Thermal Behaviour of Kaolin of Tamazert (Algeria) Deposit

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Kaolin from Tamazert deposit in the north Algeria was used in this study. The physical and chemical properties were determined by the performance of several analyses as well as the X-ray fluorescence, X-ray diffraction, thermal behaviour (ATD, TG), dilatometric and granulometric distribution. The study of ceramic behaviour as function of firing temperature has been investigated by shrinkage, adsorption both density and mechanical tests after gradually increasing from room temperature to 1500 ºC. The modification of the structure of the raw material samples has been observed after fining and the crystallization of mullite and amorphous silica phase were confirmed by scanning microscopy SEM and evaluated by XRD. The suitability of kaolin for ceramics process was discussed from the linear shrinkage, both density and open porosity. The amorphous phase content is varied from 27-34 % and the tests of flexion have been carried out as depending of temperature, revealed a suitable mechanical properties and the relationship between amorphous phase and sample properties. The adsorption rate was found to be about 35 %.

Key Words: Kaolins, Mullitisation, Sintering, Thermal treatment.

INTRODUCTION

Kaolin is present in many industrials process in Algeria, such as ceramic materials industry (fire-clays, whitewares) and coating and pigment filler for paper and building materials. Kaolin is collected from the Tamazert deposit which have a great reserve and is situated at 70 Km from Constantine town in the east of the country[1]. The present work is a part of a research program undertaken in order to valuate the kaolin raw material which is marketed by the Algerian company of kaolin. It focuses on the chemical and physical phenomena involved during the kaolin thermal transformations. The kaolinite is the main mineral component of the kaolin. It also contains minor phases like quartz, mica and impurities such as iron[2]. Theoretical formula of kaolinite is $Si_2Al_2O_5(OH)_4$ most often presented in the form $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$. It may have highly ordered or disordered structures[3], according to the contained crystalline defaults. Empirical relations have been established in order to evaluate these disorders. They are based on the intensity, the height and the shape of the peaks of diffraction band (hk$_0$). When the disorder increases in the plan (a, b), the correspondent lines become large and their intensity decreases. They may also form a whole without peaks. Hinckley[4] describes a crystallinity index HI, sensitive to all present defaults in the plan (a, b) and defined from the peaks of the bands (02l) and

(11l) by the expression: $HI = (A + B)/A_t$, A and B are reflexions (1-10) and (11-1), respectively according to local background of the band (02l) and (11l). A_t is the height of the peak (1-10) measured from continuous line existing out of these bands.

The shape and positions of the peaks (00l) of the diffraction spectra of the kaolinite may also be used to estimate the defaults number of implement through the c axis. These reflexions are sensitive to the thickness of the coherent areas in the direction [001]. The position of the peaks (00l) and their width, namely (001), depend on the distribution law of the number of sheets. It was proved the relationship between the evolution of the crystallinity index and the number of the structural defaults present in the plan (a, b) of different kaolinite at each time[5].

Kaolinite firing induces numerous complex structural and microstructural transformations leading to the formation of mullite and a silica phase, mainly in a amorphous form, according to the following reaction[6]:

$$3(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O) \rightarrow 3Al_2O_3 \cdot 2SiO_2 + 4SiO_2 + 6H_2O$$

The main product phase after firing kaolin is the mullite which is, thus, an important constituent in refractories, whitewares. Many investigations have concerned structural modifications that occur during the raw material transformation to metakaolinite, spinel Al-silicium and to mullite. The metakaolin and spinel Al-silicium phases showed small order

TABLE-1 PHYSICAL CHARACTERISTICS OF KAOLIN							
Oxides	Al_2O_3	SiO_2	Fe_2O_3	CaO + MgO	$Na_2O + K_2O$	TiO_2	LF
KF3	32,94	48.10	2.53	0.43	2.82	–	1260
KGa-1b	39.70	42.20	0.20	–	0.03	2.4	13.78
KGa-2	38.50	43.90	1.10	0.03	0.06	2.1	13.77
K bio	36.70	47.10	1.16	0.21	2.28	0.07	11.80

in crystal structure. The mullite crystallizes above 1000 °C. The amorphous phase often surrounds the formed mullite. The mechanical behaviour of firing materials is governed by the amorphous phase that is important for ceramics materials, with a high mechanical strength resisting to cracking initiation[7,8].

The selective dissolution in hydrofluoric acid is a simple and so used method for quantifying the silica amorphous phase. The principle consists of estimating the dissolution kinetics in an aqueous solution of hydrofluoric acid. The amorphous dissolution rate is more rapid than that of the crystalline phases[9]. Amorphous silica, with a relatively porous structure, dissolves faster than silica quartz. The dissolution reaction is:

$$SiO_2 + 6HF \rightarrow SiF_6H_2 + 2H_2O$$
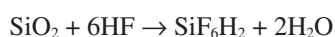
This studies deal with physical and chemical phenomenon occurring in the transformation of kaolin; growth of mullite in kaolin based ceramics and following properties evolution during the sintering of kaolin powder compacts.

