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Mullitization and Densification of ($3Al_2O_3 + 2SiO_2$) Powder Compacts by Microwave Sintering

P. Piluso, L. Gaillard, N. Lequeux & P. Boch

Laboratoire Céramiques et Matériaux Minéraux, Ecole Supérieure de Physique et de Chimie Industrielles, 10 rue Vauquelin, 75231 Paris Cédex 05, France

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Abstract

Reaction sintering of ($3Al_2O_3 + 2SiO_2$) powder compacts was studied using either a conventional electric furnace or a 2·45 GHz microwave furnace. Special attention was paid to temperature measurement within the microwave furnace. The reality of a microwave effect that accelerates the kinetics and therefore, decreases the temperatures of mullitization and densification, remains uncertain. In any case, such an effect does not exceed ≈ 50°C, which is in the order of the temperature gradient between the core and the surface of microwave heated specimens.

1 Introduction

Many studies have been devoted to microwave sintering of ceramics.[1–5] Microwave treatments have been reported to lead to a decrease in the temperature of sintering. In alumina, this decrease was said to be as large as 400°C,[6–8] which suggests the existence of a 'microwave effect' that accelerates the diffusion kinetics. However, there are large discrepancies in experimental data, and no definitive explanation has been proposed for the microwave effect.

The microwave effect has been most studied for densification without chemical change, but if it is not an artefact it should affect chemical reactions as well. Reaction sintering is a good way of combining reaction mechanisms and densification mechanisms. The present work was devoted to the preparation by reaction sintering[9–14] of mullite ceramics. The influence of conventional heat treatments was compared to that of microwave treatments in order to investigate the existence of a microwave effect on densification and reaction (mullitization). The evidence of a microwave effect being related to a decrease in the temperature of densification (or of reaction), the accuracy of the temperature measurements is of major importance. Therefore, special attention was paid to temperature measurement in the microwave furnace.

2 Experimental

2.1 The microwave furnace

The microwave-energy per unit volume (U) that is absorbed within a given material is expressed as:

$$U \approx 2\pi \cdot f \cdot E^2_{\text{int}} \cdot \epsilon_0 \cdot \epsilon'' \quad (1)$$

E_{int} being the microwave electric field within the material, f the frequency, and ϵ'' and ϵ_0 the permittivity of free space and the effective relative loss factor, respectively.

Ceramic oxides such as Al_2O_3 or SiO_2 exhibit low dielectric losses, and are, therefore, difficult to heat in a commercial microwave furnace. We have built a microwave furnace specially designed to heat such low-loss materials.[10–14] The furnace is shown in Fig. 1. It consists of a 2·45 GHz microwave generator with an adjustable 1·2 kW power output. The microwaves are directed into the applicator (which is a resonant, TE_{10n} single mode cavity) through a waveguide. A coupling iris minimizes the reflected power. The resonance of the cavity is controlled using an adjustable short-circuit. The incident and reflected powers are measured using two microwave-power meters and are recorded via a computer. The specimen is a cylinder of 13 mm in diameter and 3·5 mm thick. Its temperature is measured by a thermocouple (10% Rh–90% Pt/Pt) located in a hole drilled to the center of the specimen. The heating cycle is monitored by a programmable controller that regulates the incident power to follow a programmed temperature-to-time law.

In the absence of a theoretical model for the microwave effect, there is no evident choice for the frequency that would optimize the effect.

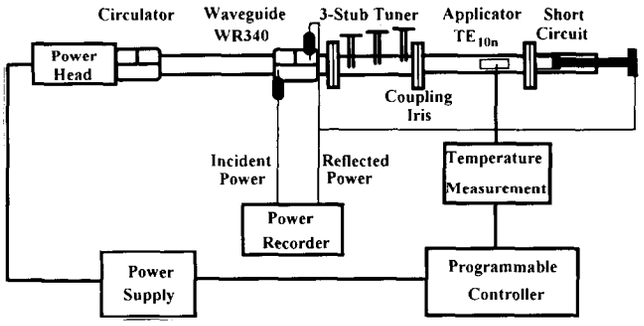

Fig. 1. The microwave furnace.

However, the frequency of 2·45 GHz is practically imposed by international regulations, which severely limit the industrial use of other, (e.g. 28 GHz) frequencies. Any industrial development of microwave sintering should satisfy the regulations and this is the reason why we have chosen a frequency of 2·45 GHz.

