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Comparative study of microwave and conventional processing of $MgAl_2O_4$-based materials

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Abstract

A comparative study of microwave and conventional processing of ceramic materials based on $MgAl_2O_4$ is presented in this paper, in particular sinters obtained from MgO and Al_2O_3 with 1 wt.% of CaO as an additive, and Al_2O_3–$MgAl_2O_4$ composites. Microwave processing took place under air at 800 W and 2.45 GHz during 4.5 min, conventional processing in an electrical resistance furnace, also on air, was conducted at 1400 °C for 96 h. The MgO:Al_2O_3 weight ratio employed for the synthesis of $MgAl_2O_4$ was 1:2.45. According to semi-quantitative X-ray diffraction analysis, approximately 90% of $MgAl_2O_4$ was produced with both processing methods. Scanning electron microscope (SEM) images of the microstructure revealed a similar morphology for the two methods, nevertheless the grain size was different. The Al_2O_3:$MgAl_2O_4$ weight ratios for the production of the composites were 9:1, 1:1, and 1:9 using the two methods and the conditions already described. A heterogeneous microstructure was observed in the specimen processed by microwaves. Due to the different nature of the processes, an extensive property was compared against an intensive one, therefore, the aim of this work was to have a realistic comparison between the materials obtained with these processes by taking into account energetic as well as kinetic aspects.

Keywords: A. Microwave processing; A. Sintering; $MgAl_2O_4$; Synthesis

1. Introduction

The solid state reaction between magnesium oxide (MgO) and aluminum oxide (Al_2O_3) can produce $MgAl_2O_4$ spinel. The spinel phase is formed by diffusion of Al^{3+} toward MgO and Mg^{2+} toward Al_2O_3 [1], producing a layer with a thickness that increases following a parabolic law. The MgO and Al_2O_3 system does not show a liquid phase at temperatures below 1900 °C [2–4], therefore, materials based on this system are good candidates for making refractories. $MgAl_2O_4$ is resistant to wear and chemical attack at high temperatures [5] and is an important refractory material employed mainly in the glass and steel industries. Heating the raw materials to temperatures above 2700 °C using electric arc furnace commonly produces it, or, when an additive such as CaO [6] is included, it can be produced at lower temperatures (around 1800 °C) that are achievable using gas burners or electric resistance elements.

The exact nature of the interaction of microwaves with the reactants during the synthesis of ceramic materials is somehow unclear and speculative. However, energy transfer from microwaves to the material is believed to occur either through resonance or by relaxation, both of which result in rapid heating. As a reference, some researchers have been able to demonstrate that electromagnetic energy can be used for the heating of ceramics at temperatures as high as 2000 °C in very short times [7], and that the synthesis of spinel-type oxides by microwaves is more than a speculation [8,9]. However, it is important to point out that microwave heating is very sensitive to the capacity of the materials to absorb this form of energy. The materials studied in this work absorb microwaves in an important amount at temperatures higher than around 400 °C. It has been reported [10] that graphite can be used as thermal auxiliary, for heating up the raw materials until they reach such temperature and start to absorb microwave energy by themselves.

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In the last few years, there has been a notorious increase in the requirements of materials and processes that the modern industry is demanding. In some cases traditional processes are not fulfilling these requirements, hence researchers are exploring new methods, such as microwave processing [11–17]. Some of them claim that microwaves are faster and more efficient for heating, sintering and crystallization of ceramic materials. However, many doubts still remain about how microwave processing compares to conventional heating. In many cases the comparisons are focused on parameters that are obviously related, such as power against temperature, but when more subtle kinetic aspects are considered the validity of the comparisons is not very clear.

The aim of this paper is to present a realistic comparison of the microwave and conventional processing, applied to $MgAl_2O_4$-based materials as an example, taking into account energetic aspects as well as the characteristics of the products obtained.

2. Experimental procedure

Two types of experiments were conducted. First, a set of tests aiming to obtain $MgAl_2O_4$ both, by conventional and microwave processing were made. In the second set of experiments, Al_2O_3–$MgAl_2O_4$ composites were synthesized in two ways: by conventional processing employing the $MgAl_2O_4$ conventionally obtained in the first set, and the second way, by microwave processing starting with $MgAl_2O_4$ synthesized by microwaves also from the first set of tests. Experimental details are given below.

