Ceramics International 42 (2016) 15471–15478

Contents lists available at ScienceDirect

Ceramics International

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

Porous mullite blocks with compositions containing kaolin and alumina waste

Valmir José da Silva, Michelle Félix da Silva, Wherllyson Patrício Gonçalves, Romualdo Rodrigues de Menezes, Gelmires de Araújo Neves, Hélio de Lucena Lira, Lisiane Navarro de Lima Santana *

Academic Unit of Materials Engineering, Federal University of Campina Grande – UFCG, Av. Aprigio Veloso, No. 882, Bodocongo, Campina Grande, PB 58109-970, Brazil

ARTICLE INFO

Article history:
Received 16 May 2016
Received in revised form
28 June 2016
Accepted 29 June 2016
Available online 29 June 2016

Keywords:
A. Sintering
D. Clays
D. Al_2O_3
D. Mullite

ABSTRACT

In the production of alumina by the Bayer process, the calcination step generates a waste containing ~90% aluminum oxide (Al_2O_3). Due to the high content of this oxide, this waste can be used as a source of alumina in porcelain formulations, especially those used in the synthesis of mullite. The purpose of this study was to produce porous mullite blocks using compositions containing kaolin and alumina waste. The compositions were formulated based on a mullite stoichiometry of 3:2. Heat treatments were carried out in a conventional furnace at temperatures of 1450 to 1500 °C, applying a heating rate of 5 °C/min and a 1-h hold time at the firing temperature threshold. The powders were characterized by means of X-ray fluorescence (XRF); X-ray diffraction (XRD); thermal analysis (TGA-DTA); scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The physic mechanical properties of the test specimens: water absorption, apparent porosity, linear shrinkage and flexural strength were also evaluated. The XRD results revealed the formation of mullite as the major phase. The morphological analysis by SEM revealed typical mullite needles originating from clay minerals. The size of the mullite needles was calculated based on the TEM analysis, which indicated diameters smaller than 400 nm, confirming the nanometric dimensions of the needles. The flexural strength test of the specimens indicated that this parameter tends to increase as the temperature is raised.

1. Introduction

Clay minerals have played an important role in human development. Originally, clays were only used as raw materials for the production of traditional ceramics. However, over the years, advances in technology have led to the widespread use of clay minerals, and it is possible that these materials have applications in practically every industrial field today. Kaolinite ($Al_4(OH)_8 \cdot Si_4O_{10}$) is a clay mineral that represents the main component of kaolin [1,2].

Kaolin is an important raw material with a wide range of industrial applications, such as paper, rubber, plastics, cement, glass, ceramics and refractories [3]. In the synthesis of mullite, it is an extensively studied low cost starting material when subjected to heat treatments at high temperatures, above 1200 °C. The phase transformations that take place in kaolinite when subjected to heating are extremely important in the production of mullite. However, the literature differs with respect to the temperature range and the subsequent steps in which the phase transformations from kaolinite to mullite occur. Researchers generally agree that kaolinite undergoes a dehydroxylation process in the temperature range of 450–600 °C, forming a disordered phase called metakaolinite ($Al_2Si_2O_7$). Metakaolinite is converted into aluminum-silicon spinel and amorphous silica, $Si_3Al_4O_{12}$, between 925 and 950 °C. The first mullite crystals begin to nucleate and grow above 1050 °C. Cristobalite (SiO_2) crystallizes from amorphous silica starting at 1200 °C. Large quantities of crystalline mullite are formed at temperatures above 1250 °C [1,4,5].

Mullite is the only stable phase of the Al_2O_3-SiO_2 binary system at atmospheric pressure. This mineral exhibits a unique combination of properties when subjected to high temperatures, such as high melting point, chemical stability, low coefficient of thermal expansion, corrosion resistance, low dielectric constant and high creep resistance. These properties enable mullite to be used in a wide range of structural, electrical, chemical and optical applications [2,6,7]. According to the literature, mullite formation depends on the type of precursor, particle size, and heat treatment, and one of the most important factors to obtain the majority phase

* Corresponding author.
E-mail address: lisiane.navarro@ufcg.edu.br (L.N. de Lima Santana).

http://dx.doi.org/10.1016/j.ceramint.2016.06.199
0272-8842/

of crystalline mullite is the appropriate composition of alumina and silica [8].