2.2 Green body preparation

Mullite ceramics were prepared by reaction sintering of alumina + silica powder compacts:

$$3\ Al_2O_3 + 2\ SiO_2 \rightarrow 3Al_2O_3{\cdot}2SiO_2$$
(Stoichiometric '3:2' mullite)

Alumina was α-Al_2O_3 (CR30 Baikowski®, 99.99% pure, d_{50} = 0·5 μm). Silica was cristobalite (M5000 Sifraco®, 99% pure, d_{50} = 1·8 μm). Powder mixtures were ball-milled for 5 h in a jar with dissociated $ZrSiO_4$ (ZrO_2 + SiO_2) balls in alcoholic medium (ethanol) with deflocculant (0·3 wt% of phosphate ester). A binder (3 wt% of polyvinylbutyral) was then added to improve the mechanical strength of the green material. Powders were granulated through a 200 μm sieve, then uniaxially pressed (150 MPa) to form pellets of 13 mm diameter and 3·5 mm thick.

2.3 Heat treatment

The first stage of heat treatment was pyrolysis of organic-binder and pre-sintering (2 h at 1000°C, in a conventional furnace). The resultant relative density (d/d_{th}) was 0·50. The second stage of heat treatment was reaction sintering, in either the conventional electric or the microwave furnace. The temperature cycles were similar in both cases: heating at 20°C mn^{-1} from room temperature to the firing temperature (T_f), soaking for 1 h at T_f, then cooling at 20°C mn^{-1} to room temperature. T_f ranged from 1300 to 1600°C. Figure 2 shows a temperature-to-time curve for a ($3Al_2O_3$ + $2SiO_2$) powder compact, microwave heated to 1500°C.

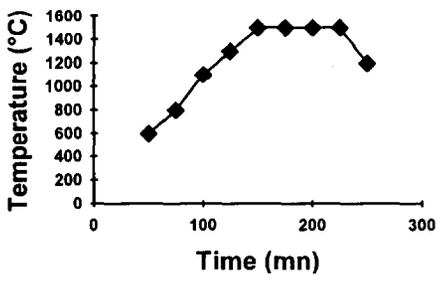

Fig. 2. Temperature versus time for a ($3Al_2O_3$ + $2SiO_2$) powder compact microwave heated to 1500°C.

2.4 Characterization of materials

Density of sintered materials was estimated by Archimedes' method. Portions of specimens were diamond sawn, polished with diamond paste, and thermally etched to observe the microstructure by optical and scanning electron microscopy. Microwave reaction-sintered specimens were sawn to cut a slice along the diameter parallel to the thermocouple hole, then the slice was cut into three portions labelled as left, central, and right. X-ray diffraction experiments (Cu–Kα radiation) were performed on those portions and the results were compared to XRD data of reference mixtures of known composition, to analyze the extent of reaction quantitatively. Two ratios of XRD peak areas were considered:

$$I_{(220)\text{mullite}}/(I_{(220)\text{mullite}} + I_{(204)\ \text{alumina}}) \text{ and}$$
$$I_{(121)\text{mullite}}/(I_{(121)\text{mullite}} + I_{(204)\text{allumina}}).$$

3 Results and Discussion

3.1 Temperature calibration

A study of the microwave effect requires that the accuracy of temperature measurement be as accurate as possible. However, temperature measurement is difficult in a microwave furnace. Firstly, microwave heating is a volumetric process that generates temperature gradients that are the opposite of what conventional heating produces, the core being warmer than the surface ('inverse gradients'). Secondly, the dielectric-loss factor of the heated material usually rises very rapidly when temperature exceeds a critical value. This leads to a sudden increase in the temperature of the specimen ('thermal runaway'). Thirdly, the large electromagnetic field inside the applicator can disturb temperature measurement.

Both radiation pyrometers and thermocouples can be used. Pyrometers are best suited to measure the surface temperature of a specimen whereas thermocouples are best suited to measure the core temperature. Pyrometers do not interfere with microwaves whereas metallic thermocouples can disturb the electric field in the cavity or be affected by it. We tried using both radiation pyrometers and thermocouples. Pyrometers require

knowledge of emissivity of the ceramics that were tested, which do not behave as a black body. Thermocouples gave reproducible results if placed perpendicularly to the electric field and protected by a metallic shield. We used thermocouples with small diameters (1 and 0·5 mm) to limit the heat losses by conduction.

The thermocouples were calibrated as follows:

3.1.1 Using 1 mm diameter thermocouples

These were tested using eutectic composition (49·4 wt% CaO + 50·6 wt% Al_2O_3), which melts at 1360°C,[15] as confirmed by the experiments in the conventional furnace. The assumption was that eutectic melting is not sensitive to any microwave effect. However, the eutectic temperature that was measured in the microwave furnace was 1320°C. This meant that the temperature in the microwave furnace was under-estimated by about 40°C (furnace was at T ≈ 1360°C) and the discrepancy must be due to heat conduction through the thermocouple. Because conduction decreases when the thermocouple diameter decreases, 0·5 mm thermocouples should behave better than 1 mm ones, as will be confirmed later on.

