



Short communication

# Synthesis of magnesium aluminate spinel by periclase and alumina chlorination

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## ABSTRACT

A pyrometallurgical route for the synthesis of magnesium aluminate spinel by thermal treatment of a mechanical mixture containing 29 wt% MgO (periclase) and 71 wt% Al<sub>2</sub>O<sub>3</sub> (alumina) in chlorine atmosphere was developed and the results were compared with those obtained by calcining the same mixture of oxides in air atmosphere. Isothermal and non-isothermal assays were performed in an experimental piece of equipment adapted to work in corrosive atmospheres. Both reagents and products were analyzed by differential thermal analysis (DTA), X-ray diffraction (XRD) and X-ray fluorescence (XRF). Thermal treatment in Cl<sub>2</sub> atmosphere of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture produces magnesium aluminate spinel at 700 °C, while in air, magnesium spinel is generated at 930 °C. The synthesis reaction of magnesium aluminate spinel was complete at 800 °C.

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## 1. Introduction

Magnesium aluminate spinel (MgAl<sub>2</sub>O<sub>4</sub>) is a widely used ceramic material in the fields of metallurgy, chemistry, and electrochemistry due to its refractory properties, mechanic resistance, and good thermal shock resistance, high chemical inertia, and excellent optical and dielectric properties [1,2].

The traditional spinel synthesis method involves reactions in solid state which occur at high temperatures [3]. Spinel has recently been prepared through different methods, which include hydrothermal techniques, sol–gel, spray plasma, cool drying, controlled hydrolysis, co-precipitation, mechanical activation and aerosol method [4].

The pyrometallurgical process of chlorination has been effectively used in the extraction of various metals in the last decades. This is due to the high reactivity of the chlorinating agent, the selectivity of the reaction, the relatively low working temperature, the simple treatment of effluents, and the low cost of the processes. Various studies have reported the effect of thermal treatment in chlorine atmosphere on the transformation phases of some materials, such as oxides and minerals, as well as the fact that

the formation of intermediate chlorinated compounds favors the generation of products whose obtention by other means requires a more energetic treatment [5,6].

The effect of the presence of Cl<sub>2</sub> on the decrease in the temperature of magnesium aluminate spinel synthesis by thermal treatment of periclase and alumina was studied in this work. The objective of this study was to develop a simple, selective, and low-cost technique to obtain magnesium aluminate spinel.

## 2. Experimental procedures

### 2.1. Materials and procedure

The solid reagents used for spinel synthesis by chlorination were periclase (MgO) 99% and alumina (Al<sub>2</sub>O<sub>3</sub>) 99%, Sigma–Aldrich. The gases used in the different thermal treatment assays were chlorine 99.5%, supplied by Cofil, Argentina, and nitrogen 99.99% and chromatographic air 99.99%, provided both by Air Liquide, Argentina.

The proper reagent quantities were weighted so that a composition stoichiometrically approximate to that of spinel could be obtained. The ratios used were: 71 wt% alumina, and 29 wt% periclase. The minerals were mixed in a disk mill during 4 min to obtain a homogeneous mixture.

Isothermal and non-isothermal calcination assays were performed in a thermogravimetric system designed to work in corrosive and non-corrosive atmospheres [7]. Mass powder

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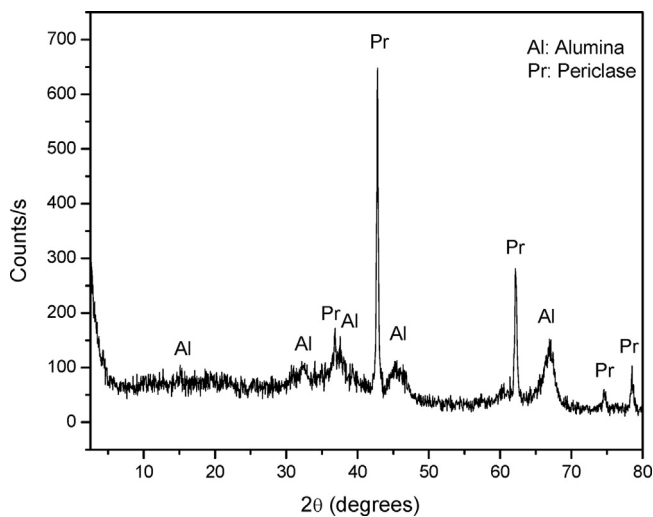


Fig. 1. Diffractogram of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture.

samples of approximately 1 g, and gas flow rates of 50 ml/min were used.