EXPERIMENTAL

Raw materials: In this work, kaolin used is designated by "KF3". Two rich kaolinite, as KGa-1b, KGa-2 from Georgia deposits in the USA and the kaolin "K bio" (French), are used as standard minerals in the study of crystallinity. Their chemical composition, the fire mass loss "LF" are indicated in Table-1.

Chemical composition (Table-1), was obtained from a sequential fluorescence X spectrometer type SIEMENS. SRS. 300. The phase identification was carried on an X-rays diffractometer (Philips PW1710,) with a radiation of Cu K_α λ = 1.541 Å. Thermal analyses was realized with LINSEY equipment at 5 °C/min under atmosphere air. We used a laser granulometer type Siroco 2000 was used to observe the granulometric distribution.

A device of type Flow Sorb II 2300 was used for measuring specific surfaces. The principle of functioning is based on the B.E.T method (Brunnauer-Emmet-Teller) which analyzes the isotherm of adsorption of a gas on a solid. Powders have previously degassed at 200 °C under scanning of nitrogen during 4 h. Specific area results are shown in Table-2.

TABLE-2 SPECIFIC SURFACE AREA AND DENSITY OF KAOLIN POWDERS				
Sample	KGa-1b	KGa-2	KF3	K bio
Specific surface (m^2/g)	11.8	17.92	14.466	15.466
Absolute density ± 0.01 (g/cm^3)	2.52	2.60	2.66	2.65

The samples shaping was made by uniaxialle dry compaction with a pressure of 25 MPa. The samples have a cylindrical form of 30 mm diameter and 50 mm height. The green samples were dried and fired during 1 h at 100 ºC. They are fired from

room temperature to 1500 °C. Others KF3 samples are shaped, as parallelized 10 mm × 5 mm × 5 mm, dried for 2 h at 100 ºC. The kinetic agglomeration of these samples was measured with a differential dilatometer (DIL-24) from 20-1500 ºC, in air atmosphere.

The morphology of grains constituting the raw materials has been observed by the scanning electronic microscopy (SEM). A drop of a suspension of powder scattered is put on a sample carry, then dried and metalized to Au/Pd. The resulting micrographics give information about the aspects of different powders. The amorphous phase of product is attacked by an HF acid corresponding for dissolution before observation by SEM of mullite grain.

In order to quantify amorphous phase, fired samples were crunched to obtain finely grains. This powder was cured in 2 % of hydrofluoric acid solution (1.10 mol/L), for different dissolution periods in order to measure the mass loss. A powder sample of 10 g was mixed with 250 mL of HF solution. The dissolution kinetic of the powder (mass loss *versus* attack duration) is made to deduce the amorphous phase rate.

Bulk density was measured by Archimedes's method and the absolute density by using an automatic helium pycnometer (ACCUPYC 1300). Mechanical tests were evaluated from tests using prismatic samples 50 mm longer, by technique of three-point flexion, at room temperature. The deformation rate was 0.5 mm/min.

RESULTS AND DISCUSSION

Characterization of kaolin mineral: The chemical analysis shows a mass ratio SiO_2/Al_2O_3 = 1.47 for KF3. That is higher than for a pure kaolinite (1.178). It is due to the presence of quartz. The high percentage of K_2O suggests a micaceous phase. Iron present in considerable quantity confers a yellowish colour on KF3. The mineral phases revealed for kaolin by X-rays diffraction are kaolinite, mica and quartz (Fig. 1). Chemical analysis coupled to the X ray diffraction, done the mineralogical composition presented in Table-2. KGa-1b and KGa-2 kaolin are so rich kaolinite. Both KF3 and K bio are constituted with same minerals phases. KF3 is the lowest in kaolinite.

The kaolinite plates of the kaolin KF3 are gathered in irregular clusters (Fig. 2). The intermediate size of the plates of hexagonal form, is from 1-3 µm for the length and *ca.* 0.2 µm for the width. The surface of the irregular plates shows distortions. This morphology is generally corresponding of kaolinite fairly crystallized[10]. KGa-1b is constituted in regular and hexagonal homogenous clusters signed of so ordered structure. Kbio shows structure less deformed than KF3.

