Synthesis and characterization of cordierite ceramic through reaction sintering kaolin and spent magnesia-carbon bricks

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Abstract. The main objective of this work is to study and characterization of a refractory material made of a mixture of natural raw material and spent refractory bricks. Relative weight ratios of 25/75 and 75/25 were studied in order to obtain cordierite ceramics having an important class in the field of refractories with the stoichiometric formula (2MgO. 2Al₂O₃. 5SiO₂), by mixing the raw material of Kaolin with spent brick powder magnesia-carbon (MgO-C). The mixtures were sintered at 1200, 1300 and 1400°C for 2 h. The phase composition of the sintered samples was analyzed by X-ray diffraction and scanning electron microscopy (SEM), porosity and density are presented and discussed. The results obtained reveal that when the level of spent brick is high ≥75%, the formation of only a spinel phase and periclase were observed, however where the kaolin level is predominant we observe the formation of the cordierite phase at 1300°C. The morphology obtained by SEM confirmed these results.

1. Introduction
Cordierite is one of the important phases of the MgO - SiO₂ - Al₂O₃ System used in many industrial applications such as: refractory materials [1]. Cordierite is a material that has attracted a lot of attention in recent decades because it has a unique combination of properties related to mechanical strength, chemical stability, low coefficient of thermal expansion, as well as good optical and dielectric properties [2-4]. Many studies have been carried out on the crystallization of cordierite using various techniques such as sol-gel processes [5,6]; sintering means [7], the most usually used method of processing the cordierite ceramics is solid-state reaction [8,9]. It is synthesized from pure oxides Al₂O₃, MgO, and SiO₂ or from talc, diatomite and clays, kaolinite and alumina as raw natural materials and waste of magnesia witch is one of a very large family of refractory materials. A great number of researchers made efforts in using solid wastes as magnesia and magnesium oxides, A. Askin et al [10] prepared cordierite composition with raw magnesite and whithe waste magnesite generated during the magnesite processing, sintered at various temperatures, between 1250-1350 °C, Katsuhiro Sumi et al. [11] prepared a dense cordierite ceramic at 1350 °C from thermal reactions of magnesium compounds and kaolinite with a relative density of 97.7%. Al-Harbi et al. [12] reported a cordierite honeycomb monolith prepared by kaolin and magnesite. Rdaoui et al. [13] prepared cordierite from Algerian raw materials and magnesium oxide MgO mixtures with relative weight ratios of 59/29/12; A. Ouali et al. [14] investigated the effect of MgO additions on the formation and densification behaviour of the cordierite obtained from some mixtures of Algerian kaolin and magnesium hydroxide. After the life cycle of Magnesia-carbon refractories (MgO-C), they are replaced by new ones. As a result, a large amount of spent MgO-C is produced and stored in dump. This waste can be reused as a potential source of secondary magnesia. In this study, MgO-C was used in mixture with kaolin (source of SiO₂ and Al₂O₃), to obtain cordierite ceramics having an important class in the field of refractories. The main objective of this work is to examine the possibilities of preparing a refractory material from raw natural product (kaolin which has already been characterized
in previous works) mixed with a spent magnesia brick, the crystalline phases have been identified using X-ray diffraction as well as SEM microstructure.

2. Materials and methods

Algerian Kaolin DD1 source of silica and allumine studied in the previous work [15] (Al₂O₃-2SiO₂-2H₂O, SiO₂ 37.24%, Al₂O₃ 40%, Fe₂O₃ 0.33%, CaO 0.21%, MgO 0.85%, K₂O 0.53%, Na₂O 0.12%, MnO 1.36% and a PAF of 17.29%, was chosen as a natural raw material with different particle size (from 32 to 250 µm). Magnesium brick (MgO-C) with a percentage of MgO of 97.1% and 10% of C is chosen for this study.

- Mixtures of different proportions of kaolin and spent brick powder (75/25 and 25/75%) were prepared. The sintered samples were elaborated by compaction, and then they were sintered at different temperatures such as (1200, 1300 and 1400 °C) with a holding time of 2 hours and a heating rate of 10 °C / min.
- XRD analysis: The different phases formed after firing were detected by X-ray diffraction using Cu Kα radiation (λ=0.15405Å) on a RIGAKU θ/2θ diffractometer, XRD images are recorded in the range [5°-90°] (2θ) with a step of 0.02° and a scan speed of 4°/min.
- SEM analysis: was carried out using a scanning electron microscope type QUANTA 2
- The density and porosity measurement was carried out using an Accupyc II 1340 gas pycnometer and a mercury porosimeter of the different pellets.

3. Results and discussion

3.1 Phase composition of spent brick

The essential phases of Kaolin were identified in the previous work [15] witch are: kaolinite, halloysite, gibbsite, nacrite, dickite, magnetite and quartz.

