MICROWAVES AS AN ENERGY SOURCE FOR PRODUCING MAGNESIA - ALUMINA SPINEL

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ABSTRACT

This work describes the production of magnesia-alumina spinel using microwaves as energy source. The microwave energy was supplied by means of an 800 W magnetron operating at 2.45 GHz. The microstructure and the mineral composition were studied by means of SEM and X-Ray diffraction respectively. The resultant product shown sintered zone and incipient smelting of the reagents meaning that microwave processing could be a practical form for spinel production.

INTRODUCTION

One of the most important properties of ceramic materials is that they retain their structural properties at high temperatures, they usually present a high melting point and this property makes difficult the process of this kind of materials, because it is necessary to achieve high temperatures. Traditionally, these materials have been produced using gas burners or electric resistance elements. Since the development of the microwave devices there has been an upsurge of interest, within the scientific community, on the possible applications of microwave radiation as an energy source for the processing of materials. There are some discussions about the mechanism that governs the absorption of microwave energy, some of these mechanisms are dipolar losses, ion jump relaxation and ohmic loss effects [Binner, 1993], but in many materials the transfer mechanism is still unknown. If the ceramic that is being processed takes enough energy for conducting a process, it would be feasible to carry out processes that, for now, are limited to be smelted in an electric arc furnace. There are several papers on sintering processes with microwaves [Boch et. al., 1992]; [Brandom et. al., 1992]; [Freim et. al., 1994] and [Cheng et. al., 1994], but in this work the aim is to have reactions that produces spinel.

The objective of this work focuses on production of magnesia-alumina spinel, presenting a summary of the results of tests conducted at temperatures close to melting point, lower than those encountered in the electric arc furnace.

SPINEL PRODUCTION

Spinel production can be described as a reaction where the reagents are two different oxides forming a compound with different properties. As a process, this reaction can be described thermodynamically. In this work the spinel studied was $\text{Al}_2\text{O}_3 \cdot \text{MgO}$. The main applications of this spinel are the kilns for cement and the glass industry where it is considered as an advanced material. This spinel usually is produced basically in two ways: by smelting production and by sintering production. Smelting production allows to have liquid materials in an intimate mixture that ensures that the diffusion between species gives a stable structure, the one that is being searched for, the spinel. In the case of sintering, temperatures are lower than smelting process, and the spinel is achieved just on the external part of the grains. The spinel is formed in the neck between the grains where the driving force for diffusion is stronger. Figure 1 represents the crystal structure of the spinel. This structure is determined by the space configuration of relative large oxygen ions, with trivalent and bivalent cations between them. Due to the relative size of the oxygen, it is possible to have certain disorder without major changes in the lattice. This situation gives a wide range of compositions that contains spinel $\text{Al}_2\text{O}_3 \cdot \text{MgO}$, as shown in figure 2. In this spinel, the $\text{MgO}/\text{Al}_2\text{O}_3$ ratio is 28.2 wt% to 71.8 wt%, but this ratio varies within wide limits. Most alumina - magnesia spinel compositions have approximately the same lattice constant [Maschio D. et. al., 1988]: 0.8 nm, up to about 0.85 nm. All oxygen ions in the lattice are equivalent, forming a close packed structure, thus X rays analysis of the spinel structure does not reveal any differentiation of the oxygen ion arrangement in the lattice.

An important item for producing spinel is that the energy must be placed inside the system for having a reaction. Reviewing the forms for supplying energy, the electric arc process requires that the material be a good electricity conductor, normally ceramic materials are bad conductors, but at certain temperatures their conductive properties are quite improved. The only problem is the way for starting the electric arc, usually for doing this, conductive material is placed between the electrodes to have the first liquid that permits to continue with the process. Heating by fire is simpler because it does not depend on the material nature, it does not deal with the material properties, the process in this case is governed by pure heat transfer conditions. Even when heat transfer involve some properties of the material, to heat an ordinary stone or to heat a special refractory is practically the same. Case of microwaves supplying is very special because heating rate depends strongly on the material properties, one ceramic can be transparent to microwaves, so it does not matter how long the material stays in a microwave field, it will never warm up. While other ceramic can absorb the microwave energy very well, so the heating rate will be great. Normally, it

has been accepted that ceramics were transparent to microwaves, and it sounds reasonable to think that transparent materials could not be smelted, or at least heated, with microwaves; however transparent ceramics, such as the Al_2O_3 and SiO_2 have been sintered in a microwave field under certain conditions [Oda et. al., 1990]. MRS II, 39110].

MgO - Al_2O_3 SYSTEM

From thermodynamic considerations MgO and Al_2O_3 should react to form MgAl_2O_4 , but in practice solids do not usually react together at room temperatures over normal time scales so, for having a reaction at an appreciable rate, it is necessary to heat the MgO/ Al_2O_3 powder mixture at higher temperatures, often above 1200°C . If the reaction is taking place in a solid phase, the first stage of reaction would be the formation of MgAl_2O_4 nuclei, this nucleation is difficult because of the differences shown in the structure of reactants and products, and the large amount of structural reorganization that is involved in forming the product. MgAl_2O_4 has a crystal structure that shows similarities and differences to those of both MgO and Al_2O_3 ; MgO and spinel have a cubic close packed arrays of oxides, in contrast to Al_2O_3 which has a distorted hexagonal close packed array of oxide ions; on the other hand, the Al^{3+} ions occupy octahedral sites in both Al_2O_3 and spinel, while the Mg^{2+} ions are octahedral in MgO but tetrahedral² in MgAl_2O_4 . Spinel (MgAl_2O_4) is the only intermediate compound³ in the phase diagram of the system MgO- Al_2O_3 and its melting point is 2135°C . Spinel forms two eutectics, one of them is 45 wt% of magnesia with a melting point of 2030°C ; the other eutectic is 97 wt% of alumina with a melting point of 1925°C (Figure 2).

EXPERIMENTAL PROCEDURE

Spinel production tests were carried out using a conventional microwave oven with a magnetron working at 2.45 GHz and 800 Watts. The reagents MgO (1 μm) and Al_2O_3 (50 μm) were mixed thoroughly to get intimate contact between the powders. The used ratio was 1:1 molar (10 gr. Al_2O_3 + 3.95 gr. MgO). Fine grained materials should be used if possible in order to maximize surface areas and therefore reaction rates. Two different ways of sample preparation were used, the first one consisted in just placing the mixture inside the crucible over the carbon bed without any compact process, while the second way consisted in having a compressed (13.8 MPa) tablet of 32 mm

diameter and 9 mm thickness. The surface area of reacting solids has a great influence on reaction rates since the total area of contact between the grains of the reacting solids depends approximately on the total surface area of the grains. Some authors had found that MgO and Al₂O₃ are not good absorbent of microwaves at low temperatures, but they can absorb microwave radiation if their temperature is increased [Oda, et. al., 1990]. In order to preheat the materials to appropriate temperatures, the mixture was placed over a high purity carbon bed (3 gr.) which is a good absorbent of microwaves. Just the bottom part of the reagents layer was in contact with carbon and it heats the sample by means of conduction and then the mixture of reagents could achieve the appropriate temperature for becoming absorbent of microwaves.

The mixture was placed over a carbon bed inside a crucible made of high purity alumina and thermally insulated (Figure 3). This crucible was selected because it resists temperatures up to 2000°C, is made of the same that one of the used compounds, therefore in case of having a reaction with the sample, there will not be a new phase, and according to Oda, et. al.,[1990] it is transparent at temperatures below 600°C, thus the microwave energy could reach the carbon and the reagents inside the crucible and then above this temperature it will heat up together with the sample. The crucible was placed inside the chamber in a specific place that according to the best heating rate, that is in front of the microwave aperture at 20 cm from it (the cavity is 35 cm length, 33 cm width, 21 cm height) [Gomez and Aguilar, 1995]. The samples were exposed to microwave energy for times of 20, 40 and 60 minutes and then analyzed.

RESULTS AND DISCUSSION

Once that experimental runs were completed, the samples were removed from the crucible and analyzed by SEM and by X Rays Diffraction for confirming the spinel formation.

Test conducted to the uncompact sample shown incipient sinterization and smelting, however this fact means that temperature was close to the 2000°C. On the other hand, compacted samples shown the following profile: The place that was in contact with the carbon bed was partially smelted. The zone close to the carbon bed and above the smelted zone exhibited a shrinkage, due to sintering, while the upon side of the sample was unreacted and no sintering occurred. The samples exposed for 40 and 60 minutes to microwave energy exhibited similar sintering

profile. Spinel was mainly produced after 40 minutes of microwave irradiation, while 20 minutes test did not reacted practically.

The difference between sintering degrees across the sample could be explained from the difference of temperatures inside the sample, the upper side was uncovered and therefore it was colder than the bottom side of the sample closer to the auxiliary heating source (carbon bed). The side that is in contact with carbon reaches the temperature, at which the materials became absorbent of microwaves, more rapidly than the part that is on the top and once that they absorb microwaves, their temperature is increased because they absorb microwave by themselves. The sample that is on the top would never reach the same temperature than the part of the sample that is on the bottom because the first one is losing heat by radiation. Taking just the sintered part of the ceramic material (exposed for 40 minutes), the diffraction pattern shows spinel formation (Figure 4). In this pattern we can see, besides of MgAl_2O_4 spinel, the presence of MgO which did not react. We did not find any carbon compound thus we can say that carbon does not take place in the solid reaction.

An important aspect to confirm is that the reagents were heated mainly by microwaves better than by heat conduction from the carbon bed. A simplified thermal analysis of the tablet system with one face in contact with the carbon bed at 2135°C (liquidus temperature of the spinel, there was smelted material here) and free convection to the air in the opposite face of the disk (maximum temperature of the hot air was 100°C) was conducted. Assuming that the only heat source to the sample is the conduction from the carbon bed the maximum temperature at the face exposed to the air is 1200°C (without heat loss). The spinel was found through the whole sample but in different amounts (more at the interface carbon - sample and less at the interface sample - air). According to West, [1979] the necessary time at 1500°C for having spinel is in the days scale) thus it is demonstrated that an important source of heat is indeed coming from the sample itself (microwave heating).

The sinterization profile can be explained with the fact that temperature is not uniform. The part in contact with the carbon bed achieved the necessary temperature for become microwave absorbent before the rest of the sample, thus in this part smelting process was being conducted (actual spinel production), while depending on the position from this point the sinterization degree is getting lower and lower until the minimum at the uncover surface in contact with air. The part that was in contact with the air is rarely sintered, but there is spinel presence even in these conditions.

Figure 5 shows a comparison between the microstructure close to the carbon bed (bottom of the sample) and far from

the carbon bed (top surface in contact with the air) for a test conducted for 40 minutes. The grain size is smaller at the top than at the bottom, but in both cases the grains are characteristic of the magnesia-alumina spinel, the only difference is that at the top the time was not enough for having grain growth, however the structure is a typical spinel. Figure 6 shows the same comparison than figure 5, but for test conducted for 60 minutes, notice that the only difference is the grain size. This means that the spinel was already formed since 40 minutes (20 minutes tests just show the practically unreacted mixture) and after that the spinel grains just grew.

Figure 7 shows a SEM image of the spinel phase taken to a specimen exposed for 40 minutes to the microwave radiation, besides it exhibit the typical structure of an spinel, chemically analysis confirmed spinel presence of spinel.

CONCLUSION

In this work was demonstrated that it is possible to use microwaves as an energy source for the production of ceramic materials such as magnesia-alumina spinel.

It was confirmed that alumina and magnesia requires an auxiliary heating before they become microwave absorbent materials.

Carbon could be used efficiently as an auxiliary source of heat for processing ceramic materials that need to be heated to certain temperature, before becoming absorbent of microwave such as magnesia-alumina spinel.

Temperatures around the melting point were achieved in some parts of the samples, the part that was unreacted was on the top and was unprotected from radiative losses, then the temperature was far from the melting point.

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Figure 1 Crystal structure of the spinel. The cubic space configuration is determined by the large oxygen ions inserted between cations.

Figure 2 Phase diagram of the system MgO - Al₂O₃. Spinel is the only intermediate compound.

Figure 3 Scheme of the specimen and the isolated crucible.

Figure 4 Diffraction pattern of the sintered material (40 minutes test).

Figure 5 Microstructure of the zone close to the carbon bed (above) compared with the zone at top for the 40 minutes test. (the white zones are the grains and the gray ones are the porosity).

Figure 6 Microstructure of the zone close to the carbon bed (above) compared with the zone at top for the 60 minutes test. (the white zones are the grains and the gray ones are the porosity).

Figure 7 SEM image of the obtained spinel (40 minutes test), notice the sharp edges typical of a spinel structure.