The chemical analyses by energy dispersion of X-rays (EDS) have not allowed to detect in the kaolinite clusters the presence of other elements only aluminium, silicon and oxygen
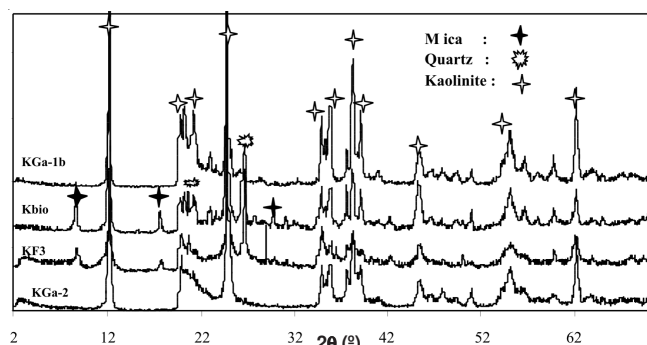
Fig. 1. X Ray diffraction patterns of kaolins KF3 and references powder
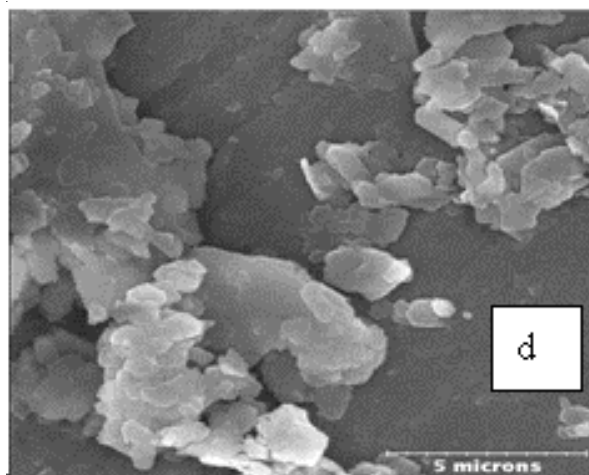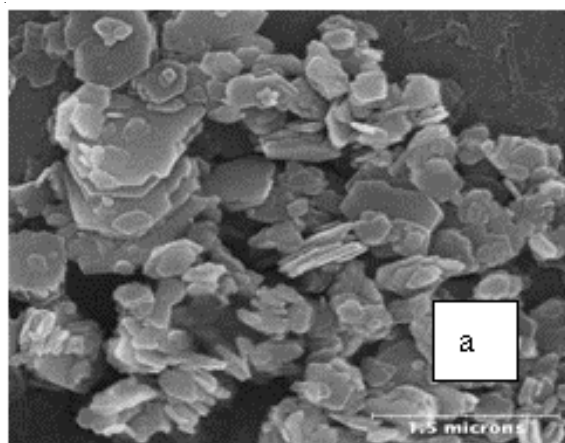

Fig. 2. Morphology of the kaolin particles (a, b): clusters of particles KF3. (c) kaolinite KGa-1b. (d) clusters of particles K bio

are identified. The contents of iron, potassium and sodium were always lower than the limit of the analysis sensitivity EDS (-1 %). Fig. 3a presents a line profile of (001) of the kaolinite contained in the kaolin KF3 and those of references. Fig. 3b shows the bandage (02, 11) spectrum of X-rays diffraction.
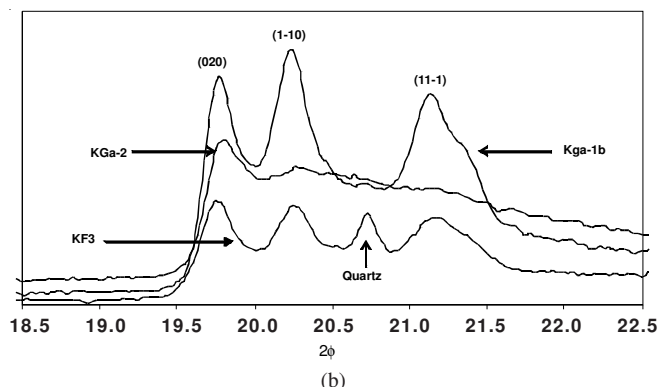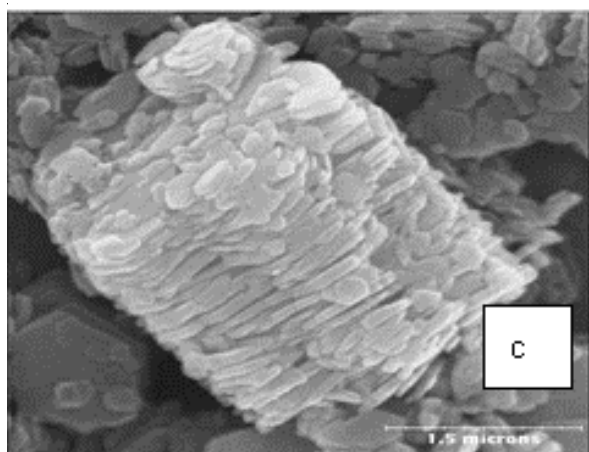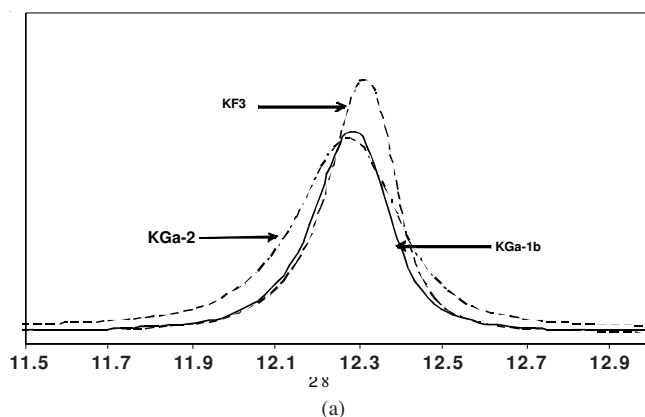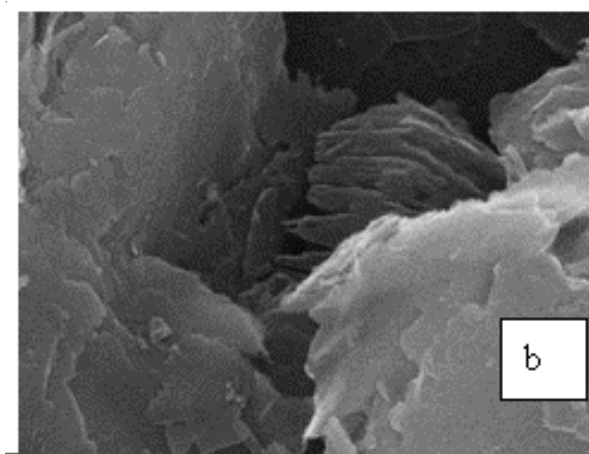