During the production of alumina (Al_2O_3) by the Bayer process, a waste is generated that is usually discarded into the environment or stored in warehouses. This waste has a high alumina content, i.e., about 90%, which can be used as a raw material in ceramic paste formulations, thus enabling an optimal stoichiometric ratio to be obtained for the synthesis of mullite as a primary phase, and thereby preventing the emergence of secondary phases that do not contribute to improve the properties of materials (e.g., mechanical strength and thermal stability at high temperatures). The reuse of alumina waste means taking advantage of its potentialities, and this procedure represents a complementary activity that contributes to diversification and reduces the cost of end products, resulting in new raw materials for various industrial applications. The reuse of this waste is environmentally attractive not only because it prevents its improper disposal in the environment, but it also because it contributes to add value to the end product by reducing mullite production costs [9,10].

In this context, this study aimed to produce porous mullite blocks based on compositions containing kaolin and alumina waste, applying high temperature heat treatments in a conventional furnace.

2. Experimental procedure

The raw materials used as starters were kaolin and alumina waste originating from the Bayer process, which had initially undergone a refining process. The kaolin was oven-dried and sifted through an ABNT No. 200 sieve (0.075 mm), while the alumina waste was heat-treated at 600 °C/2 h in a conventional furnace to remove the soot produced by oil combustion. The refined samples were then characterized by the following techniques: (a) X-ray diffraction (XRD), using a Shimadzu Lab XRD-6000 X-ray diffractometer equipped with a CuKα radiation tube, operating at a 2θ scan angle of 5–60°, scan speed of 2°/min and step size of 0.02°; (b) particle size analysis, using a Cilas particle size analyzer; (c) X-ray fluorescence (XRF), using a Shimadzu EDX-720 energy dispersive x-ray fluorescence spectrometer; and (d) TGA-DTA thermal analysis, using a Shimadzu DTG-60H differential thermal gravimetric analyzer operating at 1400 °C.

Three formulations containing kaolin+alumina waste were produced, aiming to reach a mullite stoichiometry of 3:2 ($3Al_2O_30 \cdot 2SiO_2$) corresponding to 72 wt% of Al_2O_3 and 28 wt% of SiO_2. In these formulations, 48%, 52% and 56% of alumina waste was added for each 100 g of kaolin, and the formulations are hereinafter referred to as M1, M2 and M3, respectively. M1, M2 and M3 were then heat-treated in a conventional electric furnace at temperatures of 1450 to 1500 °C, applying a heating rate of 5 °C/min and a 60-min hold time at the firing temperature threshold. The crystalline phases were identified and quantified using the Untitled XRD search/match tool for Qualitative Analysis, and the JCPDS powder diffraction files contained in the PCPDFWIN database of the Shimadzu XRD-6000 software.

The samples were treated with acid (40% hydrofluoric acid) for 10 min to remove residual glassy phase, and then morphologically characterized by scanning electron microscopy (SEM) using a FEI Quanta 200 FEG microscope, accelerating voltage 20 kV and 60.000X of magnification. The microstructural analysis was performed by transmission electron microscopy (FEI Tecnai F20 TEM), with accelerating voltage between 20 and 200 kV, 0.2 nm resolution, and images obtained between 20 and 1 million X magnification. The mullite needle diameters were measured using image analyzer software (Image J, National Institutes of Health, USA), based on the TEM images.

Table 1
Chemical compositions of kaolin, alumina waste, and formulations M1, M2 and M3.

Materials	Oxides (wt%)					
	Al_2O_3	SiO_2	K_2O	SO_3	Fe_2O_3	Others
Kaolin	35.3	56.1	1.9	4.1	1.7	0.9
Alumina waste	90.9	1.4	–	7.0	–	0.7
M1	62.0	36.6	0.5	0.5	0.3	0.1
M2	71.3	27.7	–	0.7	0.2	0.1
M3	74.2	24.8	–	0.8	0.1	0.1

The M3 formulation contained the highest ratio of Al_2O_3/SiO_2 (Table 1), so test specimens were prepared with this composition to evaluate its physicomechanical properties. To this end, the material was placed in a 30 mm × 5 mm × 5 mm rectangular mold and subjected to uniaxial pressure in a 15-ton hydraulic press (RIBEIRO-P15T, Brazil). The specimens were subjected to an initial pressure of 33.3 Kgf/cm^2/10 s and a final pressure of 66.6 Kgf/cm^2/20 s, followed by oven-drying at 110 °C for 24 h, after which their linear shrinkage was measured. The test specimens were then heat-treated in a conventional electric furnace at temperatures of 1450 and 1500 °C, applying a heating rate of 5 °C/min and a 60-min hold time at the firing temperature threshold. These fired samples are hereinafter referred to as CP1450 and CP1500 °C. The following physicomechanical properties were evaluated: water absorption (according to the Archimedes principle), linear shrinkage, apparent porosity, and 3-point flexural strