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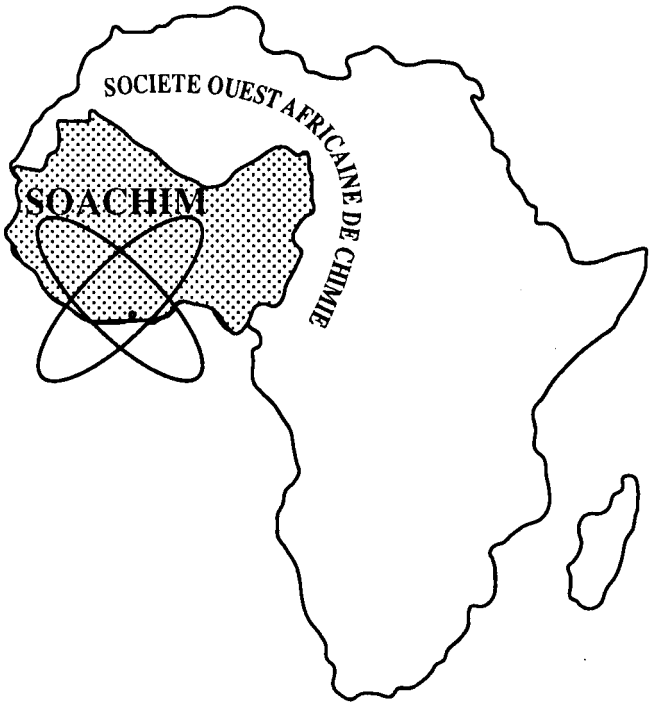

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Microstructure and mechanical properties of ceramic montmorillonitic clay

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Abstract: Natural clay SIT locally used in many traditional ceramic processes for materials manufacturing like bricks as building materials and pottery is the raw material of this study. The materials were prepared and sintered at different temperatures. Then the mechanical and microstructural properties were studied. From this survey it comes out that with a temperature programming of 1150°C for 1 h, natural clay SIT exhibits a good mechanical strength with an improvement of flexion in three points and increment in temperature associated with decrease in porosity. A look at the microstructure showed a composite microparticle material dispersed in a glassy matrix. Analysis of the porosity at the fracture surfaces was also carried out showing pores that are dimension and size varied.

Keywords: natural clay, terracotta, mechanical strength, microstructure, porosity.

Microstructure et propriétés mécaniques de céramiques d'argile montmorillonitique

Résumé: L'argile naturelle SIT, localement utilisée dans de nombreux procédés céramiques traditionnelles pour la fabrication de matériaux tels que les briques dans le domaine du bâtiment et la poterie est la matière première de cette étude. Les matériaux ont été élaborés et frittés à différentes températures. Les propriétés mécaniques et microstructurales ont été étudiées. Les matériaux élaborés et frittés à 1150 °C avec un palier final d'une heure, présentent une meilleure tenue mécanique. L'observation de la microstructure montre qu'elle est composite à l'échelle du micron montrant une phase granulaire disséminée dans une matrice vitreuse. Une analyse de la porosité au niveau des surfaces de rupture révèle la présence des pores de taille et de formes variées.

Mots clés : argile naturelle ; terres cuites ; tenue mécanique ; microstructure ; porosité.

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1. Introduction

The most important parameters which allow the use of tiles on construction sites are the flexion strength and the porosity. Both latter depending on the raw clay material is the mineralogical composition and the process of products elaboration. Generally both parameters are in relation. The flexion strength increases with decreasing porosity of the material. Studies have been carried out to explain the evolution of porosity and mechanical behavior during the heating step [1; 2]. The mechanical strength is also affected by the microstructure of the clay during the heating process. During this step, the porosity decreases giving out a formation of a liquid phase [3]. We worked on material that has a microstructure made up of individual particle then with consolidated one [4; 5]. Despite the diversity and complexity of these raw materials, we recorded a few publications in the literature [6 - 9]. Actually, much work is gradually being done as at now. The latest studies [10; 11] are related to the chemical and mineralogical characteristics of some clays of Burkina Faso and their possible applications. The use of clay for pottery and building is performed bytraditional techniques,where materials used are mostly sintered at relatively low temperatures. At these temperatures the clay materials are quite porous. For example, potters and low scale manufacturers use local clays with poor physical properties.
Studies earlier [12] about characterization of the clay that undergoes our investigation, showed a modifying parameter of the residual quartz.