(a)

(b)

Fig. 3. (a) Profile of line (001) of the kaolinite contained in KF3 and those of references; (b) bandage (02, 11) of spectrum of X-rays diffraction

It is well know that the behaviour during a rise in temperature of the kaolins depends on the degree of order of its kaolinite and its content of micaceous phase, so the existing order on the level of these minerals was studied. It is a

comparison to the degree of crystallinity of the kaolinite contained in KF3 with the kaolinite contained in the matters used like references. The crystallinity of kaolinite is developed starting from the index of Hinkley[4]. The bands (02, 11) of the spectrum of the X-rays diffraction of the reference samples and those of the two studied varieties of kaolin, are used for the calculation of the degree of crystallinity estimated starting from the index of Hinckley. They have degrees of crystallinity and chemical compositions (especially their content of transition metals) very different. Kga1 contains kaolinite crystallized very well, Kga2, although to kaolinite 97 % has a very small degree of crystallinity. The indices values calculated starting from the spectra, are characteristic of kaolinite of very well crystallized in weakly crystallized (Table-2).

The basal distance between the layers of kaolinite, increases with the number of defects of stacking[11]. The reflexion lines of the (001) become less fine when the disorder increases. The comparison of the widths to semi height obtained for the Kga1 kaolin, kaolin bio and Kga2 shows a fall of the degree of crystallinity observed for Kga2. This fall results in a disorder in the stacking of the plans along the axis (001)[5]. When the disorder increases in the plan (a, b), the corresponding lines become broader and their intensities decrease and can even constitute a whole without distinct peak. There, the results concerning the number of layers per coherent field of the kaolinite of the KF3 kaolin indicate that the order in the stacking of plans along the axis (001) approaches kaolinite weakly crystallized. The temperature of deshydroxylation is strongly decreased in the case of kaolinite with small degree of crystallinity.

Thermal analysis of kaolin KF3: The main part of the mass losing (10 %) occurs in the interval of temperature between 400 and 700 °C (Fig. 4). This phenomenon is associated with the elimination of the hydroxyl groups of kaolinite during the formation of the metakaolin and corresponds to a weak reduction in the interlayer distance because of endothermic deshydroxylation of kaolinite approximately with the formation of the metakaolin. The amplitude of this shrinkage is insensitive with the kinetics of the heat treatment.
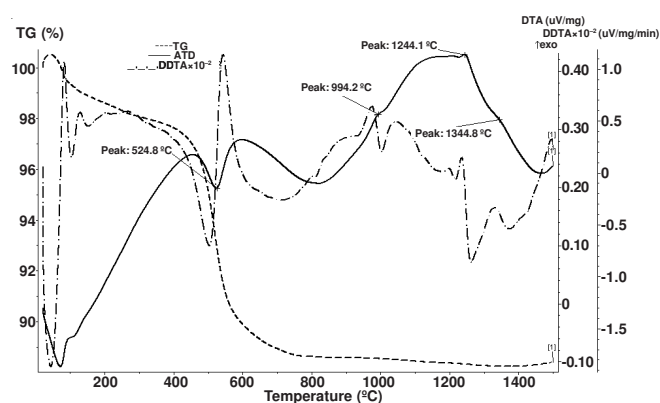
Fig. 4. Thermal analysis of KF3

The transformation of kaolinite into metakaolin is always completed towards 650-700 °C. The mass of the sample continues to decrease until 1000 °C, because the deshydroxylation of muscovite contributes to the loss of mass between[12] 700 and 1000 °C. This phenomenon would be also due to the elimination of residual hydroxyl groups. There still remains 10 % of hydroxyl OH present in the metakaolin just after its formation[6]. The deshydroxylation of kaolinite and the decomposition of the metakaolin are responsible, respectively for the endothermic peaks observed at 569 °C for the KF3 kaolin and for the exothermic phenomenon occurring with 990 °C.

A transformation associated with the first exothermic peak is observed (Fig. 4), in the range of 990-1000 °C. The exothermic peak generally attributed to the mullite formation known as secondary is observed around 1244 °C. The derivative shows the existence of this change. The cristobalite formation is responsible for a third exothermic peak detected around 1357 °C. The results of the analysis by thermal dilation made by 10 °C/min in the parallel and perpendicular directions with regard to the mould of casting are presented (Fig. 5). The global withdrawal is much higher in the perpendicular direction of platelets plans. This evolution is justified by the specific texturing of the samples. Such result may be due to the water content removing.
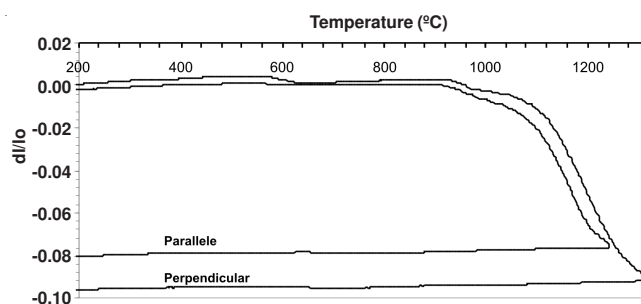
Fig. 5. Shrinkage in the parallel and perpendicular directions to kaolin layers

In the shrinkage related to the deshydroxylation of kaolinite, the elimination of water of constitution corresponds to a weak reduction in the interlayer distance because of endothermic deshydroxylation of kaolinite. It occurs at the temperatures range between 490 and 550 °C approximately with the formation of the metakaolin. This water loss is independent to speed of heat treatment. The texture of the samples implies a reduction in the interlayer distance in the perpendicular direction to the plates.

The second shrinkage is observed at approximately of 920-1000 °C. In this interval of temperature, the metakaolin decomposes in an exothermic way. The shrinkage as well as the heat released during this transformation is strongly dependent on the speed of the thermal treatment. However, the shrinkage begins at lower temperature than that from the exothermic phenomenon. It also intervenes during the structural reorganization which precedes the transformation by the metakaolin. This reorganization would be in connection with segregation[13] in fields rich in Al or in Si. The difference between the beginning of the shrinkage and the beginning of the exothermic phenomenon is the most important as the speed of heat treatment is raised and thus that the metakaolin is disordered.

The variation observed between 1000 and 1150 °C is practically independent because there is no liquid phase, therefore not of creep. A zoom of the dilatation curve of KF3 starting

TABLE-3
MINERALOGICAL COMPOSITION OF KAOLINS

Minerals	Kaolinite JCPDS: 00-006-0221	Mica	Quartz JCPDS: 01-083-2466
KF3	70 %	20 % (illite) JCPDS : 00-026-0911	10 %
KGa-1b	96 %	–	≤ 1
KGa-2	97 %	–	≤ 1 ± 0.1 %
Kbio	75.55	18.2 (muscovite)	5

from Fig. 5 indicated on Fig. 6 represents this field. This variation borders the 3 %, in a field where the liquid phase is not detected. In the argillaceous matters, a liquid is more likely to be formed during cooking. In the case of the kaolin, it could result from the phase mica alone (Tsolidus from an ideal mica = 1140 °C) or interaction between minerals of the kaolin (Tsolidus of a homogeneous mixture = 985 °C).
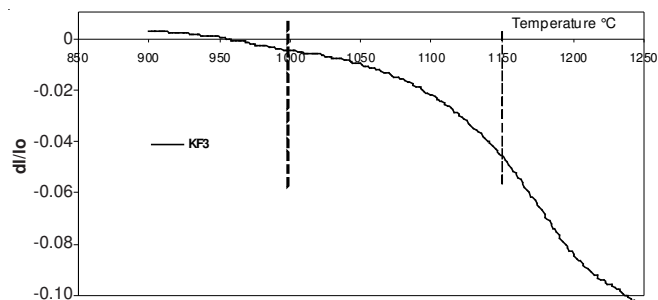

Fig. 6.   Zoom over shrinkage observed on the parts between 900 and 1250 °C by dilatometry

TABLE-4
INDICES OF HINCKLEY CALCULATED ACCORDING
TO THE SPECTRA OF THE BANDS (02.11)

Sample	Index [31]	Experimental index
KGa-1	1.03*	1.03
KGa-2	0.34*	0.44
K bio	0.98*	0.97
KF3	–	0.90

*Index of Hinkley results from previous work of Castelein et al.[7]

Between 1000 and 1150 °C, the kaolin consists of an important amorphous phase rich in silica, material whose viscous flow is well known[14]. In addition, the various transformations undergone by kaolinite and the contact with other phases present in the kaolin are likely to support defects with the interfaces. The diffusion with the solid-solid interfaces of the type grain boundary is possible. Dilatometry showed that there exists a phenomenon of creep under low stress with the higher temperatures with 1150 °C due to the existence of a liquid phase. It is clear that the principal minerals do not react between them before the appearance of the liquid phase within the mica plates. It is as in this range of temperature as are created the particles from mullite. They develop in the amorphous phase resulting from the metakaolin. This crystallization of mullite will result in a reduction in the solid volume of matter. Indeed, the quantity of mullite formed in this range of temperature is strongly influenced by the speed of heat treatment. It would thus seem that a transfer of matter likely to be the cause of an elimination of porosity must be coupled to these dimensional variations.

Fig. 7 shows diagrams of X-rays sintered samples at various temperatures from 1100-1400 °C and detected mullite at high temperature. The results of XRD analysis confirm that sintered materials made of KF3 kaolin are converted into mullite (JCPDS 01-079-1457), quartz (JCPDS 200722) and rich silica amorphous phases. Primary mullite crystallizes from 1000 °C of the heat treatment, even in small quantity. Silica shows two different forms i.e., silica amorphous and crystalline phases (the quartz as free silica), combined with the impurities.
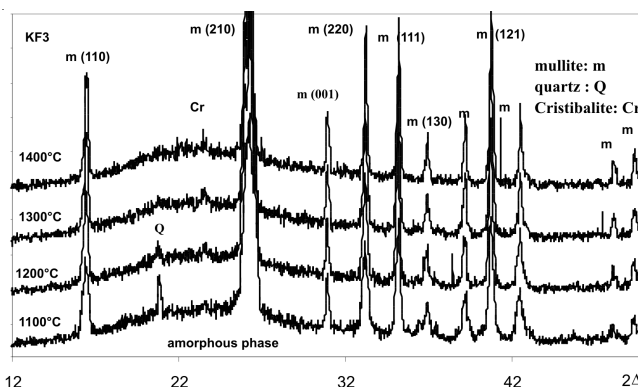

Fig. 7. X Ray patterns between 1100 and 1400 °C

At increasing temperatures, mullite is transformed into secondary mullite, at 1244 °C as also observed (Fig. 8). Presence of cristobalite (JCPDS 27-0605) is obviousness at temperature of 1350 °C. This phase appears with quartz transformation in presence of an important quantity of liquid phase. This transformation was also shown in Fig. 5. The cristobalite transformation takes place gradually. Therefore, the cristobalite intensity peak ($2\theta = 21.68$) diminishes when the firing temperature increases from X-ray spectrum made at 1400 °C and disappear. As the temperature increases, the dissolution of silica in the amorphous phase progresses and at 1450 °C the silica is totally dissolved.

As the temperature increases, primary mullite growth lightly and secondary mullite are dissolved in the amorphous phase caused by phenomena of dissolution recrystallization[15]. The difference between secondary mullite and primary mullite lies in the morphology and the face of the crystals[16]. Only the secondary mullite needles can grow bigger, while the primary mullite consists of acicular crystal aggregates. Any difference between the spectra of X-rays diffraction of the bothmullite does not detect, but differences in absorption into infrared were reported.

The amorphous phase dissolution kinetics enables to determine the amorphous content in the different samples. The results obtained are shown in Fig. 9. Amorphous phase content is about 28 % for the samples fired at 1300 and 1350 °C and increases up to 34 % for the samples fired at 1450 °C. This evolution results by the cristobalite dissolution in the amorphous phase as the temperature increases.
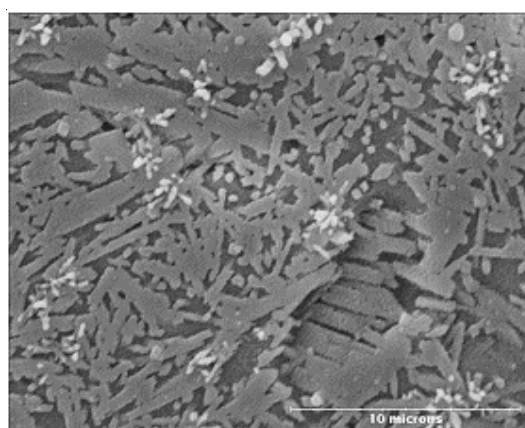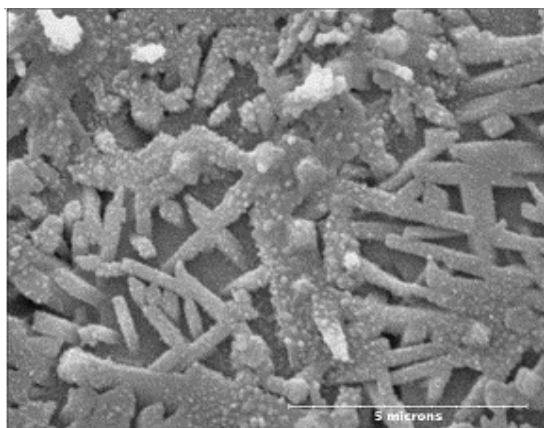
Fig. 8. Morphology mullite grains obtained from KF3 samples fired at 1400 °C
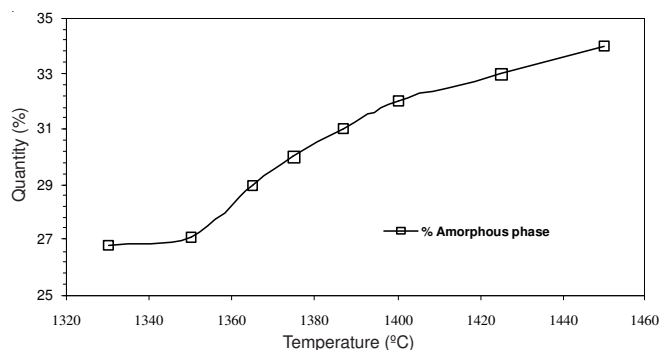

Fig. 9. Amorphous phase quantity between 1300-1450 °C

The chemical attack velocity is controlled by the reactions at the liquid-solid interfaces and by the powder grains microstructure. The corrosion occurs at the interconnected porosity where the amorphous phase may be present. The amorphous silica has a relatively more porous structure is more sensitive to the HF attack. Besides, the mullite can also be subject to a corrosion phenomena at a limited extend, as it is the case for other ceramics.

Technological properties: The measured bulk density and absorption rate obtained by the Archimedes's method, for the samples fired at different temperatures, are presented in Fig. 10. Bulk density are weakly before 1100 °C, increases between 1150 °C (d = 2.04 g/cm³) and 1300 °C (d = 2.69 g/cm³). At the firing temperature of 1350 °C, the densities remain nearly unchanged (d = 2.75 g/cm³) and a levelling settles starting

from 1350 °C. That can be explained by the fact that besides the sintering, which generally appears as the temperature increases, there are also transformation of cristobalite into an amorphous phase (d = 2.5 g/cm³) and an increase of mullite content that takes place simultaneously. These would balance the supposed densification. According to the previous report[14], the kinetics of diffusion in mullite is slow. This makes materials difficult to sinter and causes the excellent stability of the microstructure at high temperature. Furthermore, the density falls above 1350 °C. This is due to the presence of Fe_2O_3 in the kaolin powder. It was of 2.62 g/cm³ at 1500 °C. Fe_2O_3 is transformed into Fe_3O_4 and product of oxygen O_2 with the high temperature[8], of large pores are made, the density is thus decreased.
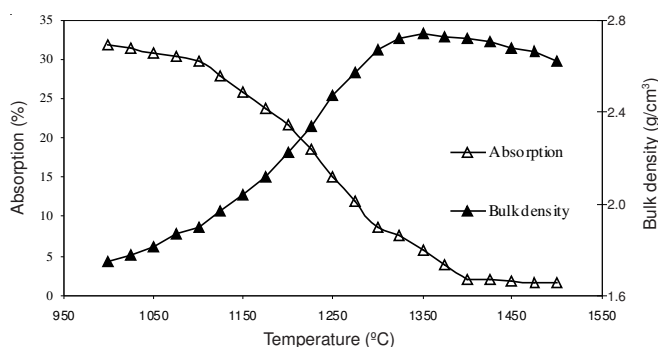

Fig. 10. Apparent density and absorption rate *versus* temperature

The intergranular liquid allows the displacement of the solid particles the ones compared to the others. A thickening is obtained under the effect of capillary forces. During the heat treatment, the liquid coming from mica phase develops and reacts with the other existing phases: the amorphous phase rich in silica, the mullite formed starting from the kaolin and quartz. As speed of heat treatment is slower, more this reaction is important and more the liquid phase is rich in silica. The existence of such a viscous liquid has a bad effect, that to make more difficult the movement of the particles solid the ones compared to the others.

In presence of liquid phase, mullite is formed in the form of needle of big size, (Fig. 8), following a phenomenon of dissolution-recrystallization[16]. These needles constitute an obstacle with the natural displacement of the solid particles. The larger their size is the more displacements will be difficult. A slow heat treatment allows this type of development. It does not support the withdrawal due to the capillary forces. It can on the other hand lead to the formation of a greater quantity of liquid phase.

The porosity represented by the means of absorption on figure 10 confirms the phenomena between 800-1400 °C. The metakaolin being porous, absorption starts to decrease only with the variations related to the phenomenon of growth of the crystalline phases, considering the big role which plays the pores. Taking into account the results of absorption, it becomes obvious that the dilatometric phenomena of shrinkages observed in lower part of 1150 °C do not lead to a thickening of compact of powder. Beyond this temperature, open porosity decreases.