2.1. Synthesis of $MgAl_2O_4$

Samples were prepared by mixing powders of MgO, Al_2O_3 (0.3 μm), and CaO in a MgO:Al_2O_3 weight ratio of 1:2.45 with 1 wt.% of CaO. The mixtures were compacted at 300 MPa to a tablet shape of 0.95 g. MgO and CaO were obtained from their respective carbonates, $MgCO_3$ (20 μm) and $CaCO_3$ (20 μm), calcined at 900 °C for 1 h. In both cases more than 90% of the carbonates were transformed into oxides. The tests conducted by the conventional method consisted simply in placing a crucible with the sample into an electrical resistance furnace at 1450 °C for 96 h.

For the microwave processing experiments, since neither of the compounds in the mixtures are able to absorb microwaves at an appreciable rate at temperatures below 400 °C, the tablets were placed over 0.05 g of graphite, which acts as a heating auxiliary. In all the cases the system was insulated for reducing heat losses, the atmosphere was air. The cavity is a cube of 25.4 cm × 25.4 cm × 25.4 cm, a waveguide conducted the energy from the source to the cavity itself. The supplied power was 800 W at 2.45 GHz for 4.5 min. The applied and reflected power, as well as temperature, were monitored during the tests in order to know the actual energy input. Temperature was recorded using an optical pyrometer through a mesh at the door of the cavity. Mesh interference was evaluated separately in order to have reliable values. $MgAl_2O_4$ obtained here was used as

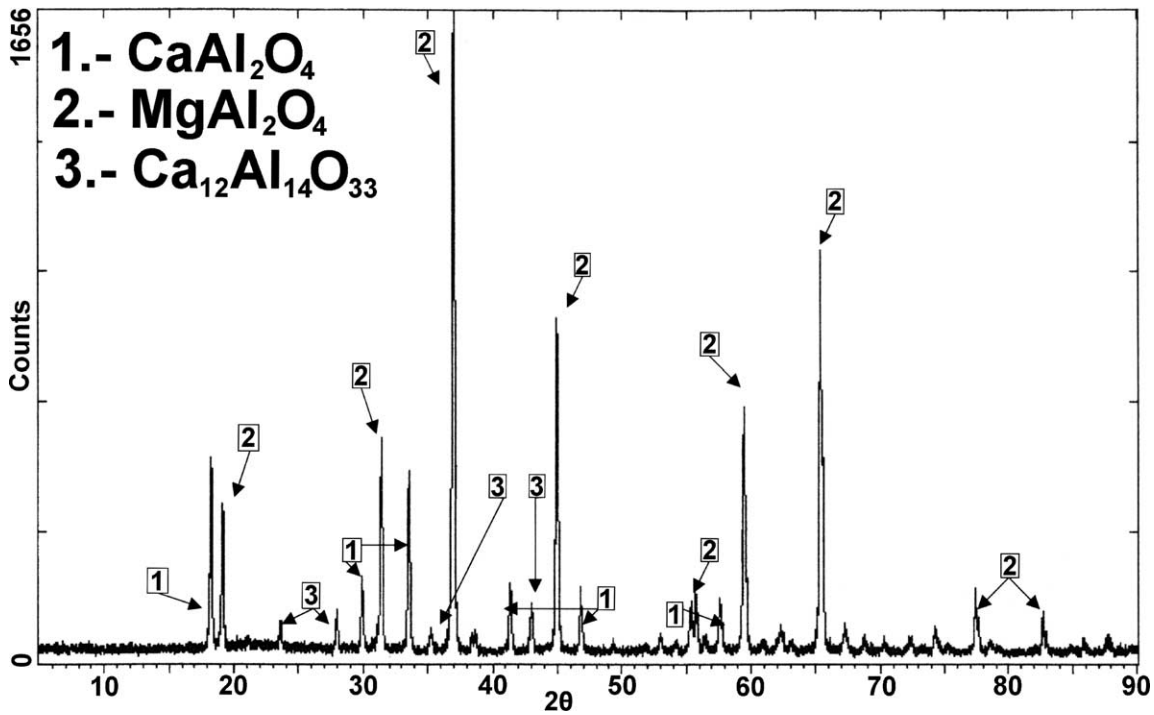

Fig. 1. X-ray diffraction pattern of a sample of $MgAl_2O_4$ synthesized conventionally.

