

Effect of Carbon Graphite on the Crystallization of Andalusite: Application to the Synthesis of Mullite and the Improvement of Refractory Quality

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ABSTRACT

Different mixtures of Moroccan silica-alumina geomaterials were used for the preparation of refractory ceramics. A formula of composition (M2) has allowed obtaining a good quality of refractory. Addition of a small quantity of carbon (1%) to the M2 formula has substantially improved the quality of the refractory. The morphological, textural and mineralogical evolution, through SEM and XRD shows that the addition of carbon, which plays a catalytic role, favors the crystallization of andalusite. Then, from 1200°C, the andalusite starts to transform to primary mullite needles. At 1400°C, the mullite becomes the major mineral phase beside cristobalite and vitreous phase.

Keywords: Refractory; Alumina-Silica; Andalusite; Mullite; Morocco

1. Introduction

Many research studies have been conducted, until now, on mullite ($3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$) as a mineral phase with many properties: low thermal expansion and conductivity, excellent creep resistance, high temperature strength, and good chemical stability [1]. These studies have focused on their synthesis methods [1,2], their phase equilibrium, their microstructures and their thermo-mechanical properties [1-7].

Different types of mullite can be synthesized according to the nature of the raw materials and the used process [8-15]. The application fields of mullite are multiple and depend on the properties of each type. Mullite synthesized from silica-alumina geomaterials by heat treatment corresponds to a fundamental constituent of refractory ceramics [16-18]. In fact, the performance of a refractory (good resistance of heat and thermal shock) is directly related to its texture and its richness in mullite.

With reference to the geological works on the metamorphism and the experimental petrology [19], silica-alumina materials, subjected to thermal metamorphism (contact metamorphism) can promote, from a temperature of 700°C, the crystallization, in solid state, of andalusite crystals.

Both crystallization and development of andalusite are done according to the diffusion processes of Si and Al through the interfaces of the rock's grains. The carbon appears to play a catalytic role in the reaction of crystallization of andalusite [20]. This is argued by the presence of coal inclusions, cross-shaped, in some varieties of andalusite (chiastolite), as well as, the development of large sticks of andalusite (up to 10 cm) in some graphitic schist's located in contact with plutonic granitoids [20]. Subjected to higher temperatures ($T > 1100^\circ\text{C}$), this andalusite can be transformed into mullite [13,14].

The objective of this study is to synthesize the mullite by high temperature treatment of local Moroccan silica-alumina geomaterials (granitic kaolin, andalusite-rich schist, silica sand, red clay and marl). Our approach consists to prepare several briquettes from various mixtures of geomaterials (M1 to M4) and adds to them variable quantities of carbon. The analysis of textures, mineral compositions and technological properties of obtained refractories allows defining the role of each of the geomaterials and the effect of carbon on the kinetics reaction of andalusite crystallization. This will permit, consequently, to better control the synthesis of mullite. These results can be used to improve the performance of re-

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fractories.

2. Nature of Materials: Localization and Composition

Among the different Moroccan geomaterials, we have chosen five varieties, that have the best profiles, and that have particular richness in silica and alumina; in addition, we have used in this work the fossil coal (anthracite) as source of the carbon.

- **Granitic Kaolin.** It is rich kaolin clay resulting from hydrothermal alteration of alkali granite of Oulmès. This late-Hercynian granitic pluton (290 Ma), located in the center of the Moroccan Meseta, is affected at its SW border, in contact with the schistic surrounding rocks, by an intense hydrothermal alteration. This alteration caused the kaolinization of alkali-feldspar of the granitic rock and gives a friable material, rich in kaolin clay with an appreciable quantity of quartz, flakes of muscovite, and chloritized biotite. The sample used in this study (ArgK) comes from the great clay quarry, which is located on the road towards the village of Oulmès; (X: 33°26'19.14"N; Y: 06°02'58.83"W; Alt: 1095 m).
- **Red Clay.** It is a very fine-grained silt of Triassic age (235Ma), rich in clay minerals and poor in carbonates. It forms deposits, which may exceed 100 m thickness. Very large outcrops of these clay deposits exist in the region of Rommani. Clays of this region are intensely exploited by the industrial ceramists for the manufacture of bricks and tiles. The sample used in this study (ArgR) belongs to a huge quarry situated at ten kilometers from the village of Rommani (X: 33°36'38.55"N; Y: 06°39'00.06"W; Alt: 323 m).
- **Clay Marl.** These correspond to marine deposits of Miocene age (6 Ma), very fine-grained and light colored (yellow to gray). The marl which is very abundant in different regions of Morocco (Rif and Meseta) forms monotonous deposits exceeding sometimes 200 m. These clays, relatively rich in carbonates are very operated by both the brick-makers and traditional potters. The Marl used in this study (MarA) comes from Benjellik careers, located at 3 km far from the city of Fez (X: 34°01'46.60"N; Y: 04°56'25.62"W; Alt.: 393 m).
- **Andalusite-rich schist.** They correspond to a schistose rock of upper Visean age (330 Ma), which constitutes the surrounding rock of the Oulmès granite. The schistose rock, of a gray-black color with a shiny and spotted surface, is affected by a high grade of contact metamorphism related to the emplacement of Oulmès granite. This metamorphism is responsible for the development of a rich andalusite zone. The