In each non-isothermal experiment, the samples were calcined in an atmosphere of either flowing air or Cl<sub>2</sub>/N<sub>2</sub> (50%) mixture at a heating rate of 5 °C/min until a temperature of 1000 °C was reached. The mass change was recorded as a function of temperature.

In each isothermal assays, the sample was placed inside of the equipment and calcined in atmosphere of N<sub>2</sub> at a heating rate of 5 °C/min, until the working temperature was reached. Once this temperature was stabilized, the gaseous mixture Cl<sub>2</sub>/N<sub>2</sub> (50%) was allowed to flow during a reaction time of 2 h. When this period of time was over, the flow of Cl<sub>2</sub> was interrupted, and the sample was purged with N<sub>2</sub> while the reactor was cooled down.

The calcination of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture was also performed under flowing air using a Shimadzu differential thermal analyzer, at a heating rate of 5 °C/min to investigate the phenomena that may occur during calcination in air.

## 2.2. Characterization and equipments

The chemical composition of the mixture between MgO and Al<sub>2</sub>O<sub>3</sub>, as well as that of the residues from thermal treatment of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture in air and Cl<sub>2</sub>/N<sub>2</sub> were determined by XRF using a Philips PW 1400 unit. The analysis by XRD was performed on a Rigaku D-Max-IIIC, Cu–Kα, which was operated at 40 kV, 30 mA.

## 3. Results and discussion

### 3.1. Characterization of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture

XRF analysis on the MgO–Al<sub>2</sub>O<sub>3</sub> mixture revealed the following chemical composition: 37.86% Al and 17.39% Mg. The characterization results of the minerals mixture performed by XRD (Fig. 1) show the presence of two crystalline phases: alumina (JCPDS 46-1131) and periclase (JCPDS 71-1176).

### 3.2. Thermal analysis of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture

Fig. 2 shows the results of thermogravimetric non-isothermal calcination assays performed in flowing air and Cl<sub>2</sub>/N<sub>2</sub> mixture, and the differential thermal analysis of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture in air.

The thermogram corresponding to calcination of the mixture in air atmosphere indicates that no changes are produced during this thermal treatment. DTA curve shows a small peak at 930 °C associated to formation of spinel by the reaction between alumina and periclase [1].

The thermogram corresponding to calcination in Cl<sub>2</sub>/N<sub>2</sub> mixture shows a mass increase in the temperature range from 500 to 800 °C, and a mass loss between 800 and 1000 °C. The differences observed between both thermograms suggest that the presence of chlorine during the thermal treatment of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture originates different phenomena from those observed in presence of air. Therefore, during a reaction time of 2 h, additional isothermal assays in flowing air and Cl<sub>2</sub>/N<sub>2</sub> mixture were performed in the temperature interval ranging from 600 to 1000 °C with the purpose of clarifying the phenomena that may occur during thermal treatments in both atmospheres. The residues of these assays were analyzed by XRD and XRF, and experimental data obtained are reported in the following sections.

### 3.3. XRD of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture calcined in air and Cl<sub>2</sub>/N<sub>2</sub>

The results of the analysis by X-ray diffraction conducted on the mixture calcined in air are shown in Fig. 3.

The diffractograms corresponding to the residues calcined at 600 and 900 °C do not vary as compared to the diffractogram of the untreated mixture. The presence of magnesium aluminate spinel (JCPDS 77-1203) is observed at 1000 °C as a consequence of the reaction in solid state between alumina and periclase. Corundum (JCPDS 83-2080) and periclase (JCPDS 71-1176) phases are also noted at this temperature. Corundum appears due to the polymorphic transformation of alumina.

Fig. 4a–e shows the diffractograms of the chlorination residues which were obtained in the temperature range of 600–1000 °C. Fig. 4a shows that the intensity of the peaks characteristic of