Table 1
Mixture compositions and conditions for the composite tests

Sample	$MgAl_2O_4$ (wt.%)	Al_2O_3 (wt.%)	Types of processing
M1	90	10	Microwaves
M2	50	50	Microwaves
M3	10	90	Microwaves
M4	90	10	Conventional
M5	50	50	Conventional
M6	10	90	Conventional

raw material for composite processing as described in the following section.

2.2. Al_2O_3–$MgAl_2O_4$ composites

Mixtures of $MgAl_2O_4$ and Al_2O_3 (0.3 μm) were prepared in a weight ratio ($MgAl_2O_4$:Al_2O_3) of 9:1, 1:1, and 1:9. More characteristics of these materials are given below together with the results from the synthesis section. $MgAl_2O_4$ conventionally obtained in the first set of experiments (synthesized) was used in the mixtures prepared for conventional processing, while the $MgAl_2O_4$ obtained with microwaves was employed in the mixtures for microwave experiments. For these experiments the mixture was compacted at 360 MPa in order to obtain the tablets of 0.95 g. Then, they were processed under the same conditions already described in the synthesis section. Table 1 presents mixture compositions and conditions.

2.3. Characterization

The resulting specimens were characterized by scanning electron microscopy (SEM) and X-ray diffraction (Cu Kα). Density measurements were also performed.

3. Results and discussion

3.1. Synthesis of $MgAl_2O_4$

3.1.1. X-ray diffraction patterns

Specimens obtained by conventional heating (Fig. 1) resulted in about 90% of $MgAl_2O_4$, while the rest of the specimen consisted of a mixture of $CaAl_2O_4$ and $Ca_{12}Al_{14}O_{33}$. The diffraction pattern of the microwave processed mixtures shows (Fig. 2) that the conversion to $MgAl_2O_4$ was also about 90%, but in this case the rest consisted of the secondary phase $CaAl_2O_4$ only. The explanation for this different behavior implies kinetic aspects. In the case of the conventional processing there is plenty of time available for the conversion to stable, low temperature phase, in this case $Ca_{12}Al_{14}O_{33}$. However, in microwave processing, the high heating and cooling rates result in very short times for the reactions to occur, thus the high temperature phase ($CaAl_2O_4$) was retained to room temperature and $Ca_{12}Al_{14}O_{33}$ was not formed.

3.1.2. Scanning electron microscopy

The two images shown in Fig. 3 correspond to the specimens obtained by conventional and microwave processing.