The analysis of the phases of the diffractogram obtained for the spent brick powder reveals that this brick contains 2 majority phases: Periclase and Graphite Figure 1:

![Figure 1. XRD patterns of spent brick (P: Periclase; G: Graphite)](image1)

3.2. Phase transformation of the sintered samples

The mixtures M1 (75 + 25%) and M2 (25 + 75%) of kaolin DD1 and spent brick powder respectively, sintered between 1200°C - 1400°C are mainly composed in the ternary system, SiO₂-
Al₂O₃ -MgO. Analysis of the DRX spectra of the different samples shows that, in this temperature range, the kaolin compounds react with those of used brick.

[SiO₄] tetrahedra reacted with [AlO₄] tetrahedra forming [Si (OAl)₂(OSi)₂] species. However, [AlO₆] octahedral species took part a complete reaction with [MgO₆] octahedral to generate MgAl₂O₄ spinel. Finally the cordierite was formed with the interaction of Si (OAl)₂(OSi)₂ and MgAl₂O₄ spinel [16,17].

\[
\text{[SiO}_4\text{]} + \text{[AlO}_4\text{]} \rightarrow \text{Si(OAl)}_2\text{(OSi)}_2; \\
\text{[AlO}_6\text{]} + \text{[MgO}_6\text{]} \rightarrow \text{MgAl}_2\text{O}_4 \text{spinel}; \\
\text{And Si (OAl)}_2\text{(OSi)}_2 + \text{MgAl}_2\text{O}_4 \text{spinel} \rightarrow \text{cordierite}
\]

Thus, we can draw the following observations:

3.2.1. For mixture M1

At the sintering temperature 1200 °C, the mixture is composed essentially of mullite and cristoballite. For a sintering temperature of 1300 °C, the mullite is transformed into cordierite which constitutes the dominant phase of the material; we are thus witnessing the beginning of the formation of a spinel and forsterite phase. At 1400 °C, the fraction of cordierite tends to increase and the intensity of the spinel peaks is increasing too (Figure 2).

![XRD patterns of the sintered M1 mixture at different temperatures](image)

**Figure 2.** XRD patterns of the sintered M1 mixture at different temperatures (Cr: Cristobalite, M: Mullite, C: Cordierite, S: Spinel, F: Forsterite).

3.2.2. For mixture M2

- At a sintering temperature greater than or equal to 1200 °C, the M2 mixture for a level of spent brick powder ≥ 75%, there is the presence of periclase phase, spinel even with the other sintering temperatures (Figure 3). The rate of cordierite increases with the increase in the percentage of kaolin. This increase is accompanied by a decrease in the rate of the mullite phases beyond 1300 °C.
3.3. SEM analysis
Figure 7 (a) and (b) shows the sintering behavior of studied mixtures (M1, M2) determined by the type and quantity of the accompanying mineral phases. In the M1 sample, certain crystals characterizing the magnesium aluminate spinel appeared. Cordierite crystals are present. In addition, some inclusions of Forsterite have been detected. The M2 sample is mainly composed of rounded crystals characterizing the mineral of periclase. These periclase crystals are directly linked together but leaving open pores in certain locations at the grain boundaries, the spinel crystals are scattered with some glassy phases in the periclase matrix resulting in a dense and compact microstructure [18].

Figure 3. XRD patterns of the sintered M1 mixture at different temperatures (S: Spinel, P: Periclase)

Figure 4 (a). Micrograph of M1 at 1300°C

Figure 4 (b). Micrograph of M2 at 1300°C
3.4. Apparent density

Figure 5 gives the variation of the apparent density as a function of the sintering temperature for different grades of spent brick. Indeed, the M2 mixture has a rapid and almost unchangeable densification. On the contrary, the M1 mixture has two stages of evolution: a drop in density between 1200 °C and 1300 °C followed by a slight increase at 1400 °C. The drop in density at the first stage can be attributed to a rearrangement of the mullite into cordierite. Comparing the density of the two mixtures with that of the crude sintered kaolin is less dense.

![Figure 5. Apparent density as a function of sintering temperature](image)

3.5. Porosity

Figure 6 shows the evolution of the open porosity as a function of the level of MgO at different sintering temperatures. Note that the porosity rate of 25% MgO at 1200 °C is high, then there is a drop in porosity for 75% MgO, the others at 1300 and 1400 °C for 25% MgO are substantially similar. However, the threshold porosity obtaining temperature is 1400 °C.
4. Conclusion

The effects of the addition of used MgO-C brick on the sintering behavior of kaolin DD1 powders were studied in this work. The results are summarized as follows:
- two phases (periclase and spinel) were detected in the sample where the rate of MgO is 75% at all sintering temperatures moreover we note the formation of cordierite at 1300 °C for the mixture or the rate of kaolin is high. The rate of cordierite increases with the increase in the percentage of kaolin. This increase is accompanied by a decrease in the rate of the mullite phases beyond 1300 °C. These results are confirmed by microstructural analysis by SEM.
- the apparent density is almost unchangeable for the M2 mixture, on the other hand; the drop in density of M1 between 1200 °C and 1300 °C can be attributed to a rearrangement of mullite into cordierite
- the porosity decreases with the sintering temperature but for the mixture M2 reaches a threshold at T = 1400 °C.

5. References

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