sample used for this study (*SchA*) comes from the schist rich in andalusite, located near to the contact with the Oulmès granite, at approximately 1.2 km far from the great quarry of kaolinic clay. (X: 33°26'21.37"N; Y: 06°03'44.04"O; Alt: 1052 m).

- **Silica Sand.** Several deposits of silica sand exist in Morocco. Silica sand used in this study (*SabM*) comes from an artisanal quarry, located at 3 km SE of the Mechraa Hammadi Dam, on the road ranging from Nador to Oujda via Layoune, (X: 34°42'56.94"N; Y: 02°47'14.27"W; Alt: 242 m). The sands appear as a thin layer of a white-pink and friable rock, belonging to the serie of limestone of the upper Jurassic (130 Ma).
- **Anthracite.** To have a pure and natural carbon, we used the fossil coal of the mine of Jerada (AntJ), located in the East part of Morocco at 45 km from the city of Oujda, (34°18'19.57"N; Y: 02°11'45.56"W; Alt: 1046 m). The coal mine from the Upper Carboniferous age (300 Ma), offers a very good variety of black coal (anthracite) with more than 95% of carbon.

X-Ray Diffraction (XRD) analyses of the three materials (ArgK, ArgR and MarA) were used to determine the nature of their clay minerals and semi-quantitative composition (**Table 1**). **Table 1** also inserts the carbonate contents, measured using Bernard's calcimeter. The mineralogical composition of ArgK consists mainly on kaolinite and small quantities of quartz and illite. The red clay (ArgR) is rather illitic. The marl (MarA) is relatively kaolinitic with very high carbonate content (34%).

The chemical compositions of the geomaterials, performed by X-Ray Fluorescence (XRF), are shown in **Table 2**.

The different samples are silica ($\text{SiO}_2 > 50\%$), however, only the two clays (ArgK and ArgR) and schist are relatively alumina ($\text{Al}_2\text{O}_3 > 19\%$). Red clay is much more ferromagnesian than the others ($\text{Fe}_2\text{O}_3 + \text{MgO} = 16.36\%$). The marl is distinguished by its richness in calcium ($\text{CaO} = 24.80\%$).

Table 1. Semi-quantitative analysis of clay mineral and carbonate content.

| Geomaterials | ArgR | ArgK | MarA |
|--------------------------|----------|-------|----------|
| <i>Kaolinite%</i> | 20 to 30 | 44.00 | 25 to 35 |
| <i>Illite%</i> | 30 to 40 | 25.67 | 15 to 20 |
| <i>Hématite%</i> | 4 | - | - |
| <i>Chlorite%</i> | - | - | 10 to 20 |
| <i>Quartz%</i> | 25 | 30.32 | 5 to 10 |
| <i>CaCO₃%</i> | 2.14 | 2.62 | 34 |

Table 2. Chemical compositions by XRF of the geomaterials used in this study.

| | <i>SiO₂</i> | <i>TiO</i> | <i>Al₂O₃</i> | <i>Fe₂O₃</i> | <i>MgO</i> | <i>CaO</i> | <i>Na₂O</i> | <i>K₂O</i> | <i>P₂O₅</i> | <i>C.L</i> | <i>Total</i> |
|-------------|------------------------|------------|------------------------------------|------------------------------------|-------------|--------------|------------------------|-----------------------|-----------------------------------|------------|--------------|
| ArgK | <u>57.20</u> | 0.08 | <u>29.40</u> | 4.50 | 0.65 | 0.26 | 1.55 | <u>3.08</u> | 0.00 | 3.28 | 100.0 |
| ArgR | <u>51.60</u> | 1.06 | <u>19.20</u> | <u>9.00</u> | <u>7.36</u> | 0.90 | 0.58 | 1.89 | 0.23 | 8.16 | 99.98 |
| MarA | <u>51.10</u> | 0.40 | 8.91 | 3.44 | 3.19 | <u>24.80</u> | 0.76 | 1.24 | 0.22 | 5.89 | 99.95 |
| SchA | <u>63.40</u> | 1.13 | <u>21.70</u> | 6.00 | 1.59 | 0.12 | 0.30 | <u>3.36</u> | 0.11 | 2.29 | 100.0 |
| SabM | <u>96.06</u> | 0.15 | 2.22 | 0.51 | 0.17 | 0.09 | 0.06 | 0.20 | 0.02 | 0.49 | 99.97 |

3. Experimental Procedures

3.1. Preparation of Mixtures

To attain the objectives of this research, we proceed in two steps.