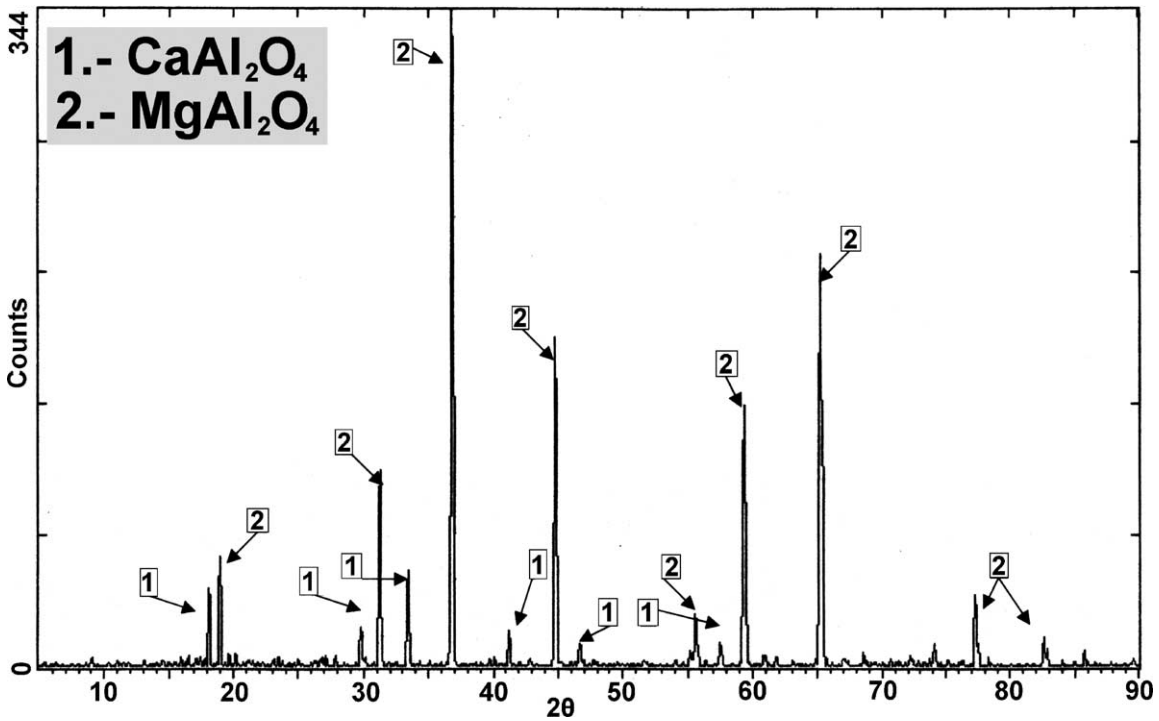

Fig. 2. X-ray diffraction pattern of a sample of $MgAl_2O_4$ synthesized with microwaves.

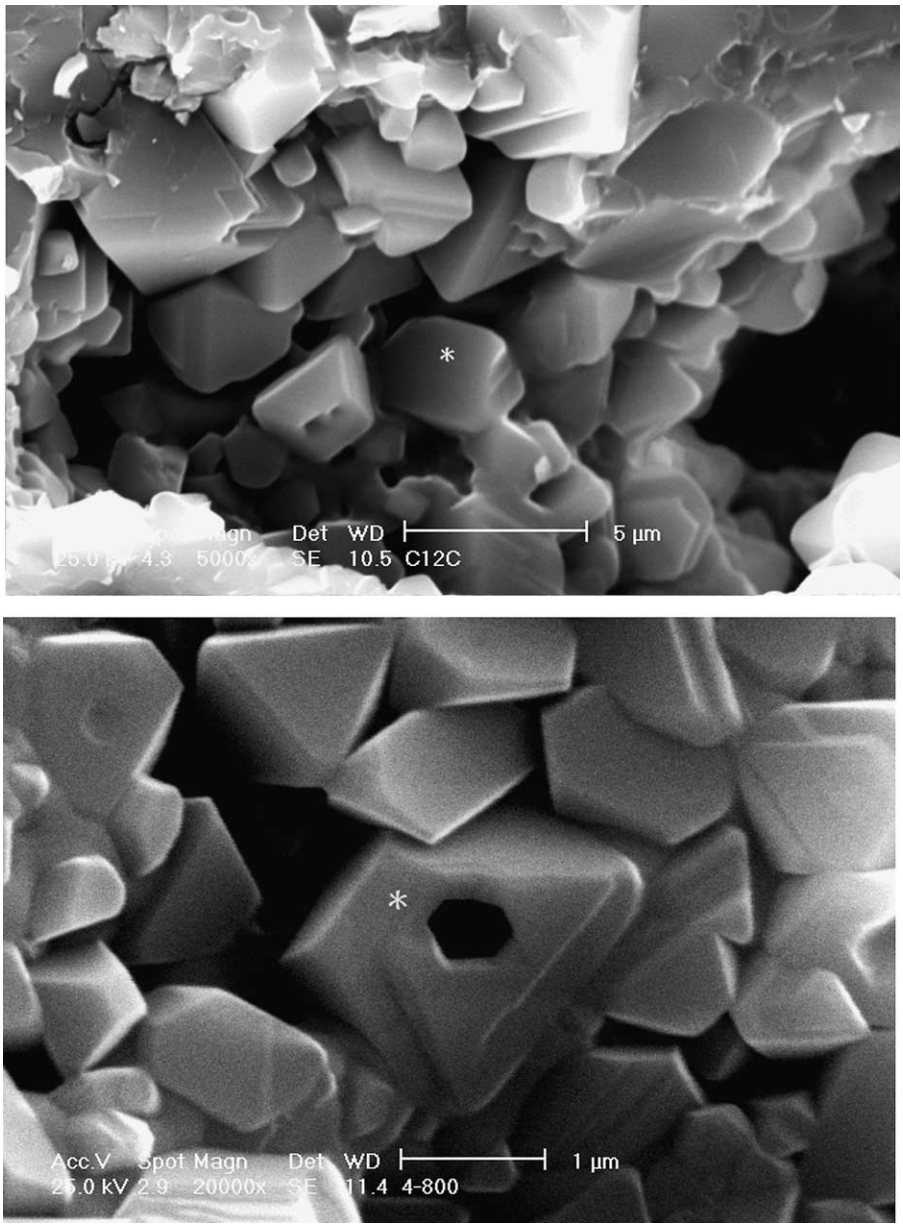

Fig. 3. SEM images of $MgAl_2O_4$ obtained by conventional (above) and microwave (below) heating.

