Effect of chamotte on the structural and microstructural characteristics of a kaolinitic ceramic.

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ABSTRACT

The main of this work is to elaborate of alumina-silica refractory bricks from Algerian kaolin and chamotte. The mixture powders of DD3 kaolin and chamotte were milled, compacted and sintered for 2 h at 1350°C. Structure and microstructure of the sintered samples were studied by means of X-ray fluorescence spectrometry, X-ray diffraction, scanning electronic microscopy and the helium pycnometer.

The results showed that DD3 kaolin has a silica content of 41% and alumina of 35%. X-ray analysis revealed that the major phases of the DD3 kaolin was kaolinite along with a muscovite and todorokite. After sintering, the ceramics composite composed mainly of mullite and cristobalite. The added chamotte increases the mullite formation, the apparent density from 2.7 to 2.75 g/cm³, decreases the porosity from 4.70 to 4.43% and a densification higher than 95%.

Key words: DD3 Kaolin; Ceramic; Mullite; XDR, DTA/TGA.

1. INTRODUCTION

The Djebel Debbagh kaolin deposit located in North East of Algeria (Guelma) is natural clay which consists of a filling of karst cavities with predominantly kaolin clays containing halloysite. Its quality varies with the extraction methods. We can find a pure kaolin with concentration of metal oxide impurities less than 5% and sometimes concentrations less than 1%. The DD kaolin of Djebbel Debbagh are rich in silica and alumina and they are classified in three categories: DD1, DD2 and DD3 according to the concentration of the metal oxide impurities and they are differentiated by their colors, white and gray because they contain manganese oxide. Due to the specific properties, DD Kaolin can be used also in several fields such as: building materials, paper, medical and cosmetic applications, thermal insulating, chemical producers, pulp and paper, food production-related industries and anything involving heat and/or hot products .... etc. The kaolin from Djebbel Debbagh (DD3) is the main refractory clays deposits mined in Algeria for manufacturing of silica–alumina refractories. These products are commonly used in the ceramics industry to manufacture kilns, and as kiln furniture, coating of laboratory furnace and refractory supports.

The main minerals constituents in kaolin are kaolinite or halloysite. The pure kaolinite theoretical formula Si2Al2O5(OH)4 is often presented in the form: Al2O3 2SiO2 2H2O [1]. This clay mineral is of great interest to the production of different types of ceramic materials for having properties interesting. Most important of these properties one is the phase mullite formation during sintering of ceramics which makes the material hard with good mechanical strength [2]. Kaolinite is one of the most used raw materials for alumina-silicate based ceramics, due to its abundance and good availability. Natural kaolinite coexists with minor constituents
such as mica and quartz [3]. Halloysite have a similar composition \( (\text{Al}_2\text{O}_3 \ 2\text{SiO}_2 \ n\text{H}_2\text{O} \ ; \ n \geq 4) \) with some excess water molecules present between the layers and often exhibits a tubular morphology [4]. At the temperature of 40°C, halloysite loses its water to form the meta-halloysite, a structure similar to kaolinite which is very difficult to differentiate. This halloysite morphology distinguishes it from the hexagonal grains of kaolinite.

The aim of the present work is to study the chamotte effect on the mullite formation and the structural and microstructural properties mullite elaborated via reaction sintering of Algerian kaolin of Djebbel Debbagh-Guelma located in the North-East of Algeria. Hence, a mixture of kaolin and chamotte powders with two compositions was mechanically milled in a high energy planetary bell mill, at room temperature for 1 h. The obtained powders were compacted into pellets and sintered at 1350°C for 2 h.

2. MATERIALS AND EXPERIMENTAL PROCEDURE

2.1. Raw materials

The studied material was kaolin grey clay designated by DD3 extracted from Djebbel Debbagh (North-east of Algeria). The DD3 kaolin was calcined to obtained the chamotte composed of mullite and cristobalite. Then, the chamotte was added to the DD3 kaolin according to the following compositions: C1 = (75% DD3 Kaolin + 25% chamotte) and C2 = (50% DD3 Kaolin + 50% chamotte). The mixture of two compositions C1 and C2 was milled and compacted into pellets under a pressure of 1 t/m² using a uniaxial hydraulic press. After drying, the green samples were sintered in an electrical muffle furnace at 1350°C for 2 h and a temperature rise rate of 10°C/min.