- **First step.** We prepare tens of mixtures (M1 to M12) from the five Moroccan geomaterials described above. Among these mixtures, we retained four mixtures (M1 to M4) that allowed obtaining ceramics resisting to a temperatures exceeding 1300°C, which we have already considered as refractories. **Table 3** gives the proportions of these four mixtures.
- **Second step.** We add to the best mixture of the first step (M2) some carbon (Anthracite: AntJ) at variable amount, from 0 at 2%, in order to define the optimal rate for improving the quality of the initial refractory. The four prepared mixtures are noted: M2C₀, M2C_{0.5}, M2C₁ and M2C₂ (The index correspond to the amount of carbon added in the formula M2). We signal that the addition of more than 3% of carbon to the mixture gives the ceramics a black aspect and increases its porosity.

3.2. Preparation of the Bricks

A quantity of 100 grams is prepared for each mixture (M1 to M4) according to the proportions indicated in **Table 3**. Each mixture is passed in planetary mill (MP100; Frequency: 150 tr/mn, time: 15 mn), which provides a very fine and homogeneous powder (mean grain size <100 μm). After 10% moistening, the powders are shaped by uniaxial pressure at 30 MPa into molds of 100 × 50 mm². The samples (briquettes) thus obtained, are submitted to a drying 110°C/24 h and a calcination at 600°C during 1h. Then they are fired at high temperatures between 1100 and 1400°C (5°C/mn) in an oven (Thermolyne 46200) [17]. During their firing, between 1150°C and 1400°C, the briquettes are analyzed to follow both their mineralogical and textural evolution and more especially the crystallization and growth of andalusite and mullite. Then, the briquettes are subjected to various tests to determine their physico-mechanical properties: thermal shrinkage, porosity, density, flexural strength

Table 3. Composition of mixtures from different geomaterials.

| Mixture | ArgK | ArgR | MarA | SchA | SabM |
|-----------|-----------|----------|----------|-----------|-----------|
| M1 | 37 | 6 | - | 37 | 20 |
| M2 | <u>30</u> | <u>3</u> | <u>3</u> | <u>37</u> | <u>27</u> |
| M3 | 40 | 50 | - | - | 10 |
| M4 | - | 50 | - | 40 | 10 |

and thermal shock. The tests were performed according to the procedures recommended by (ASTM) [21-23].

4. Results and Discussion

The presentation of the data and their interpretation will be presented in two stages: first those of briquettes from mixtures without carbon (M1, M2, M3 and M4), then those of briquettes with carbon (M2C_{0.5}, M2C₁ and M2C₂).

4.1. Refractories without Carbon

The first series of refractories obtained from the four mixtures (M1 to M4) shows variables technological characteristics according to the firing temperatures (**Table 4**).

The refractory briquette M2 has the lowest shrinkage passing under 1% at 1150°C to 2.98% at 1350°C. The shrinkage of the briquette M1 is also low, while the briquettes M3 and M4 are quite high (5% at 1350°C). Similarly, the apparent porosity is much lower in the briquettes M1 and M2 (about 5%) than M3 and M4 (respectively 12% and 10%). This porosity remains stable whatever the temperature is in the briquette M2, while it becomes slightly lower at higher temperatures in the other briquettes. In contrast to porosity, the density is maximum in briquettes M1 and M2 (2.8 g/cm³). The variations of technological parameters, between the different briquettes, are explained by both mineralogical and textural changes occurring during firing [18,24,25]. The various silica phases that compose the fired material do not have the same thermal expansion coefficient value

Table 4. Technological parameters of refractories prepared from different mixtures (M1, M2, M3 and M4). R: Thermal Shrinkage (%) P: Porosity (%), D: Density (g/cm³).