Notice the characteristic spine-like shape that is obtained in both cases, although grain sizes are somewhat different, 3–5 and 1–3 μm for conventional and microwave processing, respectively. Regarding with the raw materials, the grain size of the $MgCO_3$ powder for producing MgO was 20 μm, but there is no evidence of grains that large, this means that very fine particles were produced as suggested by West [18]. Although processing times were very different, the small difference in grain size cannot be explained on this base, hence attention must be paid to energetic aspects.

3.2. Energetic aspects

Previous experience [19] has demonstrated that powder samples exposed to temperatures between 1200 and 1400 °C in a conventional furnace take approximately 20 min to equalize their temperatures, whereas in microwave processing this equalization takes shorter. In order to establish a valid comparison for this different processes, it is useful to remember that in the conventional case, once the specimen has equalized its temperature with its surroundings, the only energy that is actually going into the specimen is the heat necessary for conducting the synthesis. In the microwave case the absorption of energy is not limited by the furnace temperature, in fact the specimen becomes a source of heat and the maximum temperature depends on the thermal balance between the heat losses and the heat for synthesis against the microwave input.

The supplied power was 800 W, but the amount of energy that was actually going into the specimen (Fig. 4) can

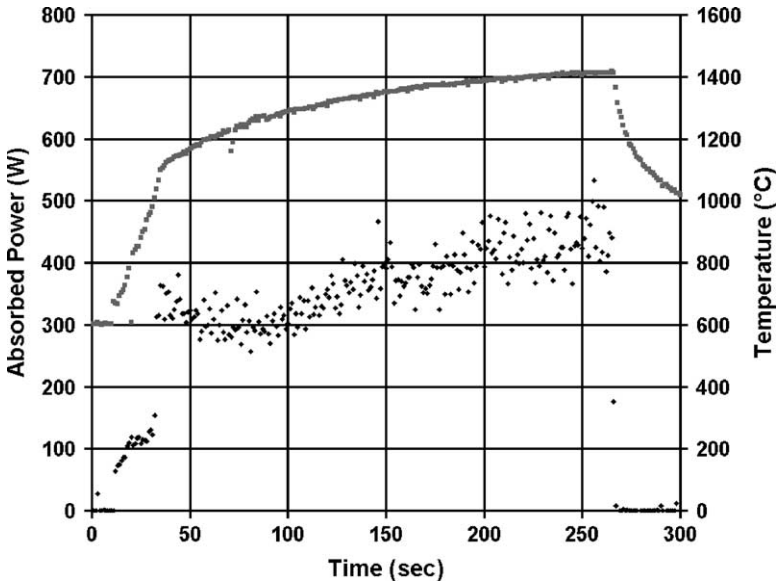

Fig. 4. Actual power absorbed by the $MgO–Al_2O_3$ mixture during synthesis. Temperature (upper line) is also shown (optical pyrometer is useful only above 600 °C).