2.2. Methods

The chemical composition was carried out by X-ray fluorescence spectrometry XRF (Bruker S8 Tiger). The microstructural characterizations of sintered samples were made by X-ray diffraction on a Rigaku diffractometer using CuKα radiation (\( \lambda_{\text{Cu}} = 0.15406 \) nm) in a (\( \theta-2\theta \)) Bragg Brentano geometry with a step size of 0.01°. The lattice parameters, volume fraction, crystallite size, \( <L> \) and microstrains, \( <\sigma^2>^{1/2} \) were obtained from the Rietveld refinement of the XRD patterns by using the MAUD program [5] which is based on the Rietveld method [6]. Morphological changes of sintered samples were characterized by scanning electron microscopy (SEM, EVO/MA25-ZEISS) coupled with dispersive X-ray spectrometry (EDX). The apparent density and open porosity of sintered samples were measured by the Archimedes method, and the absolute density was determined by using an automatic helium pycnometer (AccuPyc II 1340).

3. RESULTS AND DISCUSSIONS

3.1. Chemical composition:

The chemical composition of the DD3 kaolin given in weight percentages (wt. %) is indicated in Table 1. One notes that the DD3 kaolin is a hydrothermal rock [7], constituted mainly of two major chemical elements which are: 42% silica and 36% alumina. The great value of fire loss (17%) is due to the presence of water in the various minerals existing in kaolin [8]. In fact, it's closer to the ideal value of the fire loss recorded during the dehydroxylation of halloysite (16.85%) [9]. The high percentage of MnO (2.25%) is explained to the blackish coloration of DD3 kaolin and also supposes that the content of the associated ore (todorokite) exceeds 5%.
**Table 1**: Chemical composition of the DD3 kaolin (wt. %).

<table>
<thead>
<tr>
<th>Compounds</th>
<th>Mass %</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO$_2$</td>
<td>41.70</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>35.80</td>
</tr>
<tr>
<td>MnO</td>
<td>2.25</td>
</tr>
<tr>
<td>CaO</td>
<td>1.16</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.801</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.301</td>
</tr>
<tr>
<td>SO$_3$</td>
<td>0.801</td>
</tr>
<tr>
<td>MgO</td>
<td>0.183</td>
</tr>
<tr>
<td>P$_2$O$_5$</td>
<td>0.141</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>0.070</td>
</tr>
<tr>
<td>Cr$_2$O$_3$</td>
<td>-</td>
</tr>
<tr>
<td>Calc. loss</td>
<td>17.364</td>
</tr>
</tbody>
</table>

### 3.2. Analysis XRD:

#### 3.2.1. Phase formation of the milled powder:

The Rietveld refinement of the XRD patterns is presented in **Figure 1**. The XRD result show that the powder DD3 kaolin consists essentially of kaolinite of chemical formula [Al$_2$Si$_2$O$_5$ (OH)$_4$] or associated with halloysite [Al$_2$Si$_2$O$_5$ (OH) nH$_2$O n ≥ 4] [10, 11]. In addition to this major phase of kaolinite, the DD3 kaolin contains two phases: muscovite of chemical formula 2[Si$_3$AlO$_10$Al$_2$(OH)$_2$K] and todorokite. The todorokite phase is black mineral contains two types of manganese oxides of the chemical structural formula described as follows: 2(RO. MnO$_2$. 2H$_2$O)3 (Mn$_2$O$_3$. 3MnO. 2H$_2$O) with R = Ca, Mg, Ba, Mn) [8, 12, 13].

![Rietveld refinement of the DD3 kaolin](image)

**Figure 1**: Rietveld refinement of the DD3 kaolin.
3.2.2. Phase formation of the sintered samples:

The Rietveld refinement of sintered samples "C1" and "C2" (Figure 2) is composed of mullite (3Al₂O₃ 2SiO₂) as major phase and α-low cristobalite. The reaction of silica and alumina at high temperature provides to form the mullite (3Al₂O₃ 2SiO₂) and α-low cristobalite. The nucleation and crystals growth of mullite is done by the diffusion of silicon and aluminum at the grain interfaces. So, kaolinite undergoes a series of reactions to form the mullite which the phases transformations begins by the dissociate kaolinite from the temperature of 700°C according to the following reaction:

\[
\text{Al}_2\text{O}_3 \ 2\text{SiO}_2 \ n\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 \ \text{SiO}_2 + \text{SiO}_2 + n\text{H}_2\text{O} \quad (2)
\]

When the kaolinite is heated, the adsorbed water is liberated at above 100°C and the weakest part of the chemical bond is perturbed or broke. The dehydroxylation to metakaolinite (Al₂O₃ 2SiO₂) occurs between 400 and 550°C. For kaolinite, dehydroxylation might result in the disturbance of the Al(O,OH)₆ octahedral sheet by the extern hydroxyls, but does not have much effect on the SiO₄ tetrahedral sheet due to the more stable inner hydroxyls groups. The extern hydroxyls of octahedral sheets may be more easily eliminated by heating than inner ones that will maintain a more ordered SiO₄ tetrahedral group in structure during dehydroxylation. It's might result in the disturbance of the Al(O,OH)₆ octahedral sheet by the extern hydroxyls, but does not have much effect on the SiO₄ tetrahedral sheet due to the more stable inner hydroxyls groups [14].