3.1.2 Using 0·5 mm diameter thermocouples

These were tested by comparison with an IR pyrometer focused on a hole bored into an alumina specimen and shaped to behave as a black body, due to multiple reflections of light. In the conventional furnace, the calibration showed that the emissivity of alumina at 1000°C was of about 0·6 whereas that of the 'black-body hole' was of about 0·9 (instead of 1 for a perfect black body). In the microwave furnace, the tip of the 0·5 mm thermocouple was located at the center of the black-body hole in the alumina specimen and the specimen was thermally insulated by alumina fibers. The difference between the temperature given by the thermocouple and that given by the pyrometer was small over all the temperature range. It was of 10°C at T = 1000°C, to be compared with 40°C for the under-estimation induced by the 1 mm thermocouple. This confirms that 0·5 mm thermocouples behave better than 1 mm ones and, therefore, 0·5 mm thermocouples were used for the rest of the study.

3.2 Temperature gradients

Microwave heating is a volumetric process. In the simplest case where the absorbed power is homogeneous across the specimen, the temperature is heterogeneous, the core being warmer than the surface. This is the opposite of what is observed in conventional heating: microwave heating induces 'inverse gradients', instead of the 'normal gradients' of conventional heating. The absorbed power is not homogeneous across the specimen due to changes in E_{int} and ϵ'' (see Eqn (1)). Usually, the effect of such changes is to increase the (inverse) gradients. To minimize the gradients, the heating rate must be kept at a low value (≤ 20°C mn^{-1}) to avoid hot spots due to local thermal runaway. This requires a careful control of the microwave power, which must be kept at a low level (≤ 200 W). Moreover, the heated specimen must be situated at the place in the single-mode resonant cavity where the electric field is maximum, and the size of specimen (13 mm in diameter and 3·5 mm thick) must be small in comparison with the wavelength of microwaves ($\lambda \approx 20$ mm at 2·45 GHz). Finally, the heated specimen must be thermally insulated using low-conduction alumina fibers. In the absence of such insulation, the temperature difference between the core and the surface of specimen can exceed 500°C.

3.3 Mullitization

The extent of mullitization was quantified by XRD data obtained for reaction sintered specimens. The conventionally heated specimens were found to be homogeneously mullitized throughout their cross section, which indicated that their temperature had been homogeneous during reaction sintering. Conversely, the microwave heated specimens were found to be heterogeneously mullitized throughout their cross section, which indicated that they had been subjected to inverse temperature gradients during reaction sintering. For those specimens, the 'mulitization index' was determined from XRD data corresponding to the central section of the slice cut parallel to the thermocouple hole.

For a given mullitization index, the difference between the registered temperatures of conventional and microwave treatments was ≤ 65°C (Fig. 3). Due to the underestimation of ≈10°C in the microwave furnace, one sees that the present data are in favor of the existence of a microwave effect on mullitization whose magnitude is ≈50°C.

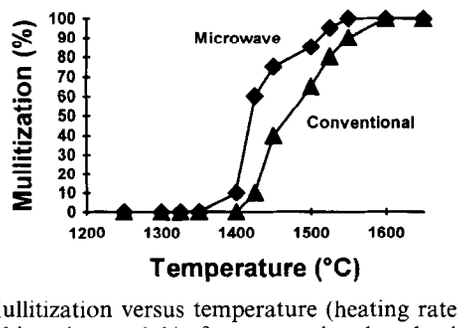

Fig. 3. Mullitization versus temperature (heating rate = 20°C mn^{-1}, soaking time = 1 h), for conventional and microwave heating.

Table 1. Mullitization and estimated temperature in a pellet microwave heated to 1400°C

Portion	*Left*	*Central*	*Right*
Mullitization (wt%) Measured	60	75	60
Temperature (°C) Estimated	1360	1400	1360

Mullitization gradients in microwave heated materials were analyzed by XRD, using various portions cut from reaction sintered pellets. For example, a specimen treated at 1400°C was found to be mullitized to 75 wt% in the central zone but to only 60 wt% in the superficial zone.

The mullitization gradients can be used to evaluate the temperature gradients, using reaction-to-temperature plots. Table 1 shows that the difference of temperature between center and surface for a pellet microwave heated to 1400°C is ≈40°C. This temperature difference is similar to the temperature difference that would correspond to the microwave effect.

3.4 Densification

Theoretical density was estimated from a rule of mixture having found the specimen composition that was given by quantitative XRD phase analysis. Apparent density was determined by averaging data from a whole specimen, which means we were not able to take into account any densification gradient.