| T (°C) | 1150 | | | 1200 | | | 1250 | | | 1300 | | | 1350 | | |
|-----------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | R | P | D | R | P | D | R | P | D | R | P | D | R | P | D |
| M1 | 0.87 | 4.61 | 2.93 | 1.09 | 4.54 | 2.91 | 2.14 | 4.29 | 2.91 | 2.89 | 3.79 | 2.91 | 3.76 | 2.65 | 2.89 |
| M2 | 0.51 | 5.61 | 2.92 | 1.12 | 5.43 | 2.92 | 1.65 | 5.37 | 2.90 | 2.13 | 5.19 | 2.88 | 2.98 | 4.93 | 2.87 |
| M3 | 1.79 | 14.01 | 2.63 | 2.22 | 13.55 | 2.61 | 3.65 | 13.12 | 2.61 | 4.14 | 12.77 | 2.59 | 4.76 | 12.34 | 2.58 |
| M4 | 3.17 | 12.06 | 2.81 | 3.48 | 11.65 | 2.80 | 4.28 | 11.19 | 2.79 | 4.56 | 11.03 | 2.77 | 5.67 | 10.87 | 2.76 |

depending on the firing temperature. The α - β quartz transformation at 570°C is accompanied by a significant variation of volume [18]. Also, the transformation of kaolinite ($d = 2.63 \text{ g/cm}^3$) to tridymite-cristobalite ($d = 2.26$ and 2.33 g/cm^3) and the formation of amorphous phase lead to a significant decrease in the density of material [17].

Andalusite-rich schist (SchA) had strengthened the composition of the kaolin clay (ArgK) of silica, alumina and potassium to promote the sintering process [16,18,26,27]. This explains why the refractory M1 and M2 show both a thermal shrinkage and a lower porosity than the others. Note that the replacement in the M2 of 7% ArgK by the SabM and the addition of 3% of MarA instead of ArgR contributes to a further decline in its thermal shrinkage. This confirms the interest of adding silica, and shows the favorable role, till a certain limit, of carbonate at the detriment of iron in the synthesis of refractory [15,26,28,29]. Scanning Electron Microscope (SEM) revealed significant variations of texture between the different synthesized refractories. Images of refractory products at 1350°C (**Figure 1**) show a fundamental difference between the refractories M1-M2 and M3-M4. The last two briquettes have both a heterogeneous and porous microstructure, however, the first ones show a homogeneous structure and particularly a high content of fine needles of mullite and a significant amount of glass phase [30]. Mullite developed from mixtures M1 and M2 probably comes from the high-temperature transformation of andalusite. Furthermore, the used andalusite-rich schist in both M1 and M2 mixture (37%) would have provided nuclei promoting the crystallization of andalusite between 700°C and 1100°C. Above this temperature, these andalusites had been transformed into fine mullite needles [13,14].

This first phase of the study, led us to retain the mixture M2 as the most favorable composition for testing the effect of adding carbon to improve the quality of the refractories.

4.2. Refractories with Carbon

Refractories obtained from the mixture M2 to which we

added varying quantities of carbon (0% - 2%) showed significant changes of their texture, mineralogy and technological properties.

- **Textural Change.** The SEM images show that, at the maximum temperature of 1400°C, the briquettes with carbon present both a homogeneous texture and a lower porosity (**Figure 2**).

The same images show furthermore a more important development of mullite, especially in the briquette M2C₁ (mixture M2 with 1% of carbon). The mullite is present as very fine needles of 10 microns long, oriented in all directions.

- **Mineralogical composition.** The X-ray diffraction (XRD) on the briquette M2C₁ (**Figure 3**), reveals a succession of phase transformations between 1150°C and 1400°C. Quartz and andalusite, well represented at 1150°C, are transformed, at high temperatures, into mullite and association of quartz, cristobalite and vitreous silicate phase. The transition from andalusite to mullite takes place between 1200°C and 1250°C. The peaks intensity of mullite indicating its abundance in the refractory material occurs to a maximum temperature of 1400°C. At this same temperature, cristobalite becomes beside to vitreous phases, the most stable form of silica [17,18].

The combined analysis of both texture and mineralogy can admit that mullite may have a double origin: a primary origin by transformation of andalusite, and a secondary origin by reaction of cristobalite-alumina [9]. This quantitative analysis shows effectively that the quantity of Mullite appears to be so important in the briquette with 1% of carbon (M2C₁), which is, originally, the richest in andalusite. Finally, note that in the briquette M2C₁, fired at 1400°C, mullite is the dominant mineral with up to 62%, whereas, in the other briquettes (M2C₀, M2C_{0.5} and M2C₂) this mullite content is significantly lower (**Table 5**).

- **Technological characteristics.** Results of the technological tests done on the carbon briquettes, fired at 1400°C, are shown in **Table 6**.