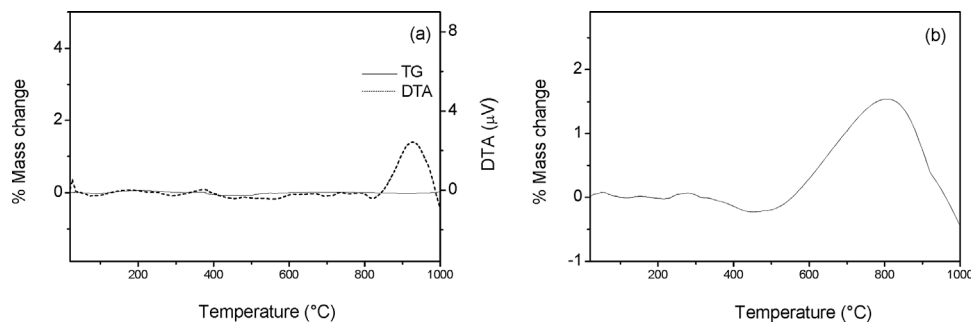
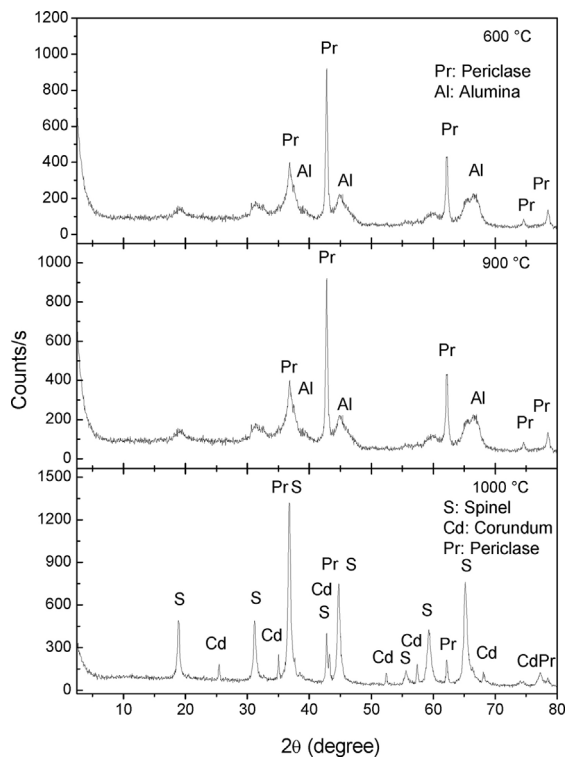


Fig. 2. TG and DTA curves of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture calcined in air and Cl<sub>2</sub>/N<sub>2</sub>.



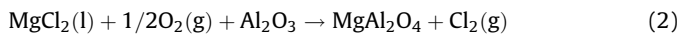
**Fig. 3.** Diffractograms corresponding to the residues obtained from the calcination of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture in air.

periclase decreases at 600 °C. This is due to the chlorination reaction of periclase, which produces magnesium chloride and oxygen, according to reaction (1).



The formation of MgCl<sub>2</sub> can be observed in the thermogram of Fig. 2b as a mass gain which occurs in the temperature ranging from 500 to 800 °C, and in the diffractogram of the residue obtained at 700 °C by the presence of MgCl<sub>2</sub> hydrated phases (JCPDS 74-1039).

The resulting MgCl<sub>2</sub> changes from solid to liquid state at 700 °C. Liquid MgCl<sub>2</sub> and O<sub>2</sub> react with alumina and produce magnesium aluminate spinel at 700 °C, according to reaction (2).