The evolution of the flexural strength is represented by Fig. 11. The values of the flexural strength vary from as low as 40 MPa with higher as 120 Mpa and are related to those of the two other parameters of sintering: apparent bulk density and absorption. They increase slightly between 950 and 1150 °C: the porosity induced by the dehydroxylation is not completely eliminated by the formation from mullite. Beyond 1250 °C and until 1350 °C, the presence of liquid phase accelerates the mullite formation and allows a better solidity (Fig. 11). The density of the samples is sufficiently high to confer on the product a great mechanical resistance. The results obtained are due to the thickening which increases as the temperature increases. Beyond 1350 °C, is a field where the presence of liquid phase can influence negatively the mechanical resistance. The flexural strength (Fig. 11) of the sintered specimens at 1500 °C is lower than that of the pure mullite specimens, because they are due to the presence of a great quantity of amorphous phase. Firing temperatures of 1250 and 1300 °C are insufficient and firing at 1450 °C leads to an excess of amorphous phase. The firing temperatures between 1350 and 1400 °C generate optimal properties.
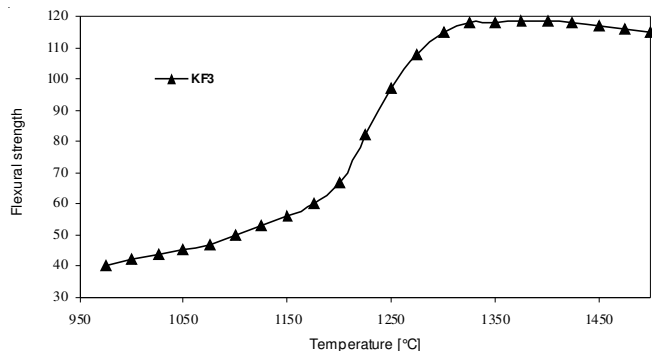

Fig. 11. Flexural strength *versus* temperature of sintering

Conclusion

In the present study, from the kaolins powder, KF3, rather slightly crystallized, the network kaolinite of KF3 is disordered compared to those standard materials. The indices of Hincley index and the form wide of half middle (00l) line diffraction, (FWHM), were not nearly of those obtained from well standard crystallized kaolinite. Thermal treatment for a strong shrinkage was notable to give a product with a perfect dimension in only one operation. For that, one often proceeds in two stages: manufacture of a grog stabilized in shrinkage, manufacture of

pressed products. The grog plays the role of grease-remover when it is used in of refractory ceramics, reduces the volumes' variation, supports the formation of the porosity, which it even slows down the propagation of the cracks and increases the resistance to thermal shock. The shrinking of grog material is relatively low compared to the raw materials. Its density is sufficiently high to confer on the product a great mechanical resistance.

The sintered materials made of KF3 kaolin contain mullite and rich silica amorphous phase. Silica shows two different forms *i.e.*, amorphous and crystalline (cristobalite). As the temperature increases, the dissolution of silica in the amorphous phase progresses and at 1450 °C the silica is totally dissolved. The amorphous phase represents between 28 and 34 % of the total product mass according to the firing temperature. Firing temperatures of 1250 and 1300 °C are unsufficient and firing at 1450 °C leads to an excess of amorphous phase. The firing temperatures between 1350 and 1400 °C generate optimal properties.

REFERENCES

1. M. Taib, The Mineral Industry of Algeria, 2009 Minerals Yearbook, U.S. Geological Survey (2011).
2. S. Caillere, S. Henin and M. Rautureau, Minéralogie des Argiles : Classification et Nomenclature, Tome, Masson, edn. 2, pp. 19-44 (1982).
3. V.A. Drits and C. Tchaobar, X Ray Diffraction by Disordered Lamellar Structure: Theory & Application to Microdivised Silicates & Carbon, Spinger Verlag, Berlin (1990).
4. D.N. Hinckley, Variability in Crystallinity Values Among the Kaolin Deposits of the Coastal Plain of Georgia and South Ccarolina, Proc. 11th National Conference on Clays and Clay Minerals, Ottawa, pp. 229-35 (1962).
5. G. Artioli, M. Bellotto, A. Gualtieri and A. Pavese, *Clays Clay Miner.*, **43**, 438 (1995).
6. J.L. Holm, *Phys. Chem. Chem. Phys.*, **3**, 1362 (2001).
7. O. Castelein, B. Soulestin, J.P. Bonnet and P. Blanchart, *Ceram. Int.*, **27**, 517 (2001).
8. D. Papargyris and R.D. Cooke, *Br. Ceram. Trans.*, **95**, 107 (1996).
9. K.R. Mikeska, S.J. Bennison and S.L. Grise, *J. Am. Ceram. Soc.*, **83**, 1160 (2000).
10. B. Tchoubar, A. Plancon, J.B. Brahim, C. Clinard and C. Sow, *Bull. Minéral.*, **105**, 477 (1982).
11. G.W. Brindley and G. Brown, *Mineral. Soc. Monograph*, **5**, 323 (1980).
12. J. Schomburg and H. Zwahr, *J. Thermal Anal.*, **48**, 135 (1997).
13. G.W. Brindey and M. Nakahira, *J. Eur. Ceram. Soc.*, **16**, 225 (1996).
14. W.G. Scherer, *J. Am. Ceram. Soc.*, **74**, 1523 (1991).
15. M.R. Anseau, M. Deleter and F. Cambier, *Trans. J. Br. Ceram. Soc.*, **80**, 142 (1981).
16. C.Y. Chen, G.S. Lan and W.H. Tuan, *Ceram. Int..* **26**, 715 (2000).