One of the four synthesized refractories that contains 1% of carbon (M2C₁), and that is, in fact, the richest one

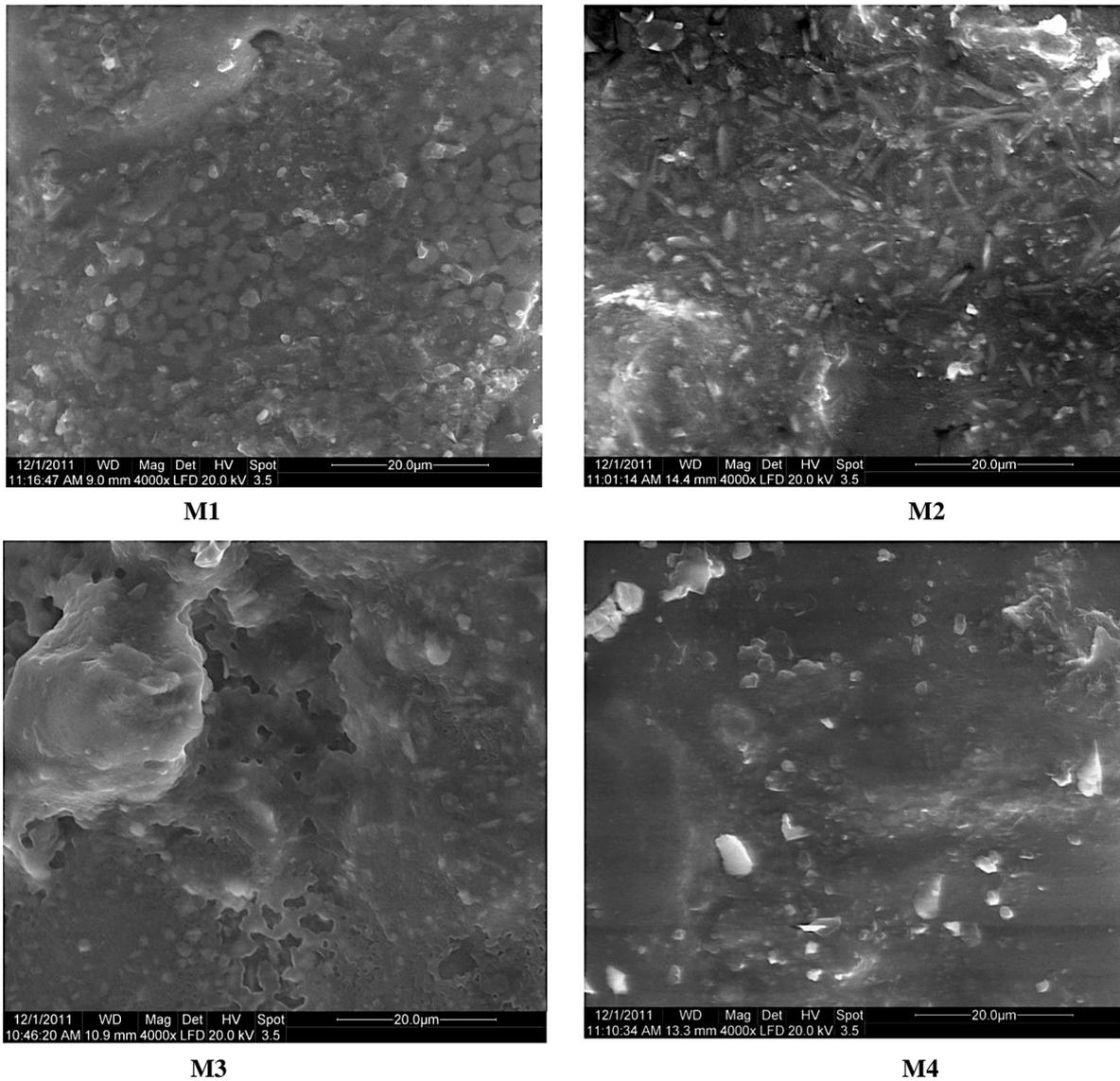


Figure 1. Photomicrographs SEM of refractories obtained from four mixtures (M1-M4) fired at 1350°C.