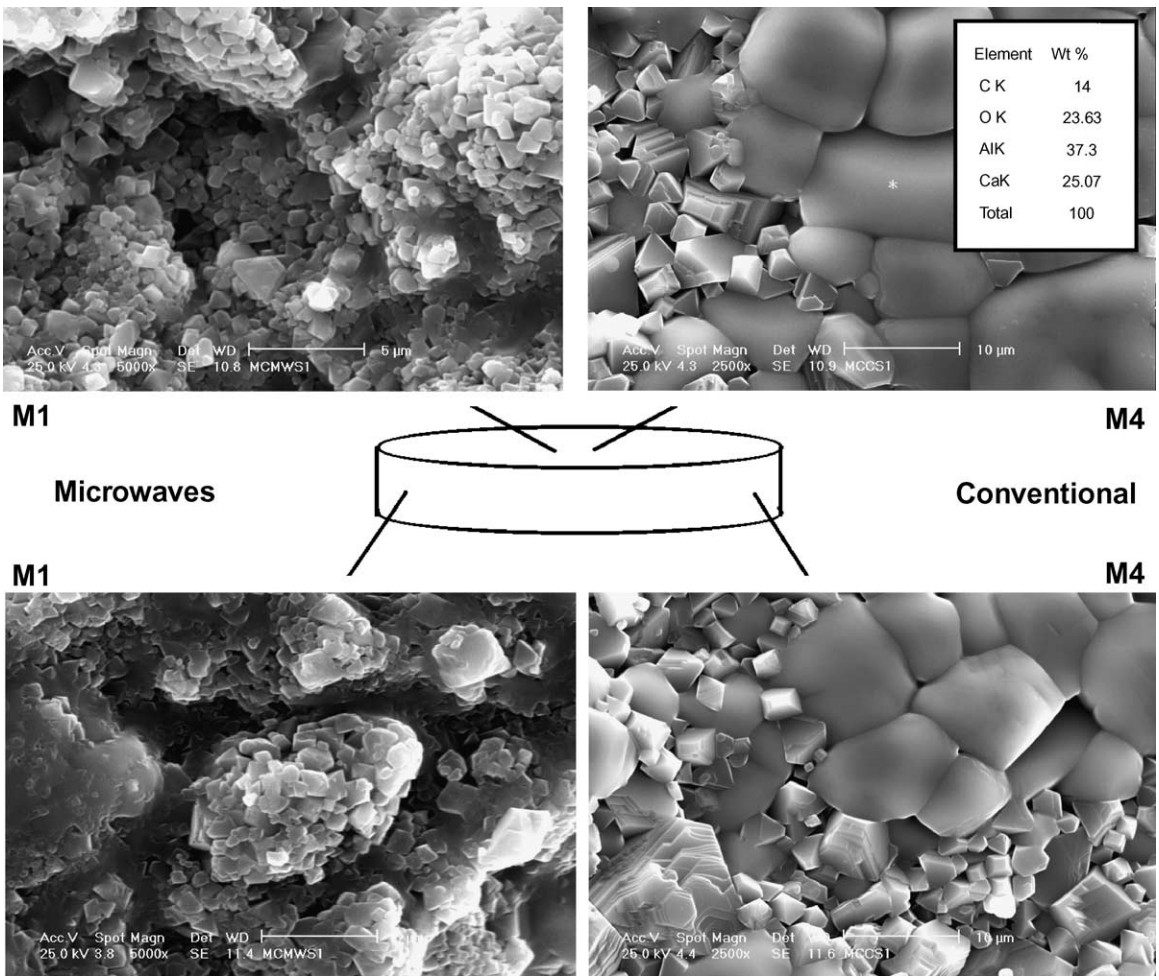

Fig. 5. SEM images of two samples, M1 (microwaves) and M4 (conventional), taken in two locations of the tablet (center and edge). Small grains are made of $MgAl_2O_4$ and large ones are made of $CaAl_2O_4$.

be estimated in the microwave case assuming a standing wave composed of the forward and reflected power inside the waveguide. Once the mixture becomes microwave absorbent, the absorbed power is estimated at around 350 W. Temperature was around 1400 °C, which is of the same order than that for conventional processing (Fig. 4). The similarity in the grain sizes suggests than a similar quantity of energy went into the specimens regardless of the difference in heating time (4 min versus 96 h.)

Equivalence time–temperature would suppose very high temperature in the microwave case for having such, about the same, grain growth in one thousand of time. However, it is known that temperature was not that high, supporting the claim related to decreasing of the activation energy as a result of an increase in the specific absorbed microwave power [20]. Another possible explanation was given by Binner et al. [21] yields on the pre-exponential factor in the Arrhenius expression without changes in the activation energy. This controversy is not solved here, but it is possible to say that different mechanisms with different activation energy might be present depending on the form of the energy source. The nature of such mechanisms and their relationship with the processing method is by itself a subject of study.

Table 2
Density of the obtained composites

Sample	ρ (g/cm^3)
M1	2.65
M2	2.33
M3	2.04
M4	1.24
M5	0.96
M6	0.71

3.2.1. $MgAl_2O_4$–Al_2O_3 composites

Density measurements (Table 2) show that only the specimens processed by microwaves were sintered appreciably. Fig. 5 shows SEM images of two specimens: M1 (microwave) and M4 (conventional) taken from two locations in the tablet. In both cases the microstructure is uniform throughout the specimen, with fine grains in the microwave case (1–3 μm) and coarser ones in the conventional process, though in this latter case the specimen shows a mixture of sizes. Two populations can be appreciated, grains of 3–5 μm along with grains of about 10 μm made of calcium aluminate.