Other studies didn't show the relation between the mechanical strength and the mullite content. We conclude that the mechanical behavior depends on porosity which depends in turn on the microstructure and this last depends also to mineralogical composition of basic raw material. The complexity and diversity of mineralogical composition of raw clay materials did not permit the compilation of results from one material to another one.

The aim of this work is to study the evolution of the microstructure and mechanical strength of montmorillonite, a raw clay material from Burkina Faso. The mechanical results have been correlated with the microstructure of heated tiles. The methods of image analysis were carried out to quantify the microstructural changes and the level of porosity.

2. Raw materials and experimental methods

2.1. Raw materials

The raw material used in this work and named was deposited in Sitiéna locality (10.36 ° North and 4.48° West, Burkina Faso).
The chemical composition show the predominance of SiO_2 (56.51 wt%) and Al_2O_3(23.24 wt%) and indicates then the alumino-silicate nature of SIT. It contains a relatively important content of alkali oxides (4.85 wt%) that are attributed to feldspars component in SIT. The high content of Fe_2O_3 (6.82 wt%) suggests the existence of structural iron in clay minerals and the presence of iron hydroxides as associated with minerals as shown Karfa and al [13].

The major identified phases in SIT are montmorillonite, quartz and albite [12]. To these important phases are added in small quantities illite, kaolinite and orthose. Illite and smectites promote the material (bricks, tiles and pottery) sintering at relatively low temperature. During the material elaboration process, smectites increase the plasticity of paste and improve the mechanical strength of dried and heated products. Feldspar component (albite, orthose) has fluxing properties and in connection with the quartz and other minerals at temperatures around 1050°C increase the formation of liquid phases. Kaolinite is more refractory and limits the spread creep at elevated temperatures.

2.2. Experimental methods

SIT was grounded until a particle size less than 100µm. Plates (12 x 5 x 1cm^3) obtained by uniaxial compacted with powder at a pressure of 15MPa, were dried for 24 hours at 40°C and heated during 1 hour in ambiant air at different temperatures (1000, 1100 and 1150 ° C) with 2.5 °C/min as the heating rate.

Rectangular specimens (length L = 47mm, width B = 8mm and thickness W = 6 mm) were cut into plates for mechanical tests using three-point bending. The testing apparatus is Instron type equipped with a load cell of 10 kN and is piloted with Bluehill 2 software. The cross head speed was 3 mm / min. The flexural strength was evaluated by the equation 1 [14].

$$\sigma_R = \frac{3}{2}\frac{LF_R}{BW^2} \qquad \textbf{(1)}$$

With F_R the applied force at rupture.

For tenacity measurement, specimens provided with a notch were tested by three-point bending. The tenacity K_{Ic}, was calculated from the maximum flexural strength bending σ_R in the configuration L/W> 4, with a length of the notch equal to a/W = 0.35 and using the equation 2. The factor Y depends

on the test configuration and the specimen geometry as shown in equation 3.

$$K_{Ic} = \sigma_R Y\left(\frac{a}{W}\right)\sqrt{a} \quad \textbf{(2)}$$

With «a» the length of the notch and $Y\left(\frac{a}{W}\right)$ the factor used to put the crack in an infinite medium.

$$Y = \frac{1{,}99 - \frac{a}{W}\left[1-\frac{a}{W}\right]\left[2{,}15 - 3{,}93\frac{a}{W} + 2{,}7\left(\frac{a}{W}\right)^2\right]}{\left[1+2\frac{a}{W}\right]\left[1-\frac{a}{W}\right]^{3/2}} \quad \textbf{(3)}$$

Y is a geometric coefficient in three-point bending [15].

For microstructural analysis, the polished and unpolished fractured surfaces of the specimens after three-point bending tests are examined with a scanning electron microscope (SEM). Carbon graphite was vaporized under vacuum on material surfaces before recording SEM images. For optical microscope observation the samples were coated with epoxy resin in vacuum under a fume hood. After polymerization, the samples were demoulded and then polished with SiC paper and with diamond paper at different grades. After rinsing and drying, the samples were directly used for observation under an optical microscope.

The porosity study was performed on the optical microscope binary image of fractured surface.

3. Results

3.1. Mechanical strength

The average values of flexural strength and tenacity for specimens heated at different temperatures are summarized in **Table 1**.

The mechanical strength improved with the increase of the firing temperature. At 1000°C, the specimen's breaking occurs at low strength (5.65 ± 0.19 MPa). This fragility is related to the low sintering temperature which does not promote the cohesiveness between grains and the silico-aluminous matrix. During the sintering until a certain temperature (around 1000°C), the decomposition and dehydroxylation of clay phases lead to the formation of gas, which during its discharge causes the formation of pores [3]. Above the critical temperature of gas formation, the porosity of the material decreases by the consolidation of specimen. At 1100 °C, the flexural strength is three fold the obtained values at 1000 °C. The obtained value at 1150 °C is higher than 1100 °C. The mechanical strength is enhanced by the formation of liquid phase provided by flux component. The liquid phase flow between the grains and reduce the porosity. This phenomenon increases with increasing firing temperature.

For tenacity measurements, the relative depth of the notch is a/W = 1/3. The measurements were not done on specimen sintered at 1000°C due to their relatively low flexural strength. Tenacity increases with temperature increasing and corroborates the flexural strength. This improvement reflects the structural changes induced by the increased energy in the material during sintering. The observation of the fracture surfaces by SEM will help us to consolidate our results over mechanical strength.

3.2. Microstructure

SEM images of the polished and unpolished fracture surfaces are presented in **Figures 1, 2 and 3**. At 1000°C, the image shows a less dense material as indicated by the strength results. At this temperature the material seems to be composed by isolated particles (clay phase and quartz) without liquid phase. At 1100°C, the SEM image shows the formation of important quantity of liquid phase showing the starting point of consolidation of specimen. The liquid phase formation, due to the action of heating temperature and flux components on the quartz, reduces the porosity. However, at this temperature the pores are in important quantity, large and connected. With the increase of firing temperature (1150°C), all the particle are embedded in the liquid phase and gives a better consolidated specimen with feeble quantity of unconnected pores.

SEM-EDAX analyses are given in **Figure 4** and **5** and the deducted chemical compositions are summarized in **Table 2**. The chemical composition shows the predominance of Al and Si in the two indexed zone. The Si percentage decreases with temperature increasing and shows the quartz dissolution to form mullite. The mullite formation is corroborated by the increase of Al percentage with the increase of temperature.

Table 1: Flexural strength and tenacity of specimens

Temperature (°C)	Flexural strength rupture (MPa)	Tenacity ($MPa.m^{-1/2}$)
1000	5.65 ± 0.19	-
1100	16.8 ± 1.4	0.45 ± 0.05
1150	21.18 ± 1.54	0.79 ± 0.08

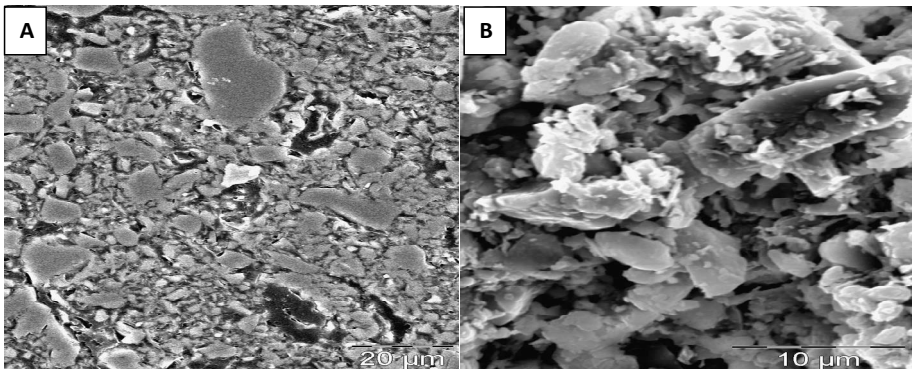

Figure1: micrograph of the fracture surface of SIT at 1000 °C:
(A) polished surface observed by optical microscope and (B) surface directly observed by SEM.

