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# Thermal Microwave Processing of Materials

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## 1. Introduction

Practically all kind of materials; namely polymers, metals and ceramics have been heated up with microwaves. There are many reasons for conducting research in this area, microwaves can be applied in vacuum and can be turned on and off in the same way than an electric resistance, but without thermal inertia. Other attributes have been investigated, such as higher efficiency and uniformity in heat transfer and high reaction rates. Researches have reported that processing of materials using microwaves for supplying energy is improved, decreasing the sintering temperature, increasing reaction rate and reducing the activation energy.

The term "microwave effect" has emerged from the many serious reports describing a higher reaction rate due to microwave application available in literature; however a satisfactory explanation has not been given because the results that are presented are often extremely specific and can not be applied to other conditions.

Some results are controversial because they consider that the energy is not being transferred to the system through conversion of microwave energy into thermal energy. It is assumed that microwaves interact directly with the molecules or atoms in the lattice considering non-thermal activation of processes such as improved atomic diffusion.

There are other explanations based on thermodynamic and kinetic effects, given by selective heating of specific reaction components, rapid heating rates and high temperature gradients due to self-generated heat within the sample rather than convection and conduction heat transfer.

Good microwave absorbers, meaning materials where microwaves are clearly converted into heat, will not show non-thermal effects. Heating mechanism due to the presence of an electric field in the frequency of 1 up to 300 GHz includes dielectric: dipolar losses, ion jump relaxation, and resistive heating. In ceramics, and especially in semiconductors, it is possible to have dielectric and resistive contributions simultaneously. These materials can be heated with microwaves, but the amount of energy that they absorb limits their application to specific processes, such as synthesis, sintering or some thermal treatment. Many examples of materials showing non-thermal effects of microwaves are taken from these materials.

The aim of this book chapter is to show some cases of microwave processing of materials considering the conditions that could explain the "microwave effect" often reported. It is necessary to consider that always that the conditions are changed over a system there will be always an effect over the process; effects where a thermodynamic or kinetic explanation is possible will not be considered as "microwave effect" just as heating water with fire is not considered a "fire effect".

Discussion in this document is centered on ceramics where it has been demonstrated that under certain conditions, microwaves heat these materials up. It is considered processing at 2.45 GHz of, calcium zirconate, spinel alumina–magnesia, silicon carbide and manganites. In each of the cases the processes are described in terms of providing an explanation for the speed up of the reaction based on thermodynamic and kinetic approaches, considering that a reaction could be speed up based on activating a given mechanism with a different activation energy, or simply having thermal gradients that are not considered when average temperatures are taken as the actual ones, rather than non-thermal diffusion which is described by the same Arrhenius equation only with the activation energy changed. Enhance in diffusion comes then from a claimed reduction of this activation energy with no further explanation or change of the phenomena or thermal considerations, such as thermal uniformity due to a combination of having small samples compared to the penetration depth of the microwaves, and high thermal diffusivity that results in smaller thermal gradients.

"Microwave effect" is described in terms of thermodynamic and kinetic aspects for the cases presented here, looking forward to extrapolate this explanation to other similar cases where this effect has been accepted without further argumentation. Although there are still many non-thermal cases that are not easily explained invoking known kinetic arguments, the purpose of this research is to reduce the amount of those cases whenever is possible.

## 2. Background

It has been reported that processing of materials using microwaves for supplying energy is improved, decreasing the sintering temperature, increasing the reaction rate (Katz et al., 1991) and reducing the activation energy (Janney et al., 1991). These kinds of reports induce to consider that the microwaves have an especial effect over the reactions. There has been outlined several possibilities for explaining this phenomenon, ranging from an improved atomic diffusion in this kind of materials (Binner et al., 1995), to iron providing local warming that causes the reactions to be more rapid (Roy et al., 2000).

There are several examples where a "microwave effect" has been proven (Binner et al., 2008). The amount of serious reports is impressive and respectfully although a satisfactory explanation has not been given. However the results that are presented are often extremely specific and can not be applied to other conditions. The mechanisms that have been proposed to explain the warming through microwaves do not seem to sustain the "microwave effect" affirmation, indeed, there are results where such effect is not observed (Roy et al., 2000), then this issue is controversial (Garbacia et al., 2003; Wittaker, 2005; Hoogenboom et al., 2005) and deserves more study.

Polymers (Popescu et al., 2008), metals (Roy et al., 1999) and ceramic (Xiang et al., 2005) have been heated up with microwaves. Ceramics can be heated with microwaves; however the amount of energy that they absorb limits their application to specific processes, such as synthesis (Rao & Ramesh, 1995), sintering (Brandon et al., 1992) or some thermal treatment (Sorescu et al., 2004).

Microwave heating is very sensitive to the kind of material that is being heated, following are some examples of processing where the potentiality of this method is presented with spinel alumina–magnesia, calcium zirconate, silicon carbide and manganites, and how some observations regarding that could be taken as non-thermal effect or special effect of microwave can be justified with classical thermodynamics and kinetics arguments.

## 3. Microwave processing

### 3.1 Microwave synthesis: calcium zirconate

Perovskite-structured oxides such as the zirconates are of considerable interest because their conductive properties at high temperature (Islam et al., 2001). One that has been often studied is the $CaZrO_3$ (Jacob, 1997; Yamaguchi et al., 2000) and in this case it is proposed that synthesis of this material using microwaves, as an energy source, is possible.

Mechanisms such as polarization increase of conductivity improving Joule effect and ion vacancy jump are explained in several references and results from other research works show that $ZrO_2$ absorbs energy from microwaves (Aguilar et al., 1996). Hence, it seems viable that this form of energy is an alternative for producing these kinds of materials. Formation of $CaZrO_3$ by heating $CaCO_3$ and $ZrO_2$ powders conducted in a microwave oven has been reported earlier (Aguilar et al., 1996). It was expected that absorption improves with temperature because it has been reported (Willert-Porada & Gerdes, 1991) that the loss factor increases as function of temperature. $CaZrO_3$ is a perovskite that is a ferroelectric material; the characteristics of these materials include high dielectric permeability, ferroelectric hysteresis and polarization saturation (Hippel, 1995). The use of a graphite susceptor has been reported (Aguilar et al., 1996), the maximum temperature that graphite alone under air atmosphere can reach is below 1200 K, but temperature in the tests would be higher because the mixture also absorbs microwaves. The purpose of this study is to process mixtures of $CaO-ZrO_2$ with microwaves for producing zirconate considering the pressing level, mass and applied power.

The experimental design was based on three parameters: pressing level, mass and applied power. The mixtures were sat over a bed of graphite as susceptor. It was found that 10 minutes are enough to reach melting point temperatures and therefore the nominal testing time was that long. The selected powers were 1000 W and 2000 W. It must be considered that not all of the applied power was actually being deposited in the sample, there are heat losses and the material itself is not a perfect absorber.

The mixtures were prepared in a 1:1 molar ratio of $ZrO_2$: CaO. The conditions of the tests are shown in table 1. Average particle sizes were 12μm for CaO and 8μm for $ZrO_2$. The pressing was carried out in just one direction thus the final shape of the sample in the compacted case was a tablet of 2.9 cm diameter and either 0.45 cm or 0.89 cm height, depending if the mixture was 8 g or 16 g.

The size of the non-compacted samples was 3.5 cm diameter, which is the inner diameter of the crucible, while height was according to the mass, 0.80 cm for the 8 g mixture or 1.5 cm for the 16 g one. The crucible was 5.0 cm outer diameter, 3.5 cm high and it was made of high purity alumina and was isolated with ceramic fibber.

The crucible with the mixture was introduced into a multimode cavity. Forward and reflected power was monitored while tuning was performed in order to keep this reflected power to a minimum value.

The power source was a magnetron working at 2.45 GHz and variable power up to 3 KW, the microwaves were conducted through a WR284 (7.2 cm x 3.6 cm) waveguide attached to the cavity, and the temperature measurement was performed by optical pyrometry.

The results and the conditions of experiments are also presented in table 1. Regarding X-rays analysis, all the samples exhibited $CaZrO_3$, although the only ones that did not present free CaO or $ZrO_2$ are those that were processed at 2000 Watts. Presence of $CaZrO_3$ at lower temperatures demonstrates that there were hot spots within the samples. In all of the cases there was formation of $(CaO)_{0.15}(ZrO_2)_{0.85}$.

| Exp. | Pressure (MPa) | Applied Power (W) | Mass (g) | Maximum temperature (K) | Time for achieving maximum temperature (sec) |
|------|----------------|-------------------|----------|-------------------------|----------------------------------------------|
| 1    | 0              | 1000              | 8        | 705                     | 553                                          |
| 2    | 147            | 1000              | 8        | 678                     | 503                                          |
| 3    | 0              | 2000              | 8        | 2488                    | 266                                          |
| 4    | 147            | 2000              | 8        | 2291                    | 352                                          |
| 5    | 0              | 1000              | 16       | 884                     | 546                                          |
| 6    | 147            | 1000              | 16       | 498                     | 525                                          |
| 7    | 0              | 2000              | 16       | 1240                    | 272                                          |
| 8    | 147            | 2000              | 16       | 1561                    | 378                                          |

Table 1. Experimental design and results.

For the samples that did not show residual CaO, or at least was not detected, the amount of $(CaO)_{0.15}(ZrO_2)_{0.85}$ must be small because the mixtures were prepared in 1:1 molar ratio and a large removal of CaO is necessary, which is rather difficult, for having an appreciable amount of this solid solution. One interesting aspect is that the compacted mixtures got molten while the non-compacted ones exhibited sintering only, even when the achieved temperatures were similar in both cases. This behavior was expected considering that pressing supplies energy to the mixture. Other aspect can be appreciated by looking at the thermal evolution (Figures 1 and 2), compacted samples took longer to achieve the maximum temperature than non-compacted, which is more notorious in the 16 g mixtures.

It is interesting to observe that in the non-compacted case the temperature remains around 1000 K until heating is activated. It is possible that this behavior is present in all of the cases, but temperatures lower than 900 K were not registered by the optical pyrometer, and
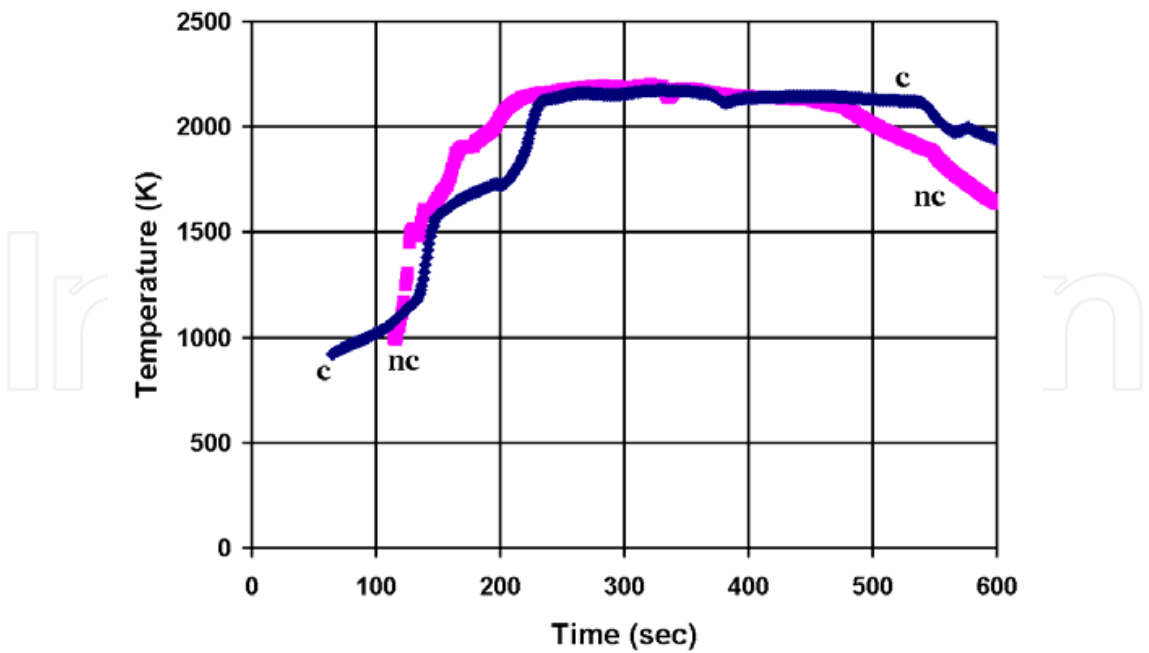


Fig. 1. Comparison between the average thermal evolution of compacted (c) and non-compacted (nc) mixtures of 8 g exposed to 2000 Watts. Temperatures below 900 K where not registered by the optical pyrometer.
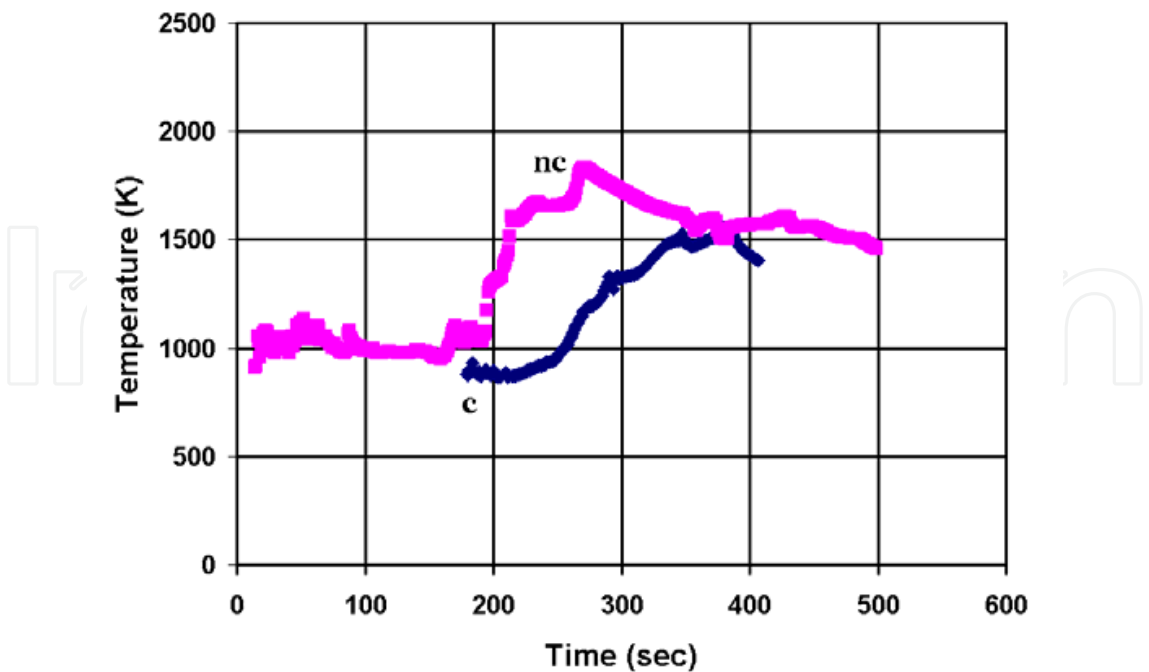
Fig. 2. Comparison between the average thermal evolution of compacted (c) and non-compacted (nc) mixtures of 16 g exposed to 2000 Watts.

therefore this "activation" temperature is not evidenced. In any case, times for activation are shorter for non-compacted mixtures than compacted and for high power/mass ratios than low (2000/8 against 2000/16).

Notice how a time for activation of the non-compacted mixture is about double when energy supply is the half (75 sec against 190 sec). The same behavior is found in the compacted case (115 sec against 250 sec), meaning that the necessary energy for having an excitable (microwave absorbent) mixture is about constant. For interpreting the differences between compacted and non-compacted mixtures, regardless the energy input, it is necessary to describe the $CaO$-$ZrO_2$ system and propose a reaction path.

There are three defined compounds in the $CaO$-$ZrO_2$: $CaZrO_3$, $CaZr_4O_9$ and $Ca_6Zr_{19}O_{44}$ (Tanabe & Nagata, 1996). They also reported the activity of $CaO$ in a $CaO$-$ZrO_2$ system, which is low compared to its (Table 2). Hence, it is possible to assume that Ca gets into the $ZrO_2$ lattice to form a solid solution in the proportions already showed. $(CaO)_{0.15}(ZrO_2)_{0.85}$ was found in all the cases. According to Tien (Tien, 1964) the electrical conductivity of this system increases with temperature and with the amount of $CaO$ up to 13 mole%, although there are other reports for electrolytes made of $CaO$+$ZrO_2$ that are higher, but in the same order of magnitude (Kingery et al., 1975).

| Temperature (K) | Cubic solid solution | |
| --- | --- | --- |
| | CaO | $ZrO_2$ |
| 1673 | 0.02051 | 0.9295 |
| 1773 | 0.02222 | 0.9295 |
| 1873 | 0.02430 | 0.9274 |

Table 2. Activities of CaO and $ZrO_2$ in a solid solution of 15 mole% of CaO.

The differences in the thermal behavior of the non-compacted and compacted mixtures can be explained by the more intimate contact among the particles in the compacted case and the energy that was already stored due to the press process. Therefore, as the solid solution is being formed, the conductivity increases and Joule effect becomes a heat contributor of the mixture and promotes even more reaction thermally. Further melting and heat losses determine the maximum achievable temperature.

Conductive material could form a shield effect, but before this happens there is dielectric heating without melting and then Joule heating as described above. The supplied power was kept to the nominal value during the test, the reflected power varied as the properties of the mixture change with composition and temperature. The absorbed power against temperature was estimated by monitoring these changes with the directional coupler (Roussy & Pearce, 1995). Notice in figure 3 how in each case, compacted and non-compacted exhibit different energy absorption related to temperature, which means a different absorption mechanism or at least different dielectric properties.
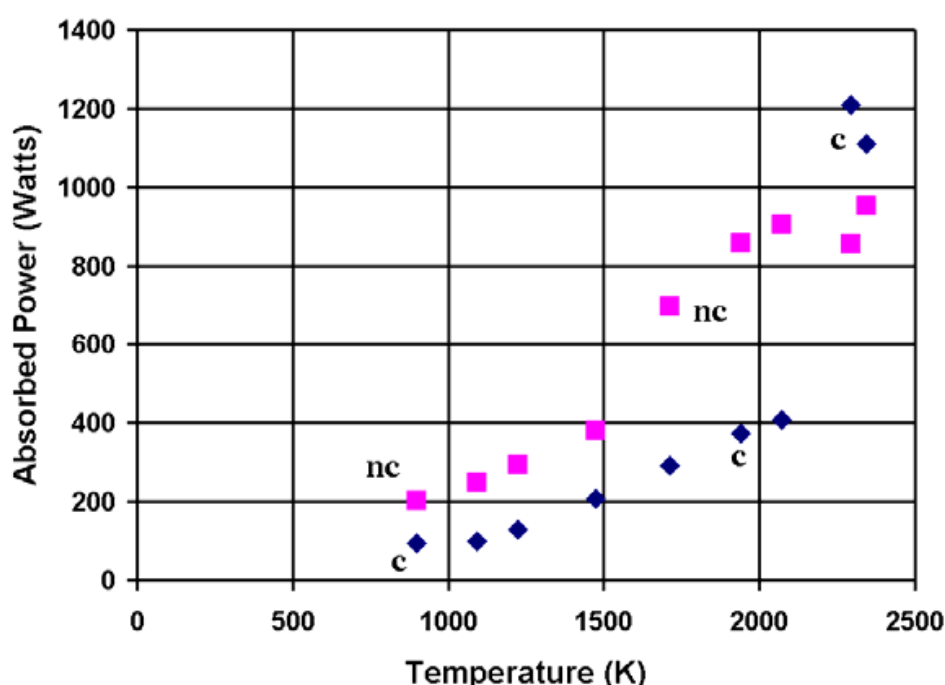


Fig. 3. Power taken by the system (cavity, crucible and mixture) estimated from the forward and reflected power ratio during the test of mixtures of 8 g Compacted (c) and non-compacted (nc) mixtures exposed to 2000 Watts.

Then, it can be suggested that heating during the reaction is aided by the formation of $(CaO)_{0.15}(ZrO_2)_{0.85}$, which was found in all the samples and has a composition close to those where the electric conductivity of a $CaO$-$ZrO_2$ solution is maximum in the experimental temperature range. $CaO$-$ZrO_2$ solid solutions are considered as a high conduction electrolyte and because any other composition was not found, it is speculated that among the $ZrO_2$, the phase, $(CaO)_{0.15}(ZrO_2)_{0.85}$, is thermally responsible of the heating with microwaves.

### 3.2 Microwave synthesis: silicon carbide

The main applications of silicon carbide are in composite materials, abrasives, high hard tools and machining equipment. It is also used as a coating material due to wear resistance.

Another application in the refractory industry is related to the manufacture of crucibles. These are just structural applications, although there are other electric ones when other elements are added (Lee et al., 1994).

Traditionally, this material is produced by means of a procedure named Acheson process, which consists in placing a mixture of silica and carbon in an electric furnace. Heating is accomplished by a core of graphite and coke placed at the center of the furnace. The mixture is set around this core where temperature is 2700 °C approximately. The graphite remains at the core, while Si reacts with carbon to form different SiC polytypes in colder parts of the oven. Among the several polytypes there are more than 200 non cubic polytypes known as $\alpha$-SiC and only one that is cubic, known as $\beta$-SiC or SiC-3C, that is interesting because of its applications. Being one among many, often $\beta$-SiC is produced in mixtures with large amounts of $\alpha$-SiC.

Since the development of the microwave devices there has been a growing interest, within the scientific community, on the possible applications of microwave radiation as an energy source for the processing of materials. Microwave synthesis of silicon carbide from silicon and activated charcoal has been reported at temperatures as low as 727 °C (Ramesh et al., 1994), which is far below the temperatures achieved in the Acheson process. From previous experiences (González et al., Aguilar, 1996) is known that temperatures around 2000°C are achievable with microwaves when the materials are good microwave absorbers.

Silicon carbide production can be described as a reaction where silicon oxide is reduced by graphite resulting in substitution of the oxygen by carbon. As a process, this reaction can be described thermodynamically as:

$$SiO_2 + 3C = SiC + 2CO \tag{1}$$

This endothermic reaction requires about 528 KJ/mole and industrially it is carried out at temperatures ranging between 1600 °C and 2500 °C.

Then, regarding microwave processing, the idea is to producing $\beta$-SiC from a mixture of silica and graphite by means of microwaves as an energy source knowing that it is possible to keep the temperature within the range of $\beta$-SiC growth.

Silicon carbide production tests were carried out using a magnetron working at 2.45 GHz and a power supply of up to 2000 Watts. Powders of $SiO_2$ and C of average size of 80 μm and 50 μm respectively, were mixed thoroughly to get intimate contact between the particles. The used ratio was 1:3 molar. $SiO_2$ and C are good microwave absorbers even at low temperatures, and then the mixture is able to achieve the required temperature for the process to occur. The mixture was placed inside a thermally insulated crucible made of high purity alumina which was in turn placed into the cavity in a specific location that was found to be the best according to the heating rate. The mixtures were exposed to the conditions given in table 3; temperature was taken optically.

The obtained samples exhibited two separated phases; first one was conformed by a black shape, while the second one consisted in a whitish material in drops. Both of phases were analyzed by X-ray diffraction of powders ($\lambda$=1.54Å), and the only compound found in the black material was SiC-3C, with un-reacted graphite, while the drops were $SiO_2$ only. One example of the diffraction pattern is shown in figure 4, which corresponds to test 8.

The X-rays diffraction patterns took from different zones in the sample show homogeneity. In all of the cases the found silicon carbide corresponded to SiC-3C, according to the diffraction center (ICSD) it is cataloged as (29-1129) which is the cubic $\beta$-SiC.

| Test number | Time (sec) | Power (Watts) | Mass (g) |
|---|---|---|---|
| 1 | 600 | 1000 | 10 |
| 2 | 600 | 2000 | 20 |
| 3 | 900 | 2000 | 10 |
| 4 | 1500 | 2000 | 10 |
| 5 | 900 | 1000 | 10 |
| 6 | 1200 | 1000 | 20 |
| 7 | 600 | 1000 | 20 |
| 8 | 600 | 2000 | 20 |
| 9 | 1200 | 2000 | 20 |
| 10 | 1200 | 1000 | 20 |

Table 3. Experimental conditions for SiC production.
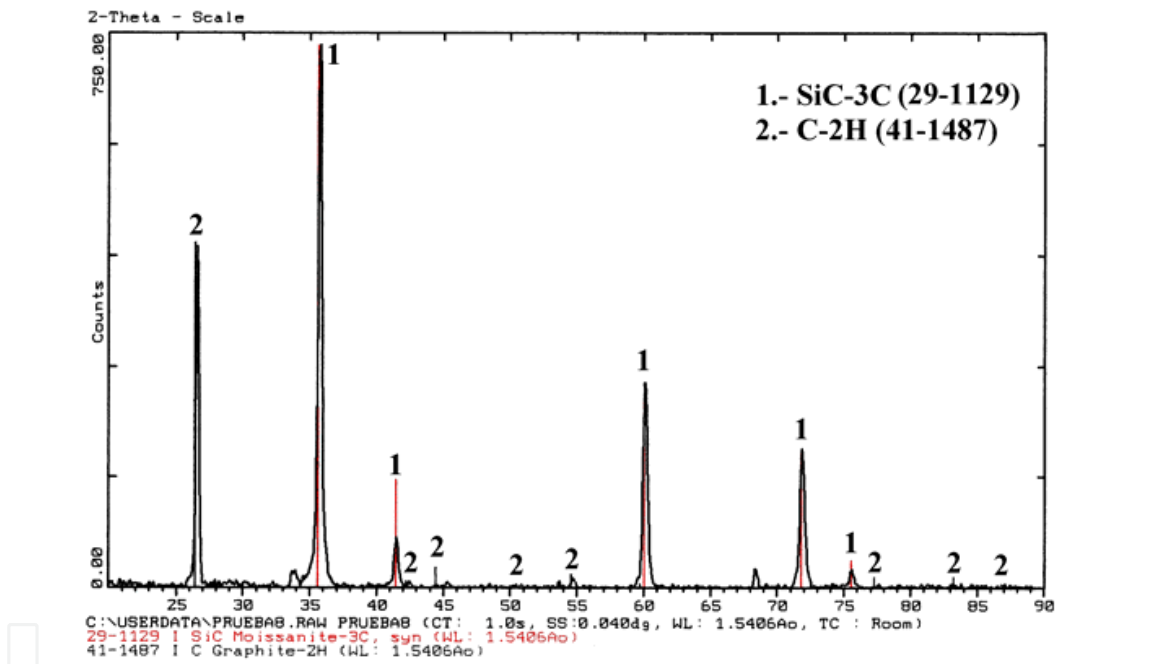


Fig. 4. X-ray diffraction pattern from the black phase in test number 8. The only species found are silicon carbide and graphite. Small unidentified peaks do not form a set for other species, although they might be other silicon carbide polytypes or silicon as element.

Table 4 shows the SiC/C ratio and the maximum achieved temperatures were between 1800°C and 2000°C, which are adequate for having growth of this particular structure. Cavity was overheated in several occasions and for that reason some tests were terminated earlier as the actual exposition time column shows. Figure 5 corresponds to the pattern of a sample of commercial SiC where β-SiC is not present.

This commercial sample, taken a resistance electrode that according to the producer was made of a single kind of SiC is made of α-SiC, which is valid considering that all of the present phases are specified that way. The microwave method gave the temperature conditions for producing β-SiC (SiC-3C) as confirmed by X-rays diffraction. SEM images

show wiskers of SiC at the center of the obtained mass (Figure 6), while grains were formed at the edge (Figure 7). Achieved temperatures are in the adequate range for producing β-SiC, no other polytype was produced, which is a difference against other methods. Then, mixtures of $SiO_2$ and C exposed to microwaves at temperatures between 1700°C and 2100°C actually produced β-SiC. The difference between the center and the edge is an evidence of thermal profile and that microwaves acted thermally.

| Test number | Achieved max temp. (°C) | SiC/C peak ratio | Actual exposition time (sec) |
|---|---|---|---|
| 1 | 1702 | 0.92 | 589 |
| 2 | 2063 | 0.17 | 605 |
| 3 | 2025 | 0.32 | 969 |
| 4 | 1968 | 1.05 | 1468 |
| 5 | 1873 | 2.76 | 830 |
| 6 | 1930 | 0.54 | 1243 |
| 7 | 1876 | 0.38 | 600 |
| 8 | 2126 | 1.55 | 605 |
| 9 | 1957 | 1.3 | 1050 |
| 10 | 2054 | 0.30 | 1100 |

Table 4. Results of the tests described in table 3.
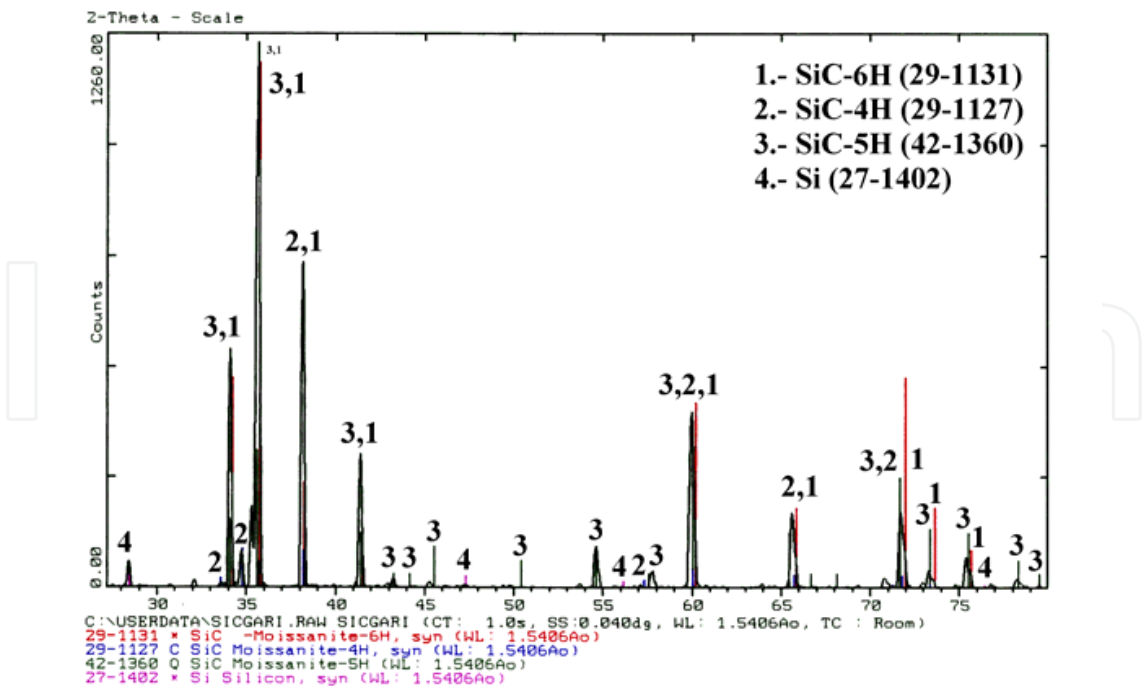


Fig. 5. X-ray diffraction pattern from commercial silicon carbide, notice the mixture of present structures, including silicon. β-SiC is not present in this case.
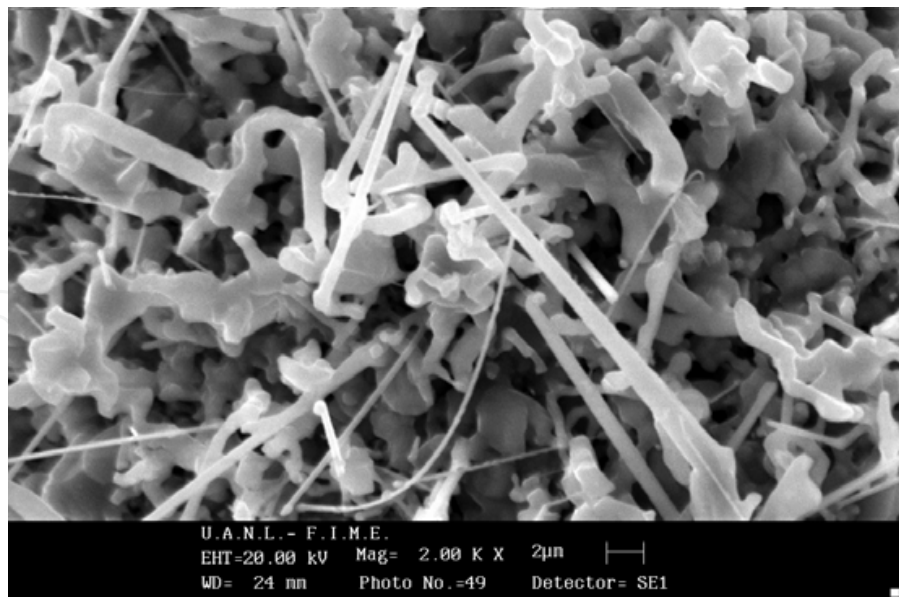
Fig. 6. Whiskers of silicon carbide (test number 5). This is one of the tests where more silicon carbide was observed; just few zones in the sample (not shown) exhibited free graphite.
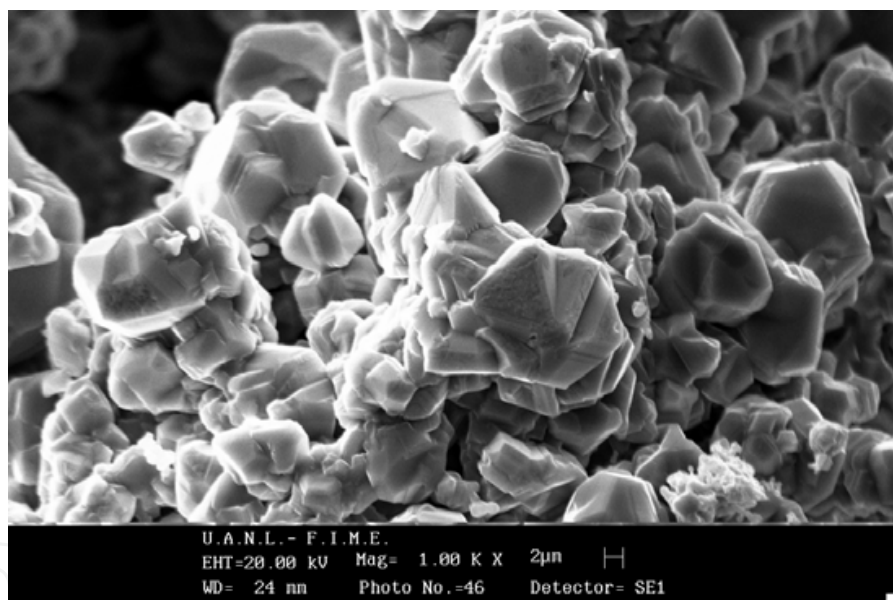


Fig. 7. Grains of silicon carbide (test number 5). This area was far from the center, closer to the crucible walls where thermal losses are higher.

## 4. Microwave effect

### 4.1 Temperature measurement

Discussions about the improvement of the processing rates when microwaves are used can not be solved while temperature is not well known for conducting kinetic comparisons. That is the reason for emphasizing the measurement techniques, optical pyrometry is a good option because it does not interact with the sample, but it is only surface measurement and does not work at low temperatures. Optical fiber is an option for low temperatures and it is claimed that they do not affect the system. Thermocouples work in a wide range of

temperature and are quite simple to use, but it is common to have arguments against them for taking temperatures in processes that are taking place under microwave fields. Thermocouples placed perpendicularly to the electric field are reliable, however this configuration is possible in waveguides only, and the test was made with two thermocouples, one in front of the other, tip to tip, with the tip at different distance from the waveguide wall and perpendicular to the electric field. The sample was an alumina crucible filled with alumina (total weight 145 g) in a WR284 waveguide. Reflected and forward power were monitored as well as temperature, power was switched on and off as points 1 to 5 (Figure 8) are switching of power and it can be noticed that there are not discontinuities in temperature. This discussion (Aguilar & Pearce, 2003) is taken in more detail below.
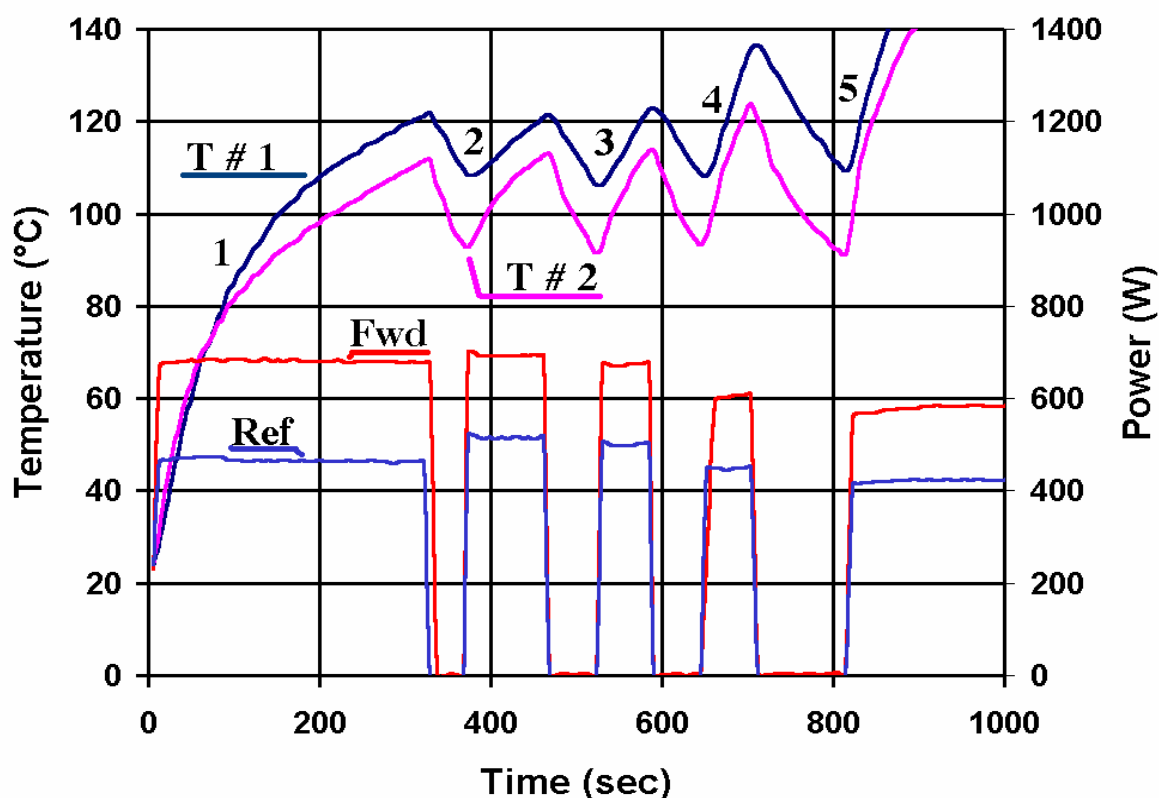


Fig. 8. Temperature measurement of 145 g of alumina, T#1 is one thermocouple located at 3 mm from the centre of the waveguide and T#2 is another one located at 1 mm. Switching of the power supply (points 1-5) shows reliability of thermocouples. Forward and reflected power is also shown.

However, its simplicity makes it attractive for being considered in multimode cavities where it is not possible to locate them in a particular position referred to the electric field. One question that arises when thermocouples are employed is if the electric field perturbs the measurement, and if the thermocouple affects the processing. Therefore, the first issue is to evaluate the reliability of the thermocouple and its possible influence on the processing in a multimode cavity.

One way for confirming reliability of thermocouples is by conducting experiments in a process that is suitable to be perform while other evidences related to temperature and reaction are considered. The chosen process was microwave synthesis of spinel ($MgAl_2O_4$) with hematite ($Fe_2O_3$). This system is interesting because alumina-based systems are very

common in refractory industry. Analysis of the obtained samples was carried out by X-ray diffraction of powders.

There are several reports of thermocouples employed for temperature measurements in a microwave field (Binner, et al., 1995; Roussy & Pearce, 1995; Gómez, et al., 1996).

The sample or powder mixture was placed into a high purity alumina crucible of 115 g (Figure 9), placed in an appropriate location in a cavity, and isolated with Kwool. The thermocouple was a shielded (3.17 mm diameter) ungrounded type K was placed at the center of the crucible.
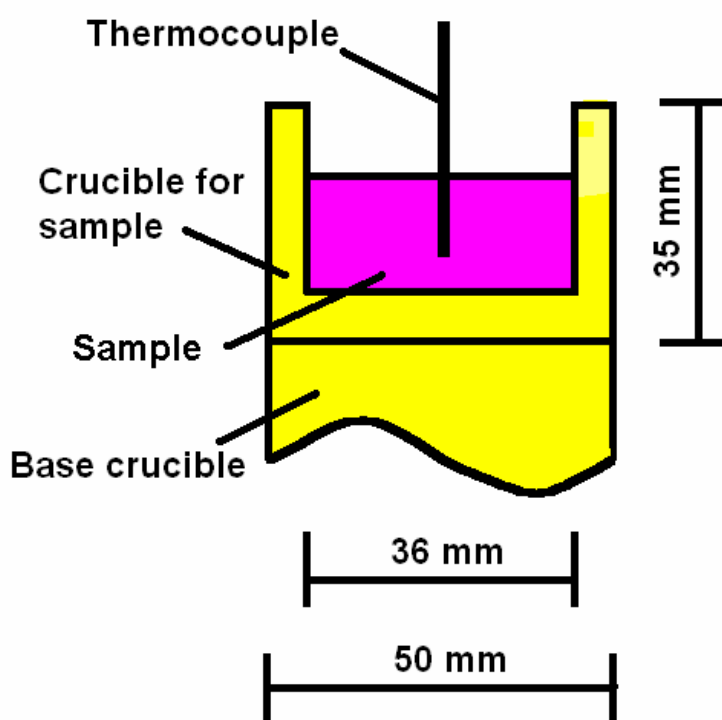


Fig. 9. Scheme of the crucible and the thermocouple inserted in the mixture.

The tests consisted in having a microwave-heating device with an on/off control. The first tests were conducted on hematite, which is know to be a good microwave absorber alone with the temperature setting to 800 °C and 1200 °C An on/off cycle produce ripples in temperature with the frequency given by the controller (Figure 10). Temperature sampling time was 5 readings per second. Notice that the line forming the ripples due to the control action is continuous even during power switching. This test proves that temperature measurement is not affected by the microwaves, although that given process would not be affected by them. Reliability of thermocouples consists on compliance of these two conditions.

Proving the second condition requires analysis of the products of a reaction. The chosen process was synthesis of $MgAl_2O_4$ spinel processed with microwaves from magnesia (MgO) and alumina ($Al_2O_3$) and hematite ($Fe_2O_3$) as a susceptor given than neither MgO nor $Al_2O_3$ are microwave absorbers (Ortiz et al., 2001). Tests were performed on the same arrangement of 7 g incompact, approximately 10 cm$^3$, and mixtures with different compositions of the system MgO-$Al_2O_3$-$Fe_2O_3$, according to table 5.

Magnesia is not a good microwave absorber, and alumina absorbs above 500 °C (Aguilar & Pearce, 2003), then $Fe_2O_3$ in the mixture acts as a susceptor that absorbs energy at room
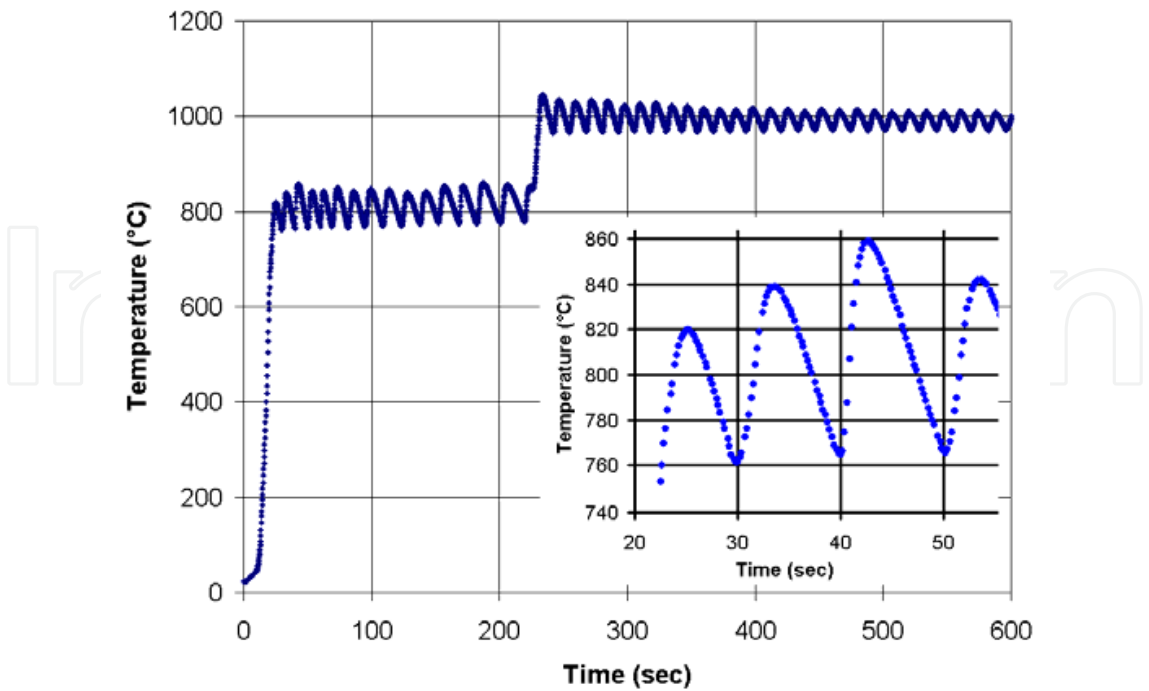
Fig. 10. Test of 20 g of hematite heated with microwaves at 2.45 GHz and 800 Watts in a multimode cavity to 800 °C and 1200°C. Notice the continuity of the temperature in the insert showing early stage of heating.

| Compound/Mixture | 1 | 2 | 3 |
|---|---|---|---|
| MgO | 45 | 35 | 30 |
| $Al_2O_3$ | 50 | 50 | 50 |
| $Fe_2O_3$ | 5 | 15 | 20 |

Table 5. Compositions of the mixtures tested in this work (mole percentage).

temperature and heats up the mixture to 500 °C where $Al_2O_3$ as well as the just formed spinel, absorb energy from the microwaves. Following the example of previous experience with this kind of material (Aguilar et al., 1997), mixtures were exposed to 800 W microwaves at 2.45 GHz for 30 minutes.

By chemical analysis of the products, it is possible to determine if the thermocouple affected the process. With this idea, a comparison against tests without a thermocouple was also performed in order to detect possible differences. In the thermocouple case, when temperature was about to exceed 1200 °C, which is the maximum for a K type thermocouple, it was removed from the system, and process was allowed to continue.

In practice, temperatures above 1200 °C are necessary for producing $MgAl_2O_4$ from MgO and $Al_2O_3$ in reasonable time scales. There are two hematite phases, $\alpha$ $Fe_2O_3$ and the $\gamma$ $Fe_2O_3$. The latter has a lattice structure similar to $Al_2O_3$. It has been reported (Bogdandy & Engell, 1971) that at temperatures between 500 °C and 700 °C, the electron diffraction of the hematite crystal is different from those of $\alpha$ or $\gamma$, meaning that there is another phase that has been designated as $\beta$ $Fe_2O_3$. It could be a superstructure effect or an order-disorder reaction. In any case, this process has been reported endothermic, absorbing 160 cal/mole at 677 °C. This property is used in this work for confirming reliability in the temperature measurement.

The samples were removed from the crucible and analyzed by means of X-Ray diffraction of powders; relative peak intensity was used for estimating amounts of the species after calibration with specimens of known composition. The maximum temperature reached was estimated to be around 2000 °C based on two aspects: the temperature of the insulator taken with an optical pyrometer at the end of the test was 2000 °C, and the melting point of the compounds found in this system range between 2000 °C and 2135 °C.

Simultaneous pyrometer – thermocouple measurements were not considered because the thermocouple was inside the mixture and the insulation was outside, hence the temperatures would not be the same. Besides, the thermocouple could not work above 1200°C and the pyrometer could not measure temperature below 600 °C. Results of tests with and without the thermocouple inserted are presented in table 6.

|  | With | Without | With | Without | With | Without |
|---|---|---|---|---|---|---|
| Added $Fe_2O_3$ (Mole %) | 5 | 5 | 15 | 15 | 20 | 20 |
| MgO | 22 | 23 | 4 | 2 | 2 | 0 |
| $Al_2O_3$ | 14 | 15 | 2 | 0 | 0 | 0 |
| $MgAl_2O_4$ | 28 | 37 | 47 | 49 | 0 | 0 |
| $Mg(Al,Fe)_2O_4$ | 30 | 18 | 36 | 38 | 98 | 93 |
| $FeAl_2O_4$ | 6 | 6 | 11 | 11 | 0 | 7 |

Table 6. Analysis of the obtained samples from the tests with and without thermocouples.

Analysis shows approximately the same composition for tests with and without thermocouple, the difference that is observed at 5% hematite can be explained considering that the melting point of the spinel decreases as hematite is added, therefore the mixture becomes molten and it is difficult to identify each zone into the sample. At this low hematite content the sample was highly heterogeneous; it was even possible to identify different portions of the sample because it was incipiently molten.

Despite this difference at that concentration, from the rest of the results it can be expressed that the thermocouple did not affect the process. Heterogeneity of the sample is an evidence of the importance of the thermal gradient that indeed is more important than the possible error introduced by the thermocouple. Sensitivity of the thermocouples can be evaluated from the thermal evolution of the three chosen hematite compositions (Figure 11).

Plotting those data as heating slopes against temperature (Figure 12) it can be noticed a drop around 600 °C in all cases, including the sample of pure hematite. The thermocouple was sensitive enough to detect that change. Magnitude of the change in the heating slope is related to hematite content, and all of them coincided at a temperature around 650 °C.

This can be related to the hematite transformation (β $Fe_2O_3$) at 677 °C. This value is above the coincidence point and although endothermic curve begins around 400 °C, a wide range of temperature for this transformation has been reported in literature (Bogdandy & Engell, 1971). However, the most important issue here is that the thermocouple is sensitive enough to follow such a thermal change.

The configuration was reliable while similitude in the chemical analyses with and without a thermocouple confirms that at least by the time that the thermocouple was inserted the mixture reaction profile was not altered. Thermocouple is a very simple device that with certain considerations can be used as a measurement probe in microwave processing and helps to have one of the most important parameters for kinetics studies.
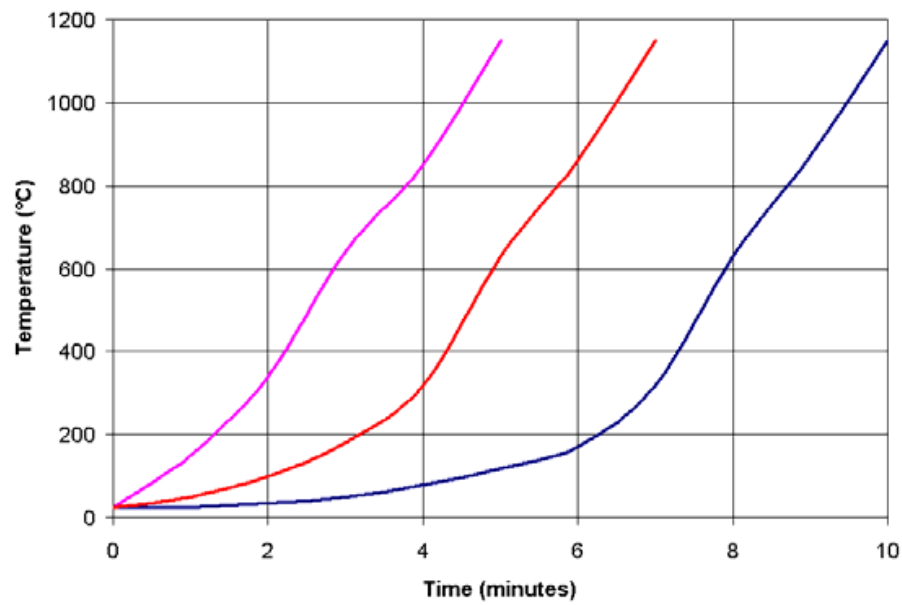
Fig. 11. Heating evolution of mixtures with different hematite content: 20 mole% (violet), 15 mole% (orange) and 5 mole% (blue).
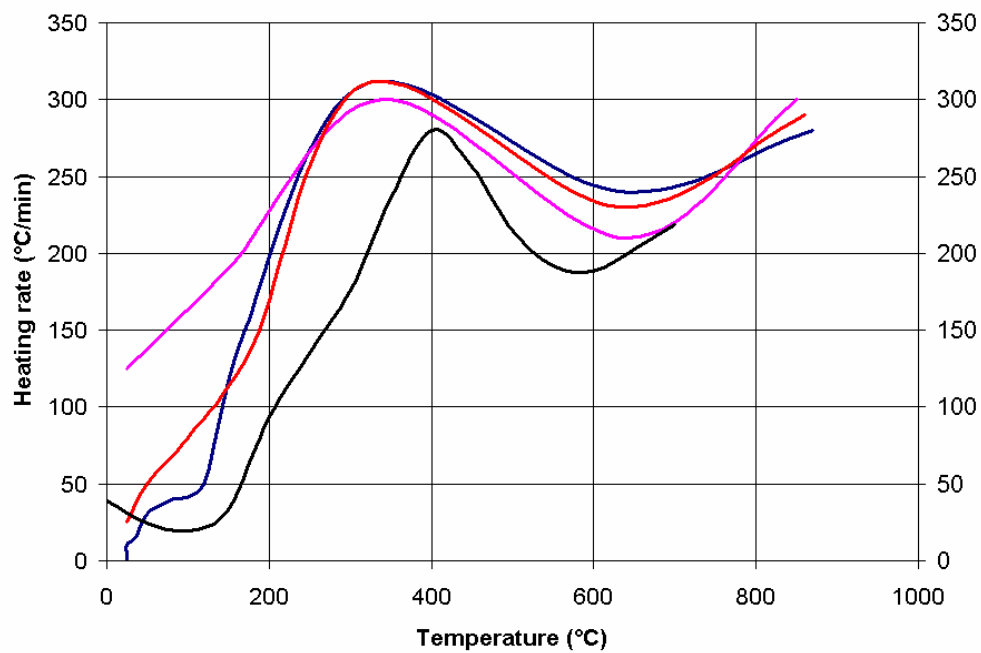


Fig. 12. Heating rates for the tests of the figure 5, as function of temperature. The hematite content are: 20 mole% (violet), 15 mole% (orange) and 5 mole% (blue). The right scale is only for the hematite (black).

## 4.2 Catalytic effect: synthesis of MgAl$_2$O$_4$

There are many papers referring to "microwave effects" of the microwaves during materials processing that consists in improvement of sintered materials as well as sintering temperatures, reaction rate increase and activation energy reduction. For instance researchers at Oak Ridge National Laboratory (Janney & Kimrey, 1991) found that activation

energy for sintering was reduced to 160KJmole$^{-1}$ for the microwave case, instead of 575 KJmole$^{-1}$ commonly reported. For crystal growth they report a reduction from 590 KJ mole$^{-1}$ to 480 KJmole$^{-1}$. In other example, Boch (Boch et al., 1992) proposes that microwaves reduce the temperature for mullite and aluminum titanate processing up to 100 °C. Therefore, one of the "microwave effects", described often as non thermal effects, concerns to "catalysis effect" which is tested with synthesis of $MgAl_2O_4$ from $MgO$ and $Al_2O_3$ as the following lines explain.

The test were conducted over 20 g mixtures of $MgO:Al_2O_3$ in a 1:1 proportion at 1200 °C for producing $MgAl_2O_4$ by:

$$MgO + Al_2O_3 \rightarrow MgAl_2O_4 \tag{2}$$

A real comparison requires two kinds of tests, the first one consisted on heating the mixture in an electric resistance furnace, and taking the temperature with a thermocouple inserted in the sample. In the second case the mixture and graphite as a susceptor, were heated in a multimode microwave cavity at 800 W and 2.45GHz with the thermocouple inserted as explained above. A very important aspect in a comparison is maintaining conditions that can be compared; in this case temperature in the microwave process was matched to conventional one at least in the range where reactions are taken place, sudden heating was not possible to control below 600 °C, but initially it was considered that the process is not being carried out under those conditions.

More tests were conducted at 2000 °C without external control; the temperature was maintained due to the heat balance between the mixtures getting energy and dispreading by radiation when at high temperature providing a self control.

Different exposition times where tried and X-rays diffraction was used for estimating the composition of the obtained sample for confirming spinel formation. X-rays patterns of known samples were used for calibration purposes and then a sample of 1 cm$^3$ around the thermocouple tip was analyzed.

Reliability and sensibility of the thermocouples has been already shown, figure 13 shows the matching temperature in the two kinds of tests. Testing time is 1800 seconds, but matching was achieved since temperature was 600 °C. The insert shows how close the actual temperature was to the setting point of 1200 °C without discontinuities during switching. Thermal runaway of alumina (Aguilar & Pearce, 2003) make difficult to control temperature, therefore the most appropriate condition in this case is to control above 600 °C after the increase of permittivity of alumina has taken place.

Once that it is confirmed that temperature measurement is reliable, the kinetic aspect can be taken in the search for a microwave effect. Accepting that the process is controlled by diffusion the following expression can be taken:

$$R^2 = 2Kt \tag{3}$$

Where R is the molar fraction of formed spinel $MgAl_2O_4$, K is the reaction constant ant t is the time.

Then it is possible to plot $R^2$ against nominal testing time as it is shown in figure 14 and 15. Testing time and temperature are not appropriate for having full transformation, nut that is the essence of a kinetic study, to have different transformation degrees for comparing against time. Error are more noticeable at low transformation because it is squared, however trends and differences are clear and they are evident despite the dispersion of the points.
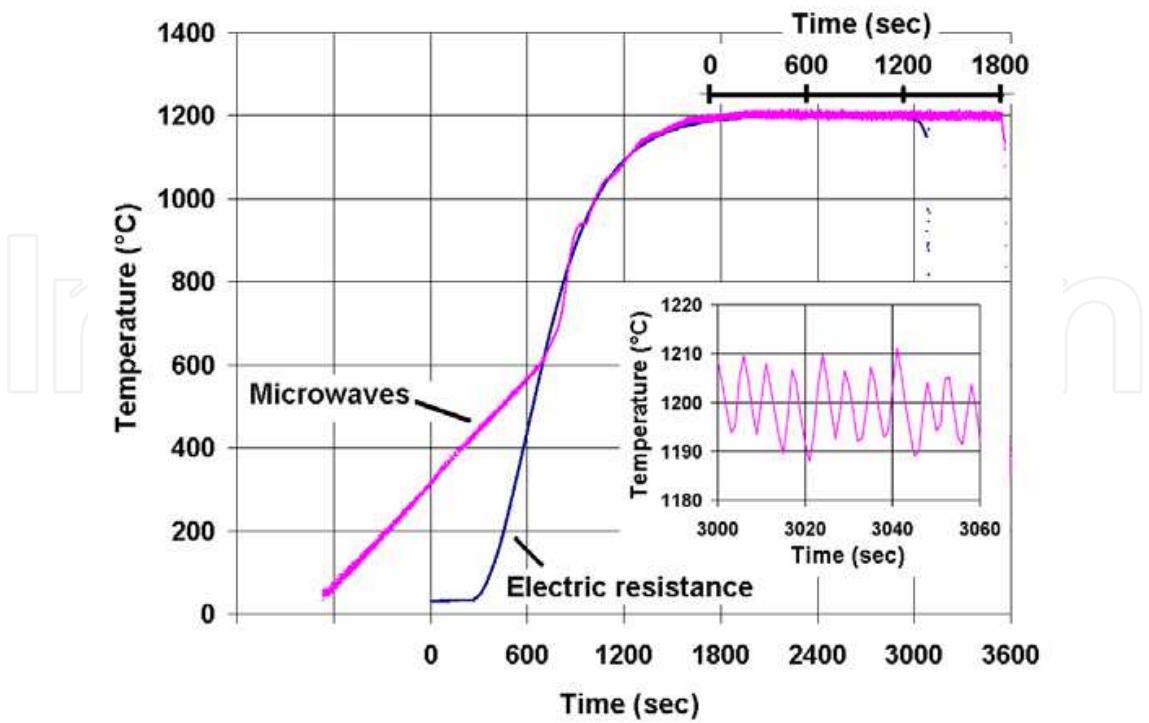
Fig. 13. Matching of the temperatures for the electric resistance and the microwave cavity. The test at 1200 °C lasted 1800 seconds. The insert shows the action of the on/off controller.
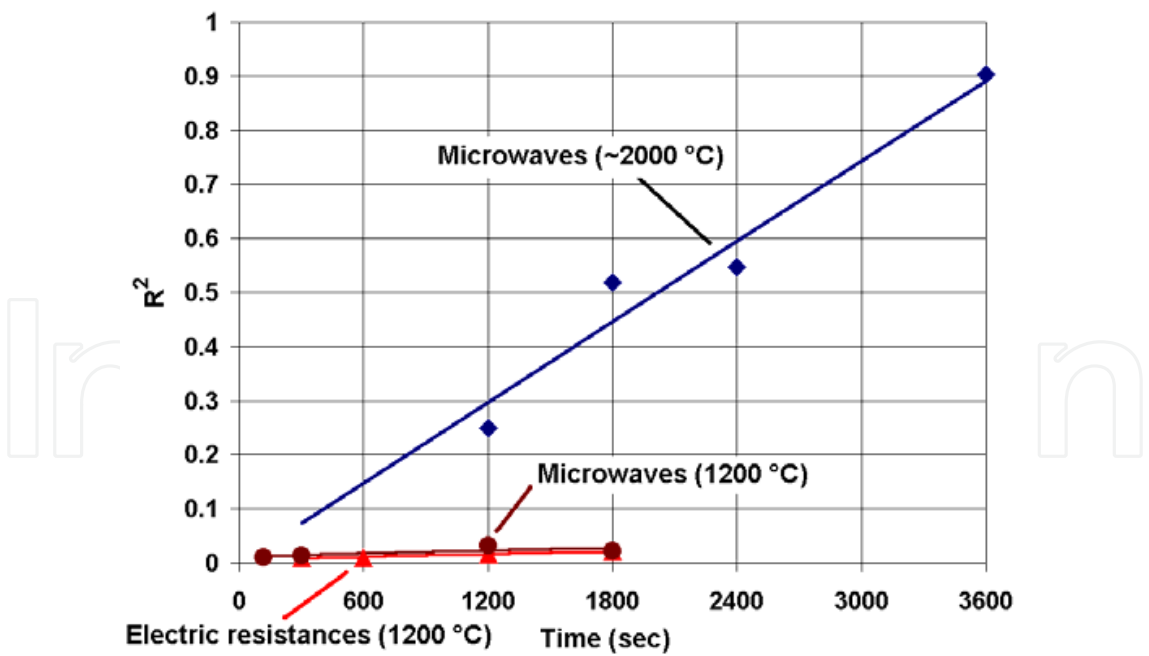


Fig. 14. Experimental results of the test at 1200 °C and 2000 °C. Parabolic regressions are also shown.

It looks like indeed the process was faster with microwaves, the slope in figures 14 and 15 represents 2K and value of K is presented in table 7.
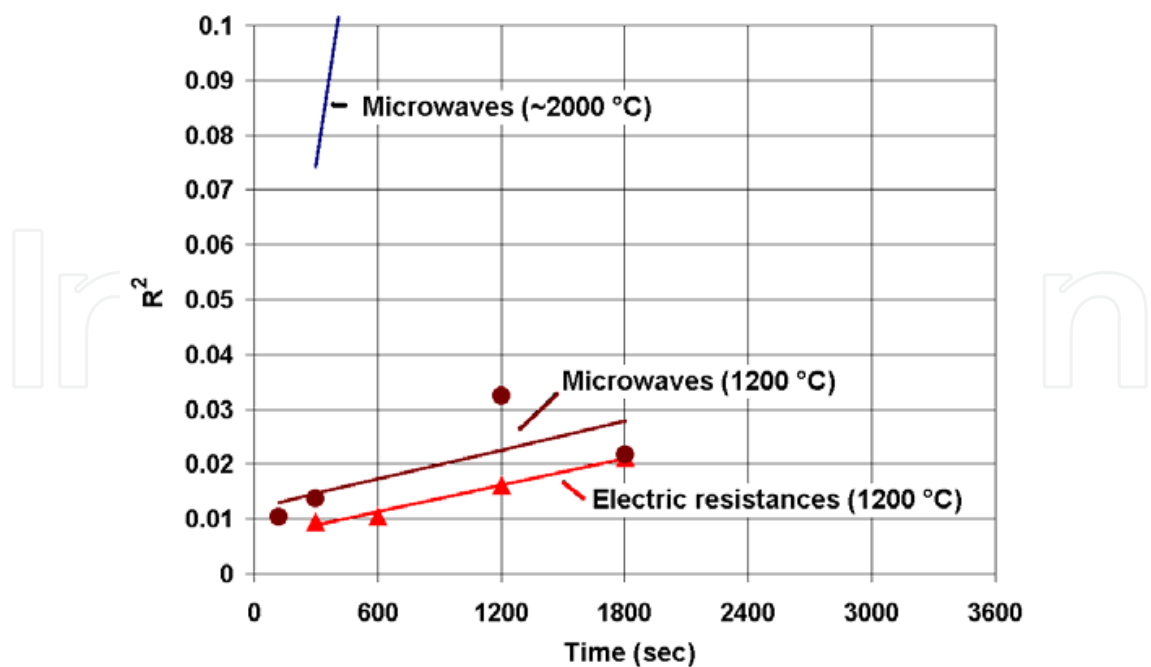
Fig. 15. Amplification of figure 13 showing the experimental results and the parabolic regressions for calculating K.

| Test | K (sec$^{-1}$) | Ordinate interception |
|---|---|---|
| Electric resistance (1200°C) | $4.07 \times 10^{-6}$ | 0.0064 |
| Microwaves (1200°C) | $4.41 \times 10^{-6}$ | 0.0119 |
| Microwaves (2000°C) | $1.23 \times 10^{-4}$ | 0 |

Table 7. Reaction constants

Interception at ordinate can not be null because the testing time begins when the temperature is 1200 °C and, although a very low rate, reaction is taking place at least since temperature exceeded 600 °C. In tests conducted previously at temperatures below 600 °C spinel was not detected by X-rays diffraction after 20 hours.

Differences in K values at 1200 °C are not extraordinary for supporting an argumentation of "microwave catalysis". Difference is in the order of 8% when catalytic effects are claimed to be around 400%.

The differences in the origin interception can be justified because the test with microwaves was at higher temperature larger than the electric resistance case before reaching 600 °C, which means higher energy transfer at that stage. This can be also justified by observing the test at 2000 °C, conducted under free heating without any control. Interception is practically null because temperature was achieved in about 600 seconds, instead of the 2400 that took to the 1200 °C tests. Reaction rate is higher at 2000 °C and hence the thermal history is less important.

Activation energy can be also estimated using the tests conducted at 2000 °C with:

$$K=Ae^{-Q/RT} \qquad (4)$$

Where T is the absolute temperature, Q is the activation energy and R is the universal constant of the gases. From the values in table 7, Q/R is -13949.64 and A is 0.0573 s$^{-1}$. These

values are useful for calculating the fraction of spinel formed in 20 hours at 600 °C, which was 0.03, too low for practical detection with X-rays diffraction of powders, being in agreement with the experimentation the assumption of no appreciable reaction below 600 °C. However, reaction took place and it is accumulative to the found spinel after the 1800 seconds of testing time.

These values are also useful for estimating the reaction degree taking into account the all the tests, including the whole thermal history, not only the portion after the mixture reached 1200 °C. This calculation is presented in figure 15, the time scale corresponds to the testing time only. Looking in first instance the curve 1 that was calculated with the temperatures recorded with the tests conducted at 1200 °C with electric resistances. The points obtained from these tests are following the kinetic equation with the calculated parameters. The curve calculated with the thermal history of the tests conducted with microwaves is practically the same, at the scale of the plot the difference can not be appreciated which corroborates that matching the tests above 600 °C is a good experimental condition and that regardless the differences in temperatures below 600 °C the samples are the same at the moment that they reached that point. It can be also noticed that at the time that the tests begins there is already some formed spinel.

However, all the microwave points, but the last one, are above curve 1 in the figure 16. The difference looks large, but it is $R^2$ and not $R$, hence it is not that large that it could be call special kinetic effect of microwaves. However it still is a difference that must be explained. Separated tests confirmed that the samples obtained from the experiments conducted in the electric resistance furnace are more homogenous than the samples from the microwave testing. It was random and although always the less reaction occurred on the surface, a profile around the thermocouple could not be determined.

An idea was that given that permittivity of alumina increases with temperature, and there is even thermal run away about 600 °C, it was possible that some parts of the mixture could
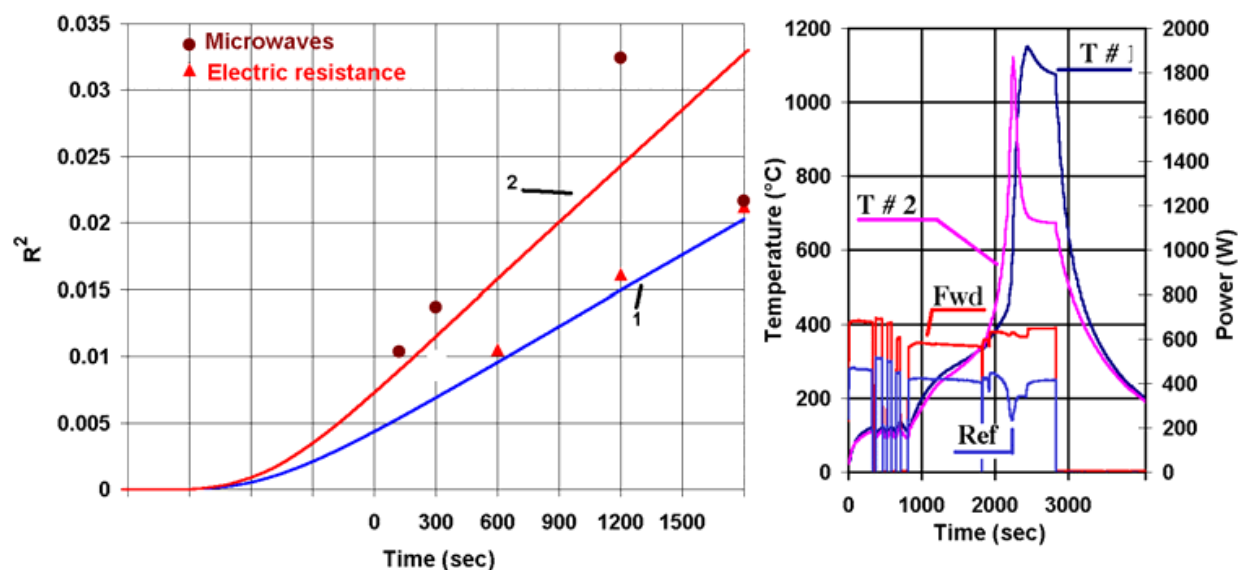


Fig. 16. The curve 1 was calculated with the parameters found in this work considering the thermal history, while the curve 2 was calculated with the same parameters at a temperature 6.4% above the registered one. Right chart shows thermal run away of alumina, T#1 and T#2 as the conditions of figure 8.

reach temperatures higher than those sensed by the thermocouple, this phenomena can not happen with the electric resistance due to the heat transfer mechanism. Thermal run away of alumina is shown in figure 16 right, alumina increase its temperature rapidly after reaching about 400 °C (T#1 and T#2) as the reflected power decrease due to the increase of the dielectric heating.With this idea it was calculated which must be the temperature in order to have the points showed by the microwave tests. It was decided to estimate an overheating error along the whole process which was 6.4%. This argument seems to be against reliability of the thermocouples, however in 1200 °C (1473 K) this error means that the average temperature was 1295 °C, which compared with test where temperature has been taken optically to the surface, could provide similar accuracy.

However, although this results could bring the idea of a microwave "kinetic effect" what is better to say according to the results is that there is a microwave effect, because the heating mechanism is different, that there is heterogeneity, which suppose selective heating rather than uniform, but all of these observations are explained thermally, described by classical thermodynamics and kinetics. There are many variables involved in the process, from the powder distribution, location of the thermocouple, and change in permittivity as the reaction evolves and heat transfer. However a non thermal kinetic effect would be much more evident.

## 5. Microwave sintering: manganites

Applications of NTC (negative temperature coefficient) thermistors ceramics such as $Fe_xNi_{0.7}Mn_{2.3-x}O_4$ are of high interest. Sintering of these materials is a crucial part in their fabrication; because electrical properties dependent of the microstructure and cation distribution. Sintering affects microstructure, including decomposition of NiO, that affects overall quality of the final product. The first approach for solving this situation is to reduce the sintering temperature below 900°C, which is the decomposition one (Töpfer et al., 1994; Csete de Györgyfalva et al., 2001) but sintering process takes too long that becomes economically impractical: Increase the sintering temperature for reducing time of processing is against product performance because the structure could be fully decomposed. There is a competition between required time for achieving full dense materials and kinetics of decomposition of the structure. Current research is dedicated to study such competition, where new and different methods that can contribute reduction of time processing are being designed. Microwaves have been used as a power source for synthesize and sinter different materials. The main benefits that many researchers claim (Bykov et al., 2001) are enhanced diffusion, selective heating, increased reaction rates, and sometimes decreased reaction temperatures. No data were reported of the application of microwave energy in the production of $Fe_xNi_{0.7}Mn_{2.3-x}O_4$ ceramics for application as NTC thermistors.

Different manganite compositions of the Mn-Ni-Fe-O system were tested in preliminary studies (Aguilar et al., 2002), the manganite $Fe_xNi_{0.7}Mn_{2.3-x}O_4$ was produced by coo-precipitation in order to have homogeneous powders to be sintered. The powders were axially compacted at 250 MPa in tablets of 6 mm diameter and 1.5 mm thickness. Conventional sintering was performed in an electrical resistance oven at 1170 °C, while the microwave sintering was conducted in a microwave oven operating at 1100 W and 2.45 GHz, modified with a temperature control within 5% error (Valdez, 2001). The samples were placed in a graphite bed, with a thermocouple located 1 mm above it. From dilatometry tests and a relationship from literature that considers the heating and cooling

slopes for determining the appropriate sintering time (Binner, 1995); temperature schedules are given in figure 17. It was confirmed by X-rays diffraction that the powders obtained to be sintered were formed of spinel type oxides (figure 18).
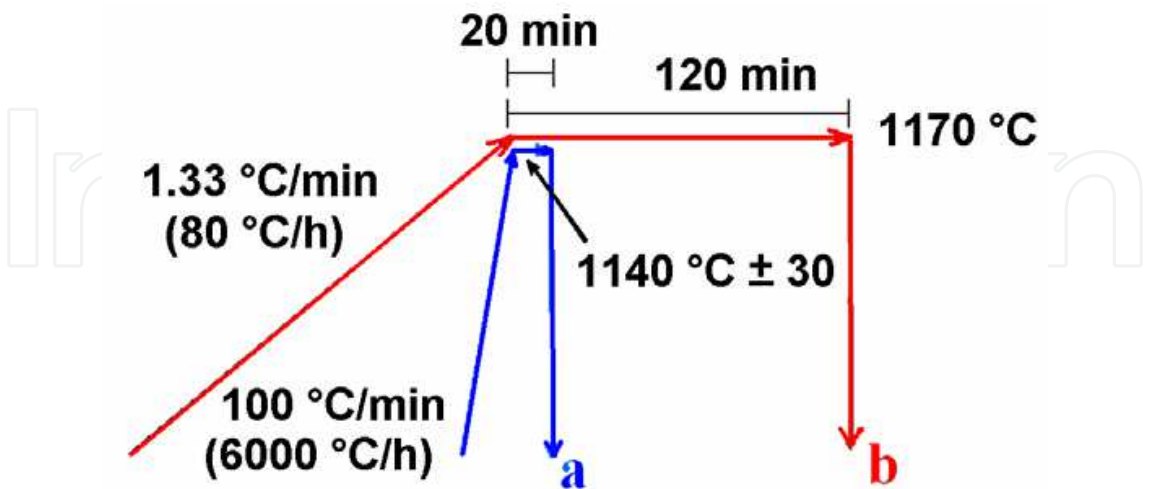


Fig. 17. Temperature schedules for the sintering, a) microwave and b) conventional processing.
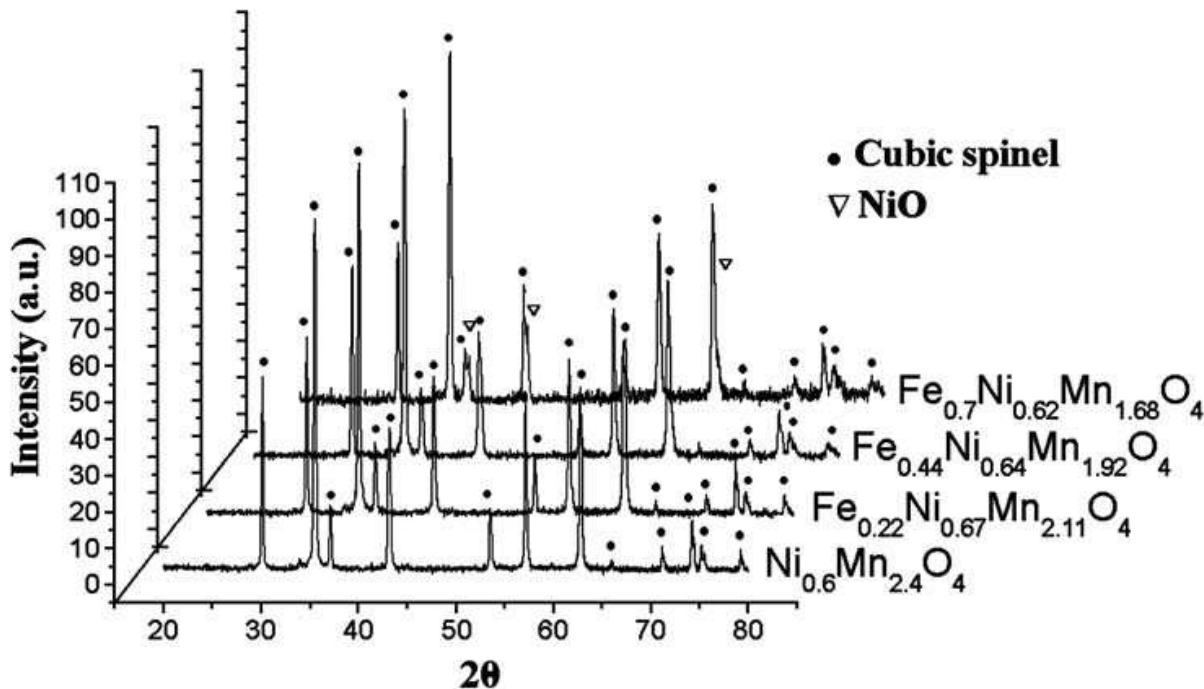


Fig. 18. X-ray diffraction pattern of the powders prior to sintering.

Apparent density of the sintered powders is compared in figure 19, final density was higher in the case of microwave sintered sample, and then it is easy to suppose that a "microwave effect" actually exists for the manganites with high iron content.

However, it is very important to evaluate if the obtained materials are the same in both processes. X-rays diffraction patterns of the samples obtained showed that the material is different for each case, free nickel was found in the sample processed with microwaves while in the conventional sintering there is no free nickel.
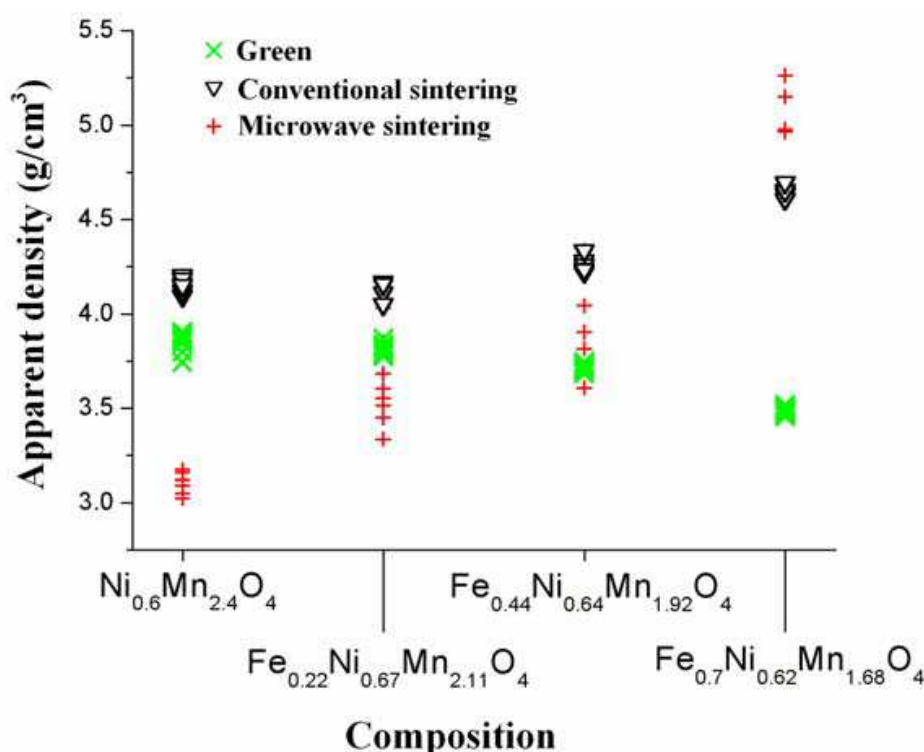
Fig. 19. Final densities of the processed powders.

An explanation is that nickel was reduced due to the presence of graphite as heating susceptor as has been suggested by Csete (Csete de Györgyfalva & Reaney, 2001). Hence, if the products are different that means that a direct comparison between microwave and conventional sintering was not actually performed and that the first idea from figure 19 is not precisely right. In studies of diffusion of isotope $^{59}$Fe in a structure type ferrite (Fe, Mn) was found that the diffusion coefficient was around $10^{-7}$ cm$^2$/s at a partial oxygen pressure of $10^{-12}$ atm and 1000 °C (Franke & Dieckmann, 1988).

Peterson (Peterson et al., 1980) found that the diffusion coefficients of $^{59}$Fe in a magnetite (Fe$_3$O$_4$) were in the order of $10^{-9}$ cm$^2$/s at an oxygen pressure of $10^{-12}$ and 1000 °C. This means that the mobility of the iron in the magnetite is different than in the ferrite, furthermore the diffusion of Mn is two orders of magnitude smaller in MnO ($D^*_{Mn}$= 2.01x10$^{-10}$ cm$^2$/s, T=997 °C, P$_{O_2}$=10$^{-12}$ atm) (Peterson & Chen, 1982) and Fe diffusion in FeO ($D^*_{Fe}$=7.29x10$^{-8}$ cm$^2$/s, T=1007 °C, P$_{O_2}$=10$^{-12}$ atm) (Chen & Peterson, 1975). Then, diffusion of iron is greater in a wustite structure (Fe, Mn)O than in a spinel, and the diffusion coefficient of manganese is smaller than the iron one. Consequently, while in the conventional heating the powders are being sintered only, in the microwaves case there is a reduction of the oxides, and what is being sintered does not have the spinel structure, but the wustite, and following the iron/manganese diffusion coefficients argument, sintering of Fe$_{0.7}$Ni$_{0.62}$Mn$_{1.68}$O$_4$ is easier than sintering of Ni$_{0.6}$Mn$_{2.4}$O$_4$. Hence, for this specific case, the "microwave effect" is actually a different processing path.

## 6. Conclusions

The tests that were presented in this document show that microwaves are a possible method for supplying energy for heating and therefore drive processes. There are several very

serious research works that present evidence of non-thermal effect that improve efficiency of the processes that are taken place.

Indeed from a strictly perspective of the final product with microwaves against any other process, there are differences due to selective heating, which is a microwave effect but it is thermal; higher temperatures than actually measured, but that is also thermal. In the case of the manganites, the found product was different; therefore the special "microwave effect" was not present.

In classic thermodynamics there is no difference in how the energy is supplied to a given system for conducting a process; it is only a matter of system states. However, kinetics depends on the path that is actually taken for the system to change its state; it could be in different stages. In endothermic processes the reaction is limited by the energy supply, changing the way the energy is being supplied could change global kinetics, without affecting the essence of the process or changing activation energies. In this case the microwave effect consists in the possibility of supplying all the energy that the system is demanding when the system is demanding it.

Each mechanism has its own activation energy; activation of a different mechanism will give as a result a change in this value, activating another process. In kinetic classes there are experiences of identifying a mechanism from evaluating its activation energy.

Assigning these effects, which are real, to non thermal phenomena deviate attention from the real challenge of the non thermal observations that are hard to explain with classical thermodynamics and kinetics. The amount of non-thermal observations available by serious researchers can not be denied. Therefore it is important to look for classical explanations always that is possible in order to identify and leave room for giving attention to those special cases.

## 7. Acknowledgements

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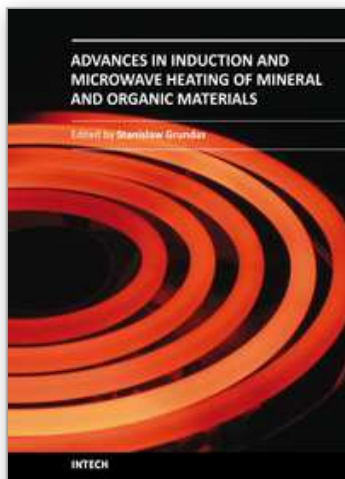
**Advances in Induction and Microwave Heating of Mineral and Organic Materials**

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The book offers comprehensive coverage of the broad range of scientific knowledge in the fields of advances in induction and microwave heating of mineral and organic materials. Beginning with industry application in many areas of practical application to mineral materials and ending with raw materials of agriculture origin the authors, specialists in different scientific area, present their results in the two sections: Section 1-Induction and Microwave Heating of Mineral Materials, and Section 2-Microwave Heating of Organic Materials.

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