Microwave heating seems to accelerate densification in comparison to conventional heating. However, specimens with the same mullitization index show the same densification, whatever the nature of heating. The temperature difference between conventional and microwave heating is a maximum for fully mullitized specimens, where densification is ≈75%. At its maximum, the microwave effect on densification is ≈50–60°C, which corresponds to the microwave effect on mullitization. This temperature difference is much smaller than the difference of 300–400°C reported by Kimrey *et al.* in 28 GHz microwave sintered alumina.[6]

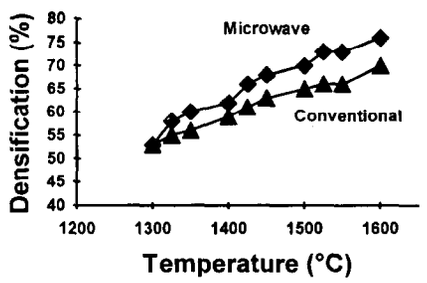

Fig. 4. Densification versus temperature (heating rate = 20°C mn^{-1}, soaking time = 1 h), for conventional and microwave heating.

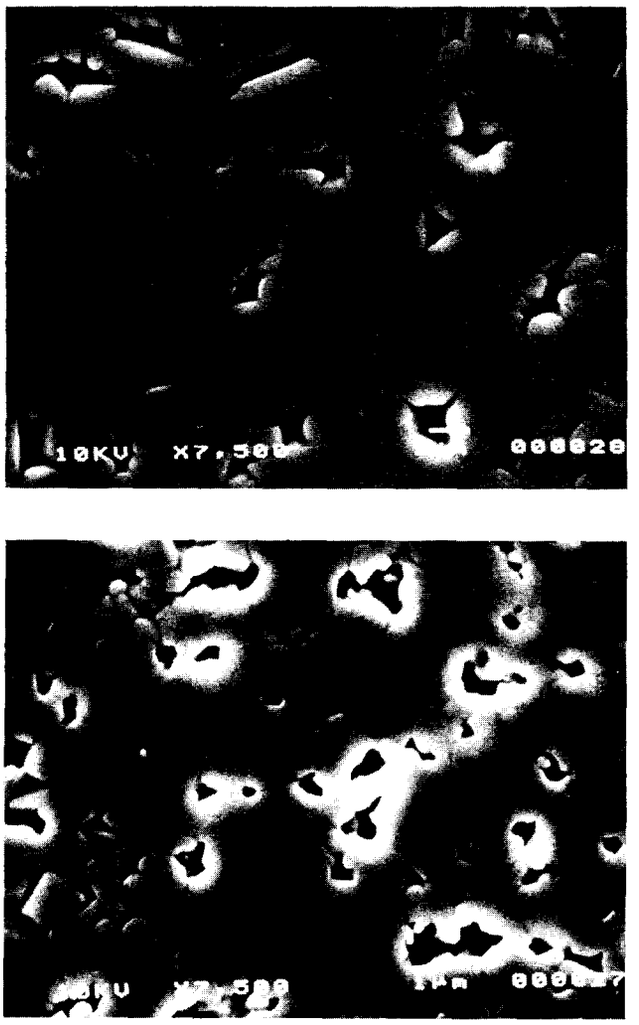

Fig. 5. SEM micrographs of a microwave heated specimen (1580°C, 35 mn): (a) core; (b) surface.

Microstructural observations confirmed that the microwave heated specimens were heterogeneous. The core exhibits higher densification and larger grain size than the surface (Fig. 5). For a given densification, conventional heated and microwave heated specimens exhibited similar microstructures, with no noticeable difference in grain shape, (i.e. equiaxial versus elongated).

4 Conclusions

The study of reaction sintering of $3Al_2O_3 + 2SiO_2$ powder compacts treated by conventional or microwave heating does not disprove the possibility of a microwave effect, which would slightly accelerate both reaction and densification. However, the decrease in temperature associated with such an effect would be ≈50°C, at most, which is much lower than what was sometimes claimed. This

temperature difference is in the order of the temperature gradients across the specimens.

It may be that the experimental conditions we used, in particular the choice of a frequency of 2·45 GHz instead of a higher frequency, were not the best to detect the microwave effect. Moreover, results on alumina-plus-silica mixtures cannot be extrapolated to results on ceramic materials having very different electric properties, in particular ionic conductors or semiconductors. However, it is a fact that, from older to newer data,[1–3,16] the trend is continuously changing toward a decrease in extent of the microwave effect. The present work shows that, for mullitic materials, the microwave effect cannot be expected to accelerate the densification (or reaction) kinetics at a rate sufficient to reimburse the extra cost of sophisticated microwave equipment. This comment refers to the preparation of homogeneous objects. On the other hand, the existence of noticeable 'inverse' gradients and the possibility of changing the heating rate by changing the dielectric properties make microwave heating an excellent technique for producing non-homogeneous objects. Objects with gradients in properties such as in the new family of functional gradient materials (FGM),[17] ceramic-to-ceramic joining, and ceramic–ceramic composites are examples.

Acknowledgements

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