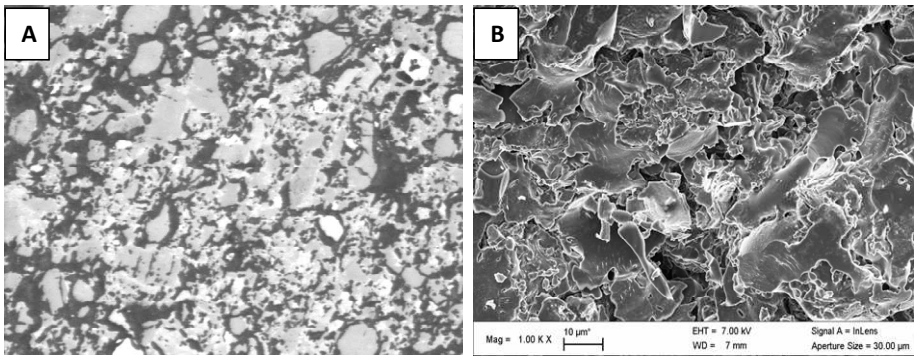

Figure 2: micrograph of the fracture surface of SIT at 1100 °C:
(A) polished surface observed by optical microscope and (B) surface directly observed by SEM.

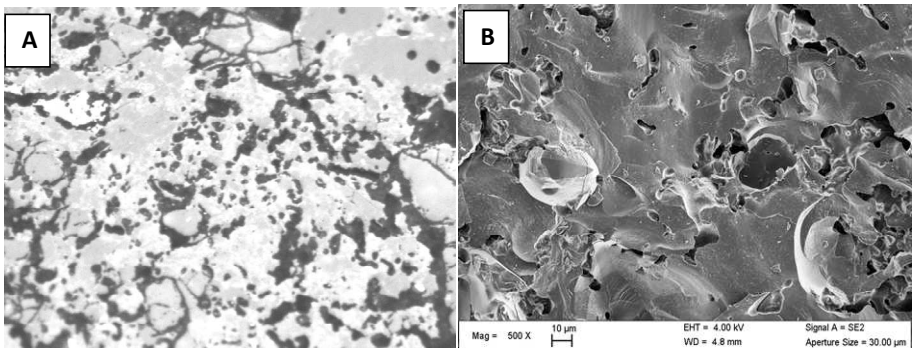

Figure 3: micrograph of the fracture surface of SIT at 1150 °C
(A) polished surface observed by optical microscope and (B) surface directly observed by SEM

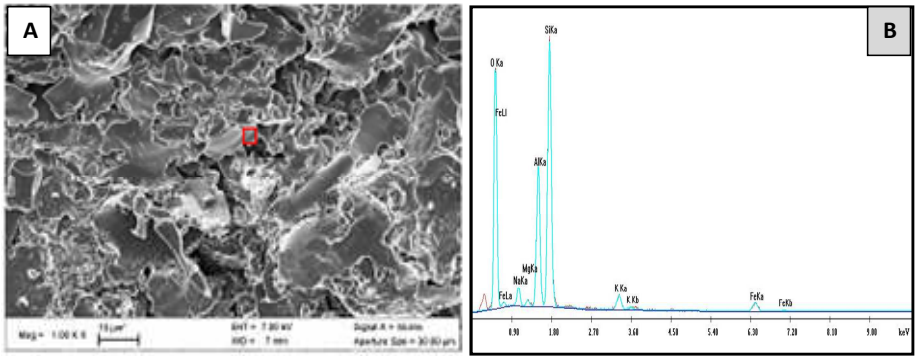

Figure 4 : EDAX analysis of a sample area of the clay SIT sintered at 1100 °C.
(A) SEM picture and (B) EDAX diagram.