The metakaolinite (Al₂O₃ SiO₂) has a monoclinic cell with parameters lattice a = 0.1514 nm, b = 0.890 nm, c = 0.68 nm and β = 100.2° [15-17]. It begins to dissociate from the temperature of 700°C to form unstable amorphous silica, which will react at high temperatures according to three reactions:

1. A part with γ alumina to form the mullite around 980°C, but inhomogeneities at the nanoscale may delay its formation up to 1300°C [18]. The mullite growth is accelerated by instantaneous nucleation process and the short distance diffusion. It's exhibits a orthorhombic structure with lattice parameters \(a₀ = 0.7588 \text{ nm, } b₀ = 0.7688 \text{ and } c₀ = 0.28895 \text{ nm and space group Pbam.} \) The mullite is the main crystalline and only stable intermediate phase in the alumina silica system, and the Al₂O₃-SiO₂ at atmospheric pressure. Mullite-based ceramics is characterized by excellent chemical and physical properties at high temperatures. It presents a good corrosion resistance, a low-dilatation coefficient and thermal conductivity, a good creep and thermal shock resistances [19]. These characteristics confer to these refractories a potential use in several industries and the ability to bear service conditions encountered in different applications. The studies showed that mullite formation process is a solution precipitation process which multiple-step process in various forms of silica–alumina mixtures [20]. They found that initial form of the alumina and silica has a large influence on mullite development because the interdiffusion of aluminum and silicon atoms between grains develops liquid phase [21].

2. The other part is crystallizing in cristobalite form, it's the β-high cristobalite with triclinic structure and represents the most stable form. It has a space group P1 and lattice parameters \(a₀ = 0.7156 \text{ nm, } b₀ = 0.7156 \text{ nm, } c₀ = 0.7156 \text{ nm, } α = 90°, \ β = 90° \text{ and } γ = 90°. \) The β-high cristobalite appears at about 1075°C and goes on increasing in between 1200°C and 1300°C after that it decreases.
3. This β-high cristobalite is subsequently transformed into α-low cristobalite between 170°C and 240°C. It has a tetragonal structure, space group P41212 and lattice parameters \( a_0 = 0.49733 \) nm and \( c_0 = 0.69262 \) nm. The most intense peak of cristobalite (21.6°) corresponding to the direction (101) represents the preferred direction of development of cristobalite crystals. Between 1100°C and 1400°C, the cristobalite is in the form of a glass phase and as an amorphous phase above 1400°C. An excess of the amorphous phase reduces the creep resistance and lowers the thermo-mechanical properties of the refractory at high temperatures. For this reason, it is necessary to reduce the rate of this phase.

Also, it is noted that the presence of manganese in the chemical composition of kaolin DD3 probably favors the formation and the development of cristobalite, so, the manganese plays a precursor role for the formation of the crystalline phase of cristobalite [12, 22]. However, the CaO element insures the cristobalite vitrification at low temperatures and favors the mullite formation [23, 24].

The Rietveld refinement of the sintered samples is summarized in Table 2. The mullite volume fraction increase with increase of chamotte content, thus, the C2 pellet (92.68 %) is higher than that of the C1 pellet (91.08 %). Indeed, the volume fraction of α-low cristobalite is about 8.92% and 7.32% for C1 and C2 pellets, respectively. The sintering treatment favors the crystallite size growth up to ~150 and 200 nm for mullite and α-low cristobalite respectively. In addition to the relaxation of microstrains that are induced into the crystal lattice by the annihilation of various structural defects.

The relative deviation of the lattice parameter of mullite reaches as much as \( \Delta a = -0.46 \% \) and \(-0.63 \% \) for C1 and C2 pellets respectively. The expansion / contraction of the crystal lattice of the sintered samples, which can be evaluated by the relative deviation \( (\Delta a = (a-a_0)/a_0) \) of the lattice parameters \( (a, c) \) from those of the perfect crystal \( (a_0, c_0) \), can be linked to the preparation method. The variation of the lattice parameter value might be related to the heavy plastic deformation, crystal defects and/or the excess/deficiency of Al and Si atoms.

Table 2: Phases, lattice parameters (a, c), relative deviation (\( \Delta a, \Delta c \)), average crystallite size \( <L> \), microstrains \( <\sigma^2>^{1/2} \), relative proportion of the sintered samples C1 and C2.