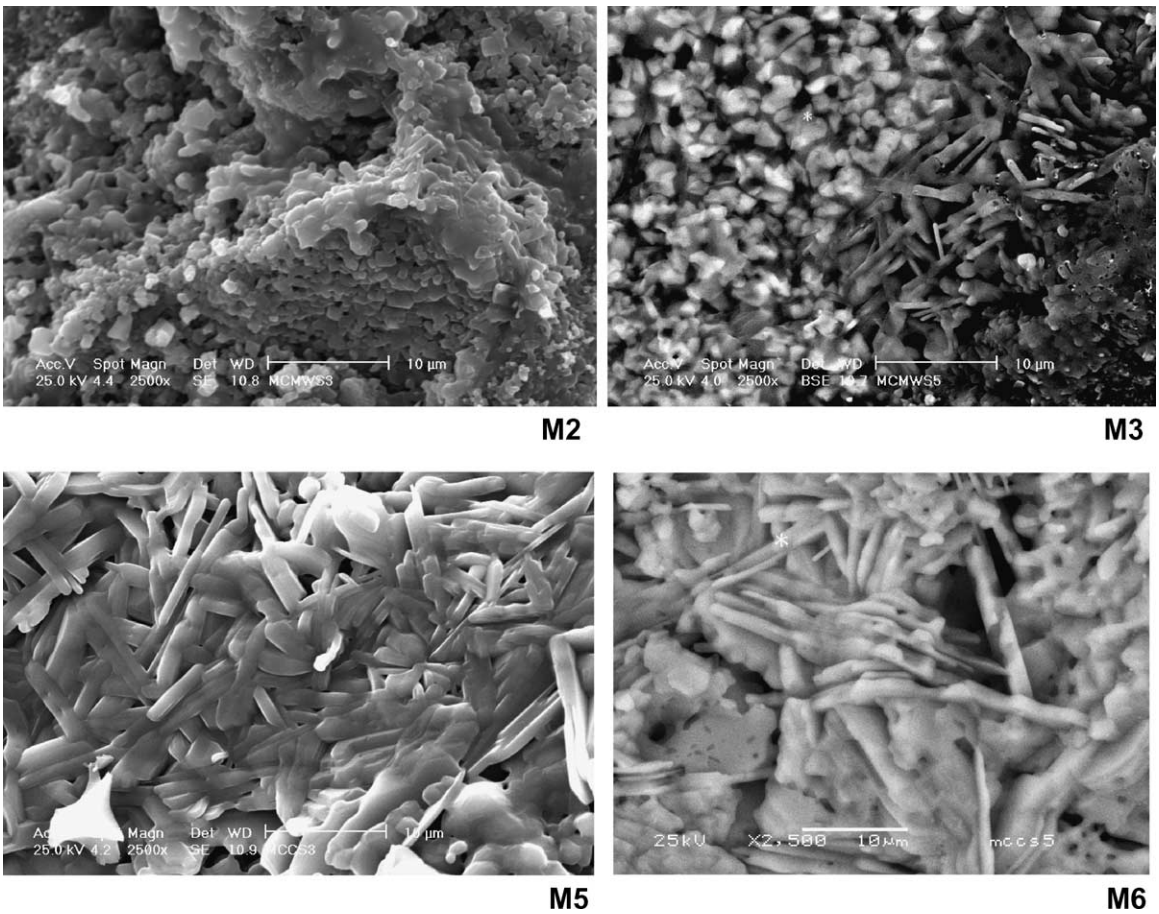

Fig. 6. SEM images of mixtures processed by microwaves (M2 and M3) and conventional (M5 and M6) heating showing the enlargement of the grains of calcium aluminates.