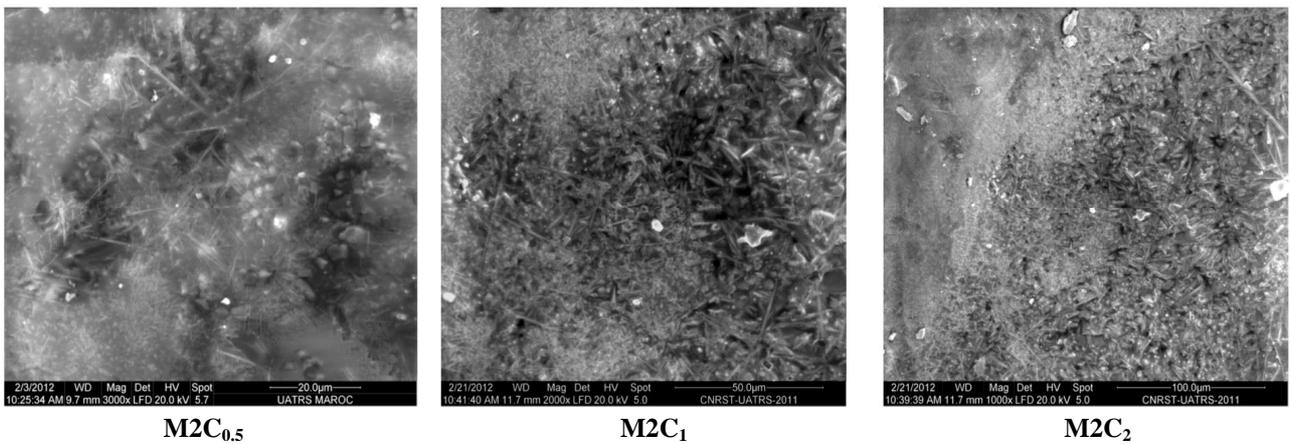


Figure 2. SEM micrographs of refractory M2 fired at 1400°C for different contents of Carbon (M2C_{0.5}, M2C₁, M2C₂).