<table>
<thead>
<tr>
<th>Phases</th>
<th>a (nm) ± 10^-4</th>
<th>b (nm) ± 10^-4</th>
<th>c (nm) ± 10^-4</th>
<th>c/a</th>
<th>( \Delta a ) (%)</th>
<th>( \Delta c ) (%)</th>
<th>( &lt;L&gt; ) (nm) ± 3</th>
<th>( &lt;\sigma^2&gt;^{1/2} ) x10^-3</th>
<th>Volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mullite</td>
<td>0.75525</td>
<td>0.77041</td>
<td>0.28866</td>
<td>0.38</td>
<td>-0.47</td>
<td>-0.10</td>
<td>147.9</td>
<td>0.69</td>
<td>91.1</td>
</tr>
<tr>
<td>Low cristobalite</td>
<td>0.50909</td>
<td>-</td>
<td>0.69268</td>
<td>1.36</td>
<td>2.37</td>
<td>0.01</td>
<td>229.1</td>
<td>3.55</td>
<td>8.9</td>
</tr>
<tr>
<td>C2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mullite</td>
<td>0.75394</td>
<td>0.76790</td>
<td>0.28770</td>
<td>0.38</td>
<td>-0.64</td>
<td>-0.43</td>
<td>145.1</td>
<td>0.39</td>
<td>92.7</td>
</tr>
<tr>
<td>Low cristobalite</td>
<td>0.50204</td>
<td>-</td>
<td>0.70005</td>
<td>1.39</td>
<td>0.95</td>
<td>1.07</td>
<td>212.7</td>
<td>2.95</td>
<td>7.3</td>
</tr>
</tbody>
</table>
Figure 2: Rietveld refinement of the sintered samples C1 and C2.
One observes that the apparent density values of sintered pellets are lower than the absolute density (Figure 3). The apparent density obtained by Archimedes method of sintered pellets C1 and C2 are 2.70 g/cm³ and 2.75 g/cm³ respectively. The absolute density obtained by using helium pycnometer show that the sintered samples C1 and C2 presented the densities equal to 2.76 g/cm³ and 2.83 g/cm³ respectively. Absolute density of mullite obtained in this work is less than that of theoretical density of pure mullite (~ 3.16 g/cm³) [1]. Usually, the increase in density is attributed to the elimination of pores during sintering. This can be explained, when the sintering temperature increases, there are transformation of cristobalite into a crystalline phase (d = 2.5 g/cm³) and an increase of mullite content that takes place simultaneously. The samples porosity C1 and C2 is about 4.70 % and 4.43 % respectively.

![Figure 3: Absolute and apparent density of the sintered samples C1 and C2.](image)

### 3.4. SEM observations:

The SEM observations of sintered pellet (Figure 4) reveal a heterogeneous structure with spherical pores ranging in size from 2 to 3 μm [25]. The chemical composition was studied by EDX analysis (Table 3) in order to investigate the qualitative analysis in the sintered samples. The EDX analysis confirm the predominance of three principal elements which are: oxygen (O~53 at. %), aluminum (Al~22 at. %) and silicon (Si~19 at. %). These elements composed of principal substances of alumina Al₂O₃ and silica SiO₂, and that determine the main heat characteristics of refractories. One notes also the presence of other elements in very small proportion such as: Ca, Mn and Fe.
**Figure 4:** SEM micrographs of the sintered pellet C2.

**Table 3:** Elemental analysis (EDX) of the DD3 kaolin.

<table>
<thead>
<tr>
<th>Chemical elements</th>
<th>Wt. %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>53.07</td>
</tr>
<tr>
<td>Al</td>
<td>21.94</td>
</tr>
<tr>
<td>Si</td>
<td>18.93</td>
</tr>
<tr>
<td>Ca</td>
<td>0.50</td>
</tr>
<tr>
<td>Mn</td>
<td>4.09</td>
</tr>
<tr>
<td>Fe</td>
<td>1.37</td>
</tr>
<tr>
<td>Mg</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**4. CONCLUSION**

In this paper, the sintered samples were elaborated by solid-state reaction from Algerian kaolin of Djebbel Debbagh-Guelma (North-East of Algeria) and chamotte. The sintered samples composed mainly of mullite and cristobalite. The results of this present study indicate that the chamotte activates the sintering by the mullite formation, and increases the density to maximum value. The sintered samples yielded a dense mullite ceramics with a relative densification higher than 95%, an apparent density in the range 2.7 to 2.75 g/cm³ and a porosity from 4.70 to 4.43%.
REFERENCE