Materials Research Bulletin 59 (2014) 337–340

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Short communication

Synthesis of magnesium aluminate spinel by periclase and alumina chlorination

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ARTICLE INFO

Article history:
Received 18 December 2012
Received in revised form 13 August 2013
Accepted 16 July 2014
Available online 19 July 2014

Keywords:
Magnesium aluminate spinel
Chemical synthesis
Thermogravimetric analysis
X-ray diffraction

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_2O_3 (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_2 atmosphere of the $MgO–Al_2O_3$ 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.

1. Introduction

Magnesium aluminate spinel ($MgAl_2O_4$) 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 pyrometallurgic 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_2 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_2O_3) 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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http://dx.doi.org/10.1016/j.materresbull.2014.07.026
0025-5408/

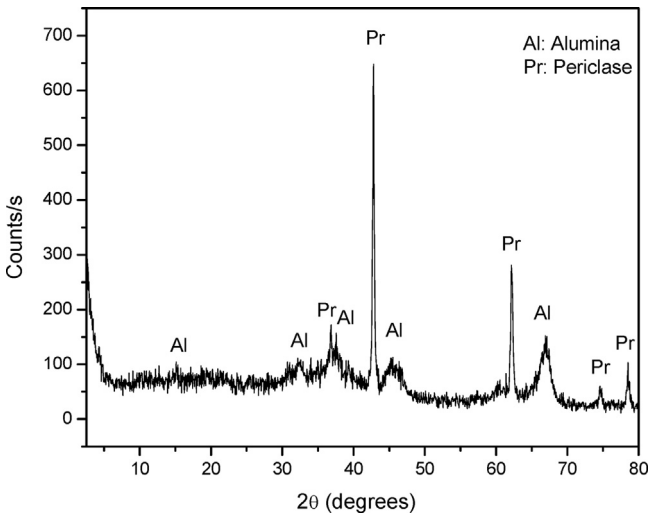

Fig. 1. Diffractogram of the $MgO–Al_2O_3$ mixture.

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_2/N_2 (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_2 at a heating rate of 5 °C/min, until the working temperature was reached. Once this temperature was stabilized, the gaseous mixture Cl_2/N_2 (50%) was allowed to flow during a reaction time of 2 h. When this period of time was over, the flow of Cl_2 was interrupted, and the sample was purged with N_2 while the reactor was cooled down.

The calcination of the $MgO–Al_2O_3$ 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_2O_3, as well as that of the residues from thermal treatment of the $MgO–Al_2O_3$ mixture in air and Cl_2/N_2 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 $MgO–Al_2O_3$ mixture

XRF analysis on the $MgO–Al_2O_3$ 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 $MgO–Al_2O_3$ mixture

Fig. 2 shows the results of thermogravimetric non-isothermal calcination assays performed in flowing air and Cl_2/N_2 mixture, and the differential thermal analysis of the $MgO–Al_2O_3$ 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_2/N_2 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 $MgO–Al_2O_3$ 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_2/N_2 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 $MgO–Al_2O_3$ mixture calcined in air and Cl_2/N_2

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

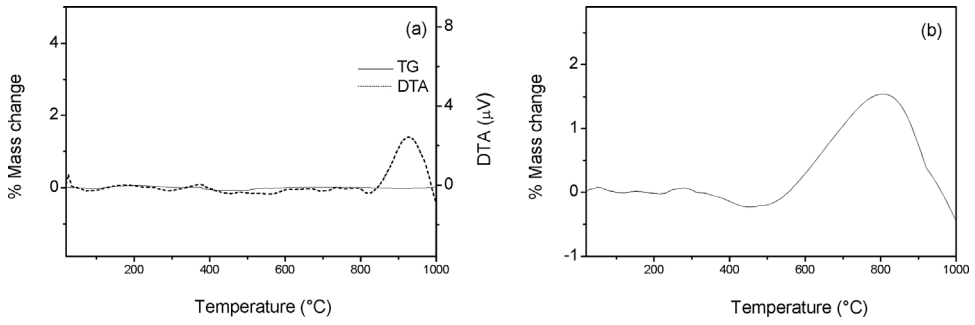

Fig. 2. TG and DTA curves of the $MgO–Al_2O_3$ mixture calcined in air and Cl_2/N_2.