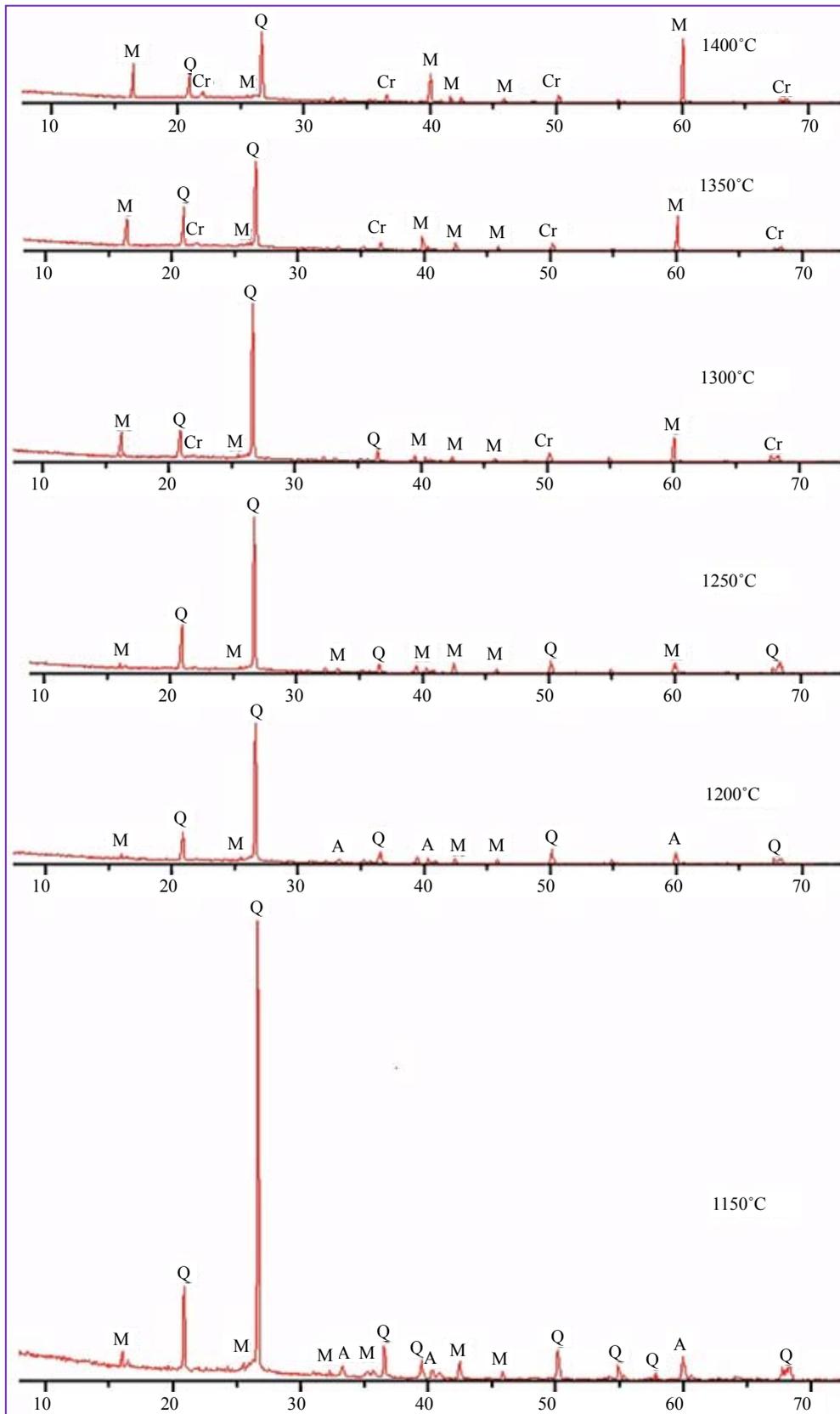


Figure 3. XRD spectrum of refractory M_2C_1 . (M: Mullite, A: Andalusite, Q: Quartz, Cr: Cristobalite).

of mullite, proves to be the most efficient one, with a porosity of 5.19% and a mean density of 2.86 g/cm³, and above all an improved flexural strength (42.05 MPa).

The cyclic thermal shock test was performed according to DIN51 068 standard [31]. The samples were heated for 15 min at 950°C, and immediately immersed in the cooling water at 25°C for 3 min. After drying for 2 h at 110°C, we proceed to examine the surface state to detect possible damage. The flexural strength is measured [5,6,17,32].

An example of a sample M2C₁ subjected to 70 cycles of thermal shock is shown in **Figure 4**. We observe only one type of cracking located on the side. The average thickness of the crack is about 537 μm. Compared to previous works, this briquette shows both a good mechanical and thermal performance [17,18].

5. Comparison with Previous Techniques

An extensive literature analysis allowed situating our synthesis technique of mullite among previous techniques. In fact, at least seven research teams have adopted several innovative approaches [4,9,17,18,26,33,34]. **Table 7** summarizes the process conditions and the synthesis temperature of mullite of each team, and compares them with those corresponding to this study.

It emerges from this comparison that our approach is simple and based on natural geomaterials that are quite abundant in Morocco as well as in many other regions of the world: kaolin clay and andalusite-rich schist. The specificity of the technique is the addition of a small quantity of carbon (1% of Anthracite) which plays a catalytic role in the crystallization reaction of andalusite

from the mixture of kaolin clay and andalusite-rich schist between 700°C and 1100°C. Then at high temperatures (T > 1250°C), andalusite transforms in a massive way to primary mullite needles. The resulting refractory at 1400°C, with an average density of 2.86 g/cm³, shows both good mechanical and thermal performance (Flexural strength = 42.05 MPa, good strength after 70 cycles of thermal shock).

6. Conclusions

The refractories are materials which are increasingly demanded and whose manufacture involves necessarily the synthesis of mullite. This study is part of numerous works aimed the synthesis of mullite from different ma-

Table 5. Quantitative mineralogical composition of the four briquettes.

| Refractory | M2C ₀ | M2C _{0.5} | M2C ₁ | M2C ₂ |
|------------|------------------|--------------------|------------------|------------------|
| Mullite% | 56 | 60 | 62 | 59 |

Table 6. Results of technological tests done on the carbon briquettes.

| Samples | Porosity (%) | Density (g/cm ³) | Flexural Strength (MPa) |
|--------------------|--------------|------------------------------|-------------------------|
| M2C ₀ | 5.20 | 2.88 | 38.1 |
| M2C _{0.5} | 5.20 | 2.88 | 40.4 |
| M2C ₁ | 5.19 | 2.86 | 42.05 |
| M2C ₂ | 5.45 | 2.85 | 37.7 |