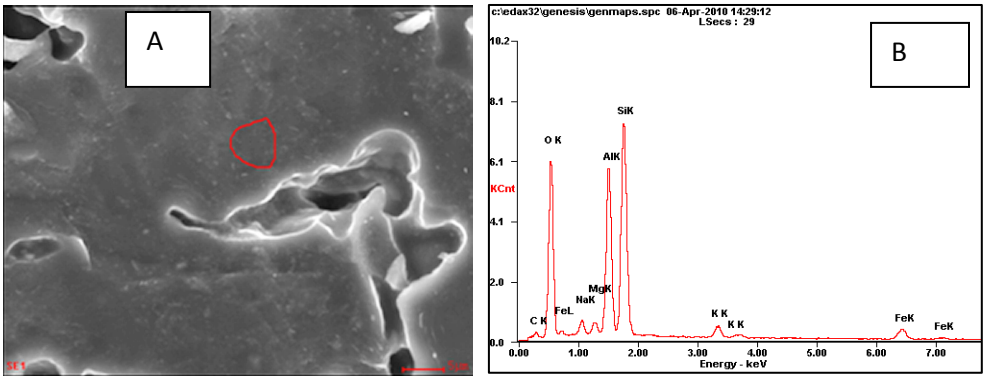

Figure 5 : EDAX analysis of a sample area of the clay SIT sintered at 1150 °C.
(A) SEM picture and (B) EDAX diagram.

Table2 : chemistry EDAX analysis zone specimen sintered at 1100 °C and 1150 °C.

Elements	Si	Al	O	Fe	Na	K	Mg	Ca	Total
1100°C									
% Wt	29.26	13.58	48.32	3.16	2.77	2.16	0.75	-	100
% Atomic	21.58	10.42	62.55	1.17	2.50	1.14	0.64	-	100
1150°C									
% Wt	26.94	19.05	42.79	4.97	2.29	2.02	1.46	0.49	100
% Atomic	20.62	15.17	57.49	1.91	2.14	1.11	1.29	0.26	100

3.3. Porosity by image analysis

Dekayir and Maataoui [16] have identified three types of pores according to the shape parameter SF defined by equation 4.

$$SF = \frac{P(x)^2}{4\pi S(x)} \qquad (4)$$

Where P = perimeter S = surface x = pore or mineral

The different pore forms according to SF value are presented on **figure 6**. The percentage of material porosity is determined according to their gray levels and is quantified according to equation 5.

Binarized images of polished fracture surfaces of specimen are presented by **Figures 7a** and **7b**. With 1100 °C, the image is composed by a great number of large gray corresponding to the pores. The three different form of pore are present, but the majorities are intermediate pore indicating that the sintering process at this temperature is not complete. With increasing of sintering temperature, at 1150 °C, the gray number and it sizes considerably reduce. The sintering of specimen at this temperature is more advanced than the previous temperature.

Vitrification is one of the sintering mechanism steps of ceramic clay. During the sintering, glassy phase is created as a result of complex reactions. The glassy phase volume, chemical composition and viscosity change with temperature. The flow of this phase in the specimen pores, increase the material shrinkage at the macroscopic level. The evolution of pore volume, bulk density and pore size distribution influence more the mechanical characteristics than the mineralogical composition evolution due to phase transformations [15].

$$\phi(\%) = \frac{\sum_{i=1}^{i=x} S_i}{S_{image}} \times 100 \qquad (5)$$

S_i = pore area (i) ; S_{image} = image surface

3.4. Mineralogical analysis by XRD

X-ray diffraction pattern of sintered specimens are shown in Figure 8. For the three sintering temperature, the materials consist of quartz, mullite, magnesium silicate and aluminium. At 1100 °C and 1150 °C, the amount of quartz, magnesium silicate and aluminium decreased, while the mullite quantity increases. Mullite seems to be abundant on specimen sintered at 1150°C than on any other. The mullite formation is responsible for mechanical properties improvement with temperature increasing.