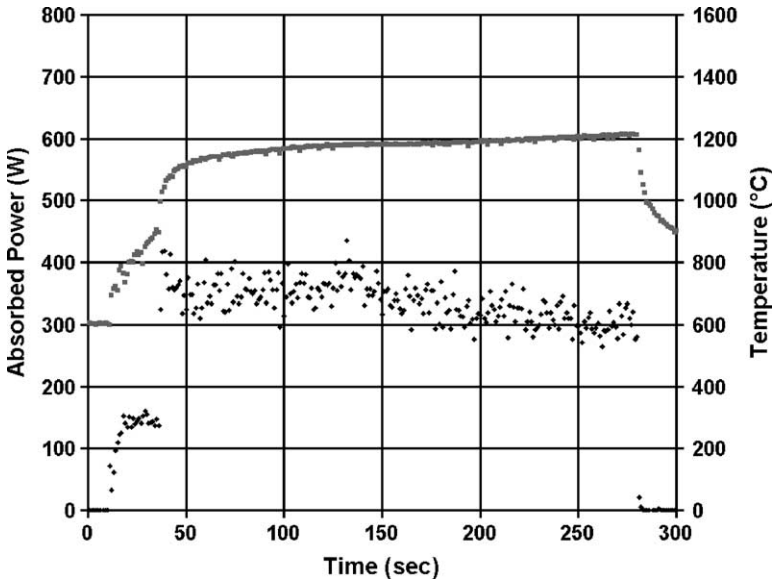

Fig. 7. Actual power absorbed by the $MgAl_2O_4$–Al_2O_3 mixture (M3) during sintering. Temperature (upper line) is also shown (optical pyrometer is useful only above 600 °C).

The effect of the different mixture compositions of $MgAl_2O_4$–Al_2O_3 can be appreciated in Fig. 6, notice the presence of elongated crystals. More Al_2O_3 (less $MgAl_2O_4$) would produce phases richer in this compound. Literature [22,23] suggests than $CaAl_{12}O_{19}$ and $Ca_2Mg_2Al_{28}O_{46}$ can be formed, although the presence of them was not confirmed here. However, microstructure exhibited by the specimens is in good agreement with that showed by De Aza et al. [24] where these compounds are present. In the case of the synthesis experiments discussed above, the difference between grain sizes for conventional and microwave processing is not as large as it is in the case of the composite formation. In the processing of the composites there is no synthesis, the only reaction that took place, either by microwaves or conventional heating, was sintering. In other words there is just one mechanism involved, witch is diffusion (one activation energy only). Therefore, the available energy is employed for grain growth, which under these circumstances is just a matter of time. The amount of absorbed energy was slightly lower than in the case of the synthesis of $MgAl_2O_4$ due to the properties of the mixture, temperature was also lower (Fig. 7). The maximum average temperature for mixtures M1, M2, and M3 were 1337, 1312, and 1261 °C, respectively. These small differences are correlated with the amount of Al_2O_3, which suggests that $MgAl_2O_4$ is a better microwave absorber than Al_2O_3, as has been pointed out in other works [25].

4. Conclusions

The results of this work allow concluding that the use of mixtures MgO–Al_2O_3 with 1 wt.% of CaO produces more than 90 wt.% of $MgAl_2O_4$ either by microwaves or by conventional heating. $Ca_{12}Al_{14}O_{33}$ is a stable compound at room temperature, but $CaAl_2O_4$ was found instead as a second phase in the microwave processing, because cooling was too fast for permitting the reaction to produce $Ca_{12}Al_{14}O_{33}$. The morphology of the synthesized grains is similar for both methods of heating because the amount of energy that actually went into the specimen was about the same. In the case of the sintering of the composite $MgAl_2O_4$–Al_2O_3, the differences in the grain size are explained by the different processing times. As mixtures became richer in Al_2O_3, the shape of the grains becomes elongated, which suggest the presence of $CaAl_{12}O_{19}$ and $Ca_2Mg_2Al_{28}O_{46}$.

Microwave processing is generally believed to be a highly efficient and high-rate method of production, but this issues should be analyzed carefully because they depend both on the materials being processed and the specific reaction involved (synthesis or sintering). In this research, synthesis by both methods resulted in similar microstructure at very different times, proving that microwave heating was faster for synthesis of $MgAl_2O_4$ than conventional heating. These results suggest that the mechanisms that take place are different for each processing method. Synthesis of $MgAl_2O_4$ was more dependent to the way the energy was supplied than to time, while sintering of $MgAl_2O_4$–Al_2O_3 gave a microstructure that was mainly depending of processing time. Despite the discussion regarding the activation energy, it can be said that at least for this case the use of microwaves for synthesis is indeed better than for sintering.

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