of the predominant amorphous phase and by the existence of a remaining order resulting from the parent phase [18], which is a phyllosilicate phase.

The latter particularity is pointed out on Fig. 8 when oriented samples are sintered at the two heating rates. Furthermore, it is shown in Fig. 9 a larger face to face interaction, compared to the edge to edge interaction. The latter phenomenon seems to be associated with the preferential shrinkage of agglomerates and the presence of elongated large pores, which cannot be eliminated (Fig. 5).

An interesting feature of the face to face interaction is that it is enhanced by higher heating rates in the temperature range corresponding to the structural reorganisation (Fig. 9), i.e. 950–1080°C. In a similar way, it was shown for a kaolin raw material that the corresponding DTA exothermic phenomenon in the same temperature range is enhanced by a more rapid heating rate [17].

The preferential face to face interaction gives rise to a local cation reorganisation inside product agglomerates having an important crystallographic relation with stacked layers of the parent mineral. The activation energy for phase crystallisation is minimised when the structural organisation is limited, therefore between remaining layers of the phyllosilicate phase. Higher heating rates favour a lower crystallinity degree of the matrix phase [17], which support an improved diffusion mechanism between large interfaces. These effects are observed during the structural reorganisation stage, but also continuously influence the sintering process, as observed on Fig. 6 where densification strain rates vary with the pre-firing heating rate.

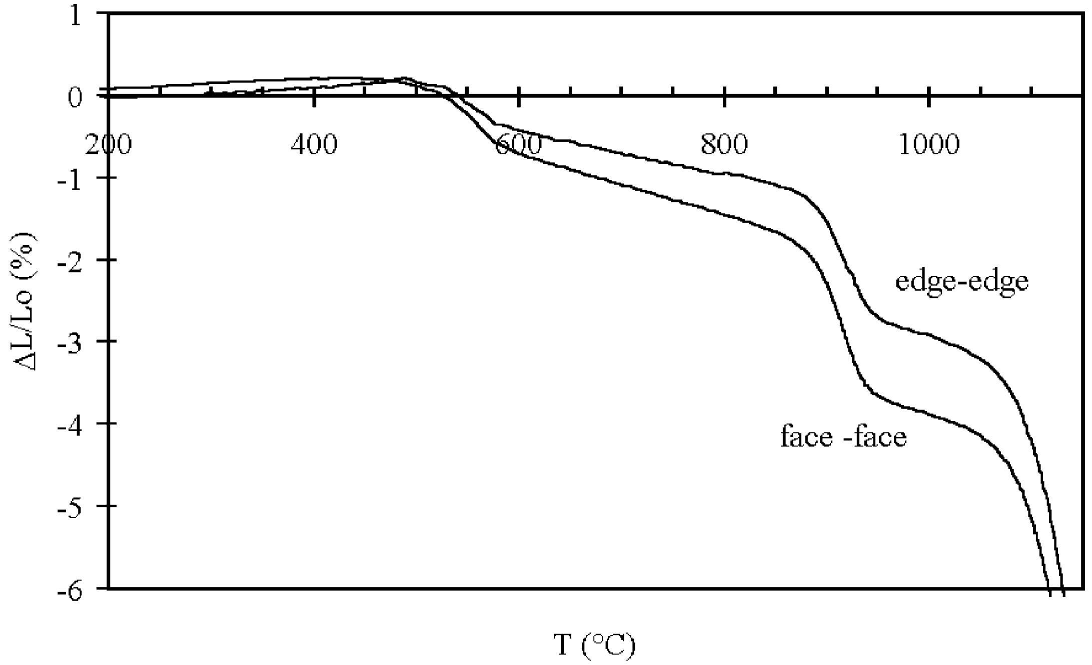

Fig. 8. Relative densification above 850°C of oriented samples, against temperature. Face to face and edge to edge densification curves.

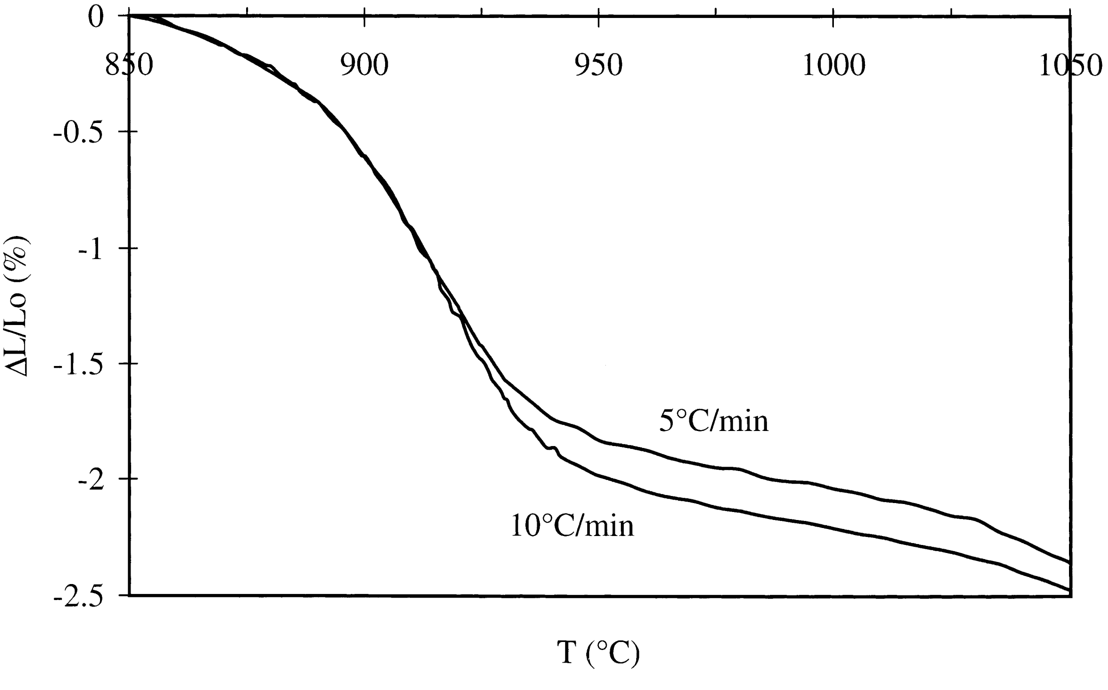

Fig. 9. Densification against temperature of face to face oriented samples in the 950–1050°C temperature range, when the heating rates vary.

5. Conclusion

The densification rate of the Poa clay material is high when the temperature increases, mainly above 1050°C. Nevertheless, during an isothermal sintering at 1120°C, the densification rate reduces to very low values. In that case, the loading dilatometry method highlights a significant creep, which can overcome the metakaolin shrinkage. The extent of this phenomenon is increased by a more rapid firing of the material. These results suggest a role of heating rate during the structural reorganisation of the material, favouring the formation of a weakly organised material above 1000°C. The existence of a solid state diffusion mechanism is also proposed, mainly at face to face contact of the remaining metakaolinite particles. It favours a preferential anisotropic densification of agglomerates and the presence of large pores, which limit the fired density of the material.

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