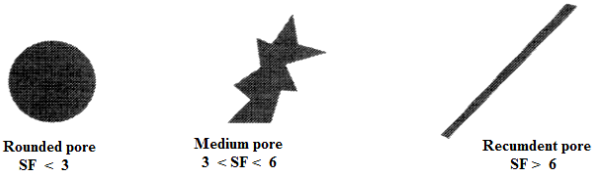

Figure 6 : Basic forms used for the classification of pores[16]

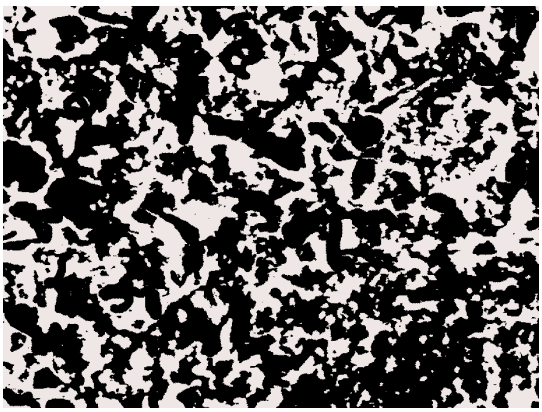

Figure 7 a : Image analysis of an area of a test piece of clay SIT sintered at 1100 °C. Porosity rate: 45%

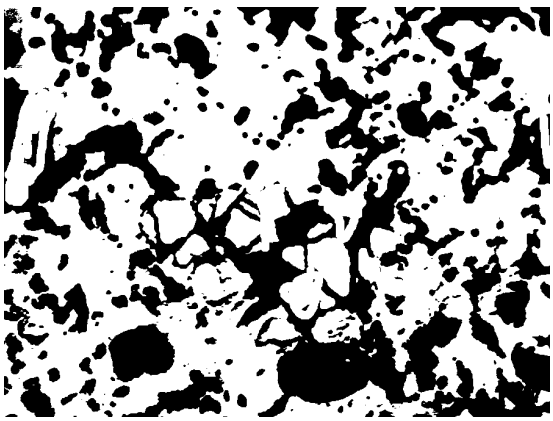

Figure 7 b: Image analysis of an area of a test piece of clay SIT sintered at 1150 °C. Porosity rate: 32%

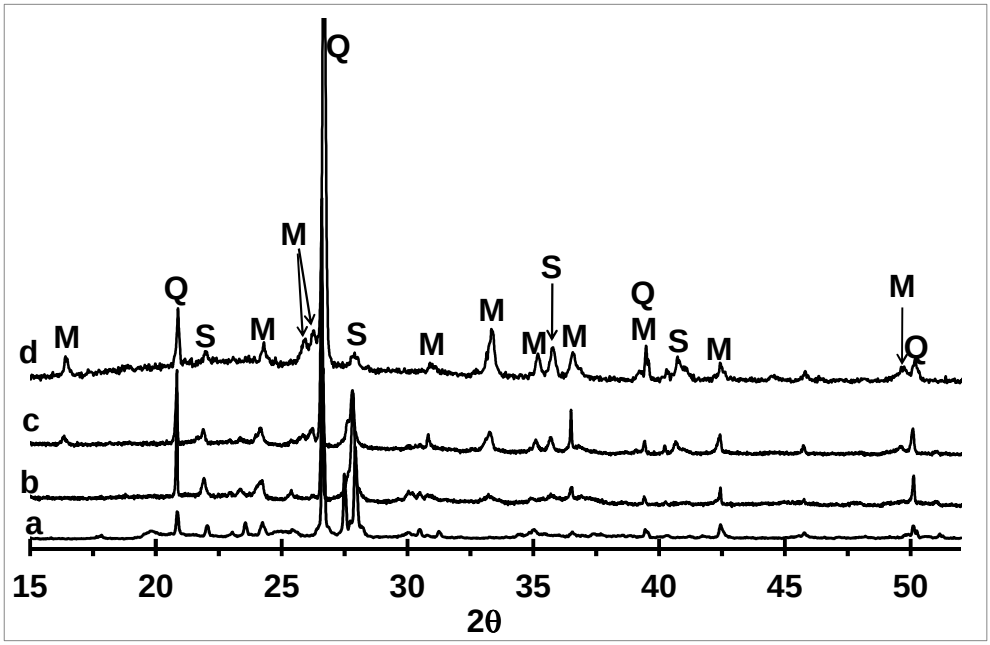

Figure 8: X-ray diffraction pattern of raw clay SIT (a) and clay SIT sintered at 1000 °C (b) 1100 °C (c) and 1150 °C (d). M = mullite ($Fe_{0.2}Al_{2.05}Si_{0.75}O_{4.88}$) S = magnesium silicate and aluminium ($Mg_2Al_4Si_5O_{18}$), Q = quartz (SiO_2)