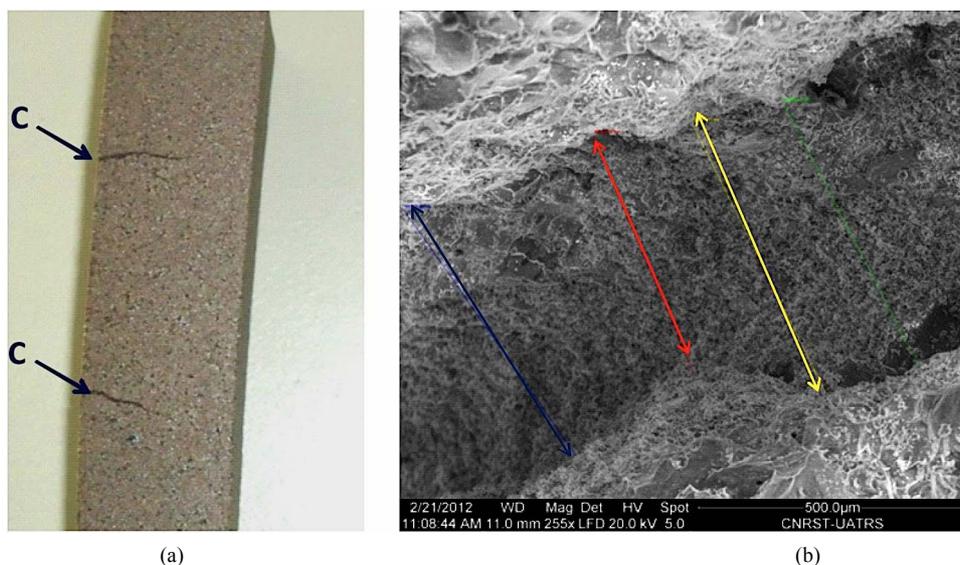


Figure 4. Damage caused by thermal shock on the M2C₁ refractory. (a): Aspect of sample (C: Crack); (b): micrograph showing the thickness of cracks caused by thermal shock.

Table 7. Comparative table of our mullite synthesis technique with the previous ones.

| Ref. Research team | Process | Special conditions | Firing temperature (°C) | Density (g/cm ³) |
|------------------------------------|---|--|-------------------------|------------------------------|
| M.A. Sainz <i>et al.</i> [4] | Thermal transformation of Kyanite | The evaluation of the grain size of mullite | 1600°C/1h | - |
| J. Santillan <i>et al.</i> [9] | Kyanite and alumina milling | Milling for 12 h | 1600°C/1h | 3.03 |
| M. Kolli <i>et al.</i> [17] | Different particle size fractions of kaolin | Pressure at 80 MPa | 1450°C | 2.75 |
| B. Amrane <i>et al.</i> [18] | Mixture of kaolin clay and halloysite | Using coarse grog | 1200°C/1h | 2.60 |
| Kong <i>et al.</i> [26] | Mixture of alumina and quartz | Addition of BaO (10%) | 1500°C/4h | 3.22 |
| Balmori-Ramirez <i>et al.</i> [33] | mixture of Kyanite and aluminum metal | Kyanite milled for 6 h and aluminum for 3 h | 1600°C/1h | 3.08 |
| Viswabaskaran <i>et al.</i> [34] | Mixture of clay and reactive alumina | Mixture (30 min) and addition of MgO (5%) and boehmite | 1600°C/3h | 3.01 |
| This study | Mixtures of natural geomaterials | Adding of carbon graphite | 1400°C/1h | 2.86 |

terials and using several techniques.

Our choice both of geomaterials and methodological approach were based on geological observations, particularly what happens at the inner zone of the aureole of contact metamorphism; pelitic surrounding rocks (silica-alumina composition) affected by the thermal effect in contact with a plutonic magma intrusion may give andalusite hornfels. On the other hand, the thermal effect affecting the pelitic rocks, originally rich in graphite, promotes the development of black schist and hornfels with large andalusite crystals. Thus, for the synthesis of our refractory, we thought to the formulation of mixtures from geomaterials rich in Si, Al, Na, K... whose composition tend to that of pelites, and to add some amount of carbon.

Thus, our choice of geomaterials was oriented to: a kaolin clay from the hydrothermal alteration of alkali granite of Oulmès (ArgK), andalusite-rich schist of the aureole of contact metamorphism (SchA), Triassic red clay (ArgR), Miocene clayey marl (MarA) and Jurassic silica sand (SabM).

The first step of this study has allowed obtaining an ideal composition for the synthesis of a refractory's good quality (M2 = 30% ArgK + 37% SchA + 27% SabM + 3% ArgR + 3% MarA). In a second time, adding a precise amount of carbon (1%) has allowed a significant improvement of this refractory (Porosity: 5.19%; Density: 2.86 g/cm³; FS: 42.05 MPa; good strength after 70 cycles of thermal shock).

Compared with other technical mullite synthesis for refractory applications, our method proves to be simple, convenient and inexpensive. Its principle is based, first, on the introduction in the mixture of andalusite rich schist (SchA), which provides the nuclei promoting the crystallization of andalusite. Secondly, adding of carbon, which plays a catalytic role, favours the growth of anda-

lusite between 700°C and 1100°C. Then, from 1200°C, the andalusite starts to transform to primary mullite needles. Finally, at 1400°C, mullite becomes the major mineral (up to 62%) beside cristobalite and vitreous phase.

On the other hand, the results of this study have a double economic interest: it contributes to the valorization of Moroccan geomaterials and leads to the local synthesis of refractories, which the national need is mainly imported from abroad.

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