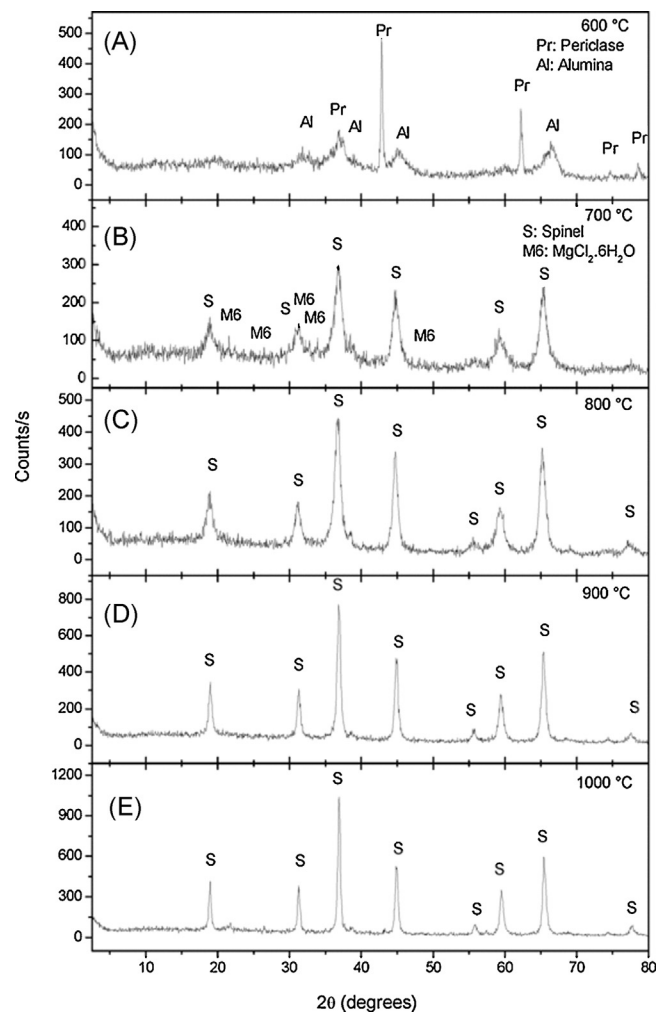


The reactions leading to the formation of spinel in presence of Cl<sub>2</sub> continue to proceed up to the final temperature in study. This can be seen in the diffractograms of the residues obtained between 700 and 1000 °C (Fig. 4b–e) as an intensity increase of the characteristic peaks of magnesium aluminate spinel, as the chlorination temperature rises. This phenomenon is proved by the information resulting from the difference between mass gain and loss which is produced in the temperature ranging from 700 to 1000 °C (Fig. 2b). The mass gain between 700 and 800 °C is produced because the formation rate of MgCl<sub>2</sub> (reaction (1)) is higher than that of spinel synthesis (reaction (2)), which releases chlorine. The mass loss produced between 800 and 1000 °C occurs because the spinel synthesis prevails over the formation of MgCl<sub>2</sub>.

On the other hand, the chlorination of magnesium aluminate spinel starts at about 1000 °C, according to the following reaction:



This chlorination results in a slight mass loss in relation to the initial mass of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture, as it shows the thermogram in Fig. 2b.



**Fig. 4.** Diffractograms corresponding to the residues obtained from the calcination of the MgO–Al<sub>2</sub>O<sub>3</sub> in Cl<sub>2</sub>/N<sub>2</sub> mixture.

The analysis of the diffractograms in Fig. 4 indicates that the reaction between the MgO–Al<sub>2</sub>O<sub>3</sub> mixture and Cl<sub>2</sub> produces magnesium aluminate spinel at 700 °C and it is highly selective between 800 and 1000 °C.

The comparison between the results obtained in Cl<sub>2</sub> and air (Figs. 3 and 4) shows that the temperature of the synthesis of spinel is reduced by 230 °C when the calcination of the MgO–Al<sub>2</sub>O<sub>3</sub> is performed in Cl<sub>2</sub> atmosphere.

### 3.4. XRF analysis of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture calcined in Cl<sub>2</sub>/N<sub>2</sub> atmosphere

Table 1 shows the results of the Mg and Al analysis on the residues obtained from the chlorination of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture samples.

Data on Table 1 indicate that a decrease in Al and Mg concentrations is produced at 700 °C in relation to that observed at 600 °C. At 700 °C, MgCl<sub>2</sub> is formed from periclase, generating a mass increase, which in turn causes Mg and Al concentrations to decrease.

Table 1 also shows that Al and Mg concentrations begin to increase between 800 °C and 900 °C due to the fact that spinel generation rate is higher than that of MgCl<sub>2</sub>. The synthesis reaction of spinel (reaction (2)) releases Cl<sub>2</sub> thus, the concentrations of Al and Mg increase. Mg concentration decreases at 1000 °C, in comparison to that obtained at 900 °C because at this temperature,

**Table 1**

Mg and Al contents (atomic %) in residues obtained from the calcination of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture in Cl<sub>2</sub>/N<sub>2</sub> atmosphere.

Element	600 °C	700 °C	800 °C	900 °C	1000 °C
Al	17.36	15.14	16.26	16.82	15.43
Mg	38.12	35.53	37.40	37.54	39.53

spinel starts to be chlorinated and this phenomenon leads to the removal of Mg as volatile MgCl<sub>2</sub> (reaction (3)).

#### 4. Conclusions

- 1) The presence of chlorine allows a marked decrease in the temperature of the process of thermal treatment of the MgO–Al<sub>2</sub>O<sub>3</sub> mixture used in magnesium aluminate spinel synthesis.
- 2) The formation of spinel in Cl<sub>2</sub> atmosphere starts at 700 °C and is totally selective at 800 °C; while spinel, together with corundum and periclase, is obtained by calcination in air at 930 °C.

- 3) The rise of the chlorination temperature between 800 and 1000 °C leads to a significant crystallization of spinel.
- 4) The results of the studies conducted by TG, XRD, and XRF confirm that the mechanism proposed for the formation of spinel through reactions (1) and (2) can interpret the experimental data obtained.

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