4. Discussion

The complexity of the microstructure of ceramic clay requires the use of multi-technical approach to identify the link between the chemical compositions and mineralogy on the one hand, and both microstructure, mechanical properties on the other hand [17].

The study shows the significant increasing of mechanical properties with sintering temperature. The bending strength is correlated with tenacity values.

The SEM image of fracture surface of material sintered at 1000°C (**Figure 1**) reveals a heterogeneous structure with pores showing size from 2 to 3 microns. There are also amorphous phase and individual particles probably corresponding to quartz. The other materials sintered at 1100 °C and 1150 °C (**Figures 2 and 3**) are well consolidated due to the formation of the liquid phase during sintering and cooling steps.

A good starting point for the multi-scale structure of the materials is the glass phase matrix, which occurs at micrometric scales by neo-mullite crystals form and other mineral accessories phases. SEM- EDAX microscopy analysis of fractured surface (**Figures 4 and 5**) revealed the presence of Si and Al as the essential components. The crystals were hosted by an amorphous alumino-silicate phase with addition of alkali oxides (**Table 2**).

Concerning the image analysis, we found that all the forms of pore described in **Figure 6** are even more complex at multidimensional scale. The matrix and the porosity form a porous structure whose behavior under strength stress increases the microcracks at the macroscale and reduces the performance of fired specimen. This is most felt in

sintered materials at 1000 °C as compared to other temperatures. This mechanism explains well the results of three-point bending tests and tenacity.

Depending on the process temperature and the morphology, the primary structure of the specimen may have scattered granular morphology or a continuous matrix with inclusions pores [17]. The granular morphology is typical of specimens heated at 1000 °C, and the continuous matrix with inclusion pore is characteristic of higher temperatures, 1100 ° C and 1150 ° C. These two morphological forms are intrinsically linked to the porosity which can occupy up to a third of the whole material [17].The pores can be reduced by the formation of glassy phases because the sintering proceeds by a mechanism of viscous flow [18].

Remaining pores are most often isolated between the agglomerated grains. The movement of grain gaskets, fast at the beginning of sintering [19] helps to trap the pores. Simultaneously, it appears that the coalescence process of the fine pores leaves a large amount of pores of large size. Ultimately, it seems that the elimination by diffusion of pores trapped in the material or pores with large size to be mobile can limit the final densification of the material.

We have noticed a continuous evolution of the solid phase and decreasing of pore area at 1100 ° C there, which intersects the qualitative observations by SEM (**Figure 1, 2 and 3**). These measurements indicate that the decrease in porosity (**Figure 7**) is related to the formation of new crystalline phases (**Figure 8**). The depletion of the surface porosity is resulted from the formation of a crystalline structure but also from the flow of the liquid phase that ~~is~~ reduced the number of pores and / or their form. Reducing the size of the pores by volume as the surface ensures the cohesion of the material and allows it to resist crack propagation and the applied load. This explains the improving three flexion strength and toughness as a function of sintering temperature (**Table 1**).

5. Conclusion

We conducted in this paper, an approach linking the mechanical behavior of materials in terracotta from local clay of Burkina Faso as to the microstructure or mineralogy. Other aspects of the microstructure, such as grain structure (grain size, recrystallized fraction) or characteristics around the grain gaskets (especially areas denuded of precipitate) may have an influence, but it is very difficult to distinguish them from that of the other parameters. However the fired materials at 1100 ° C agree best in the context of energy-cost properties: it allows us to continue the work by associating clay SIT to other natural mineral raw materials.

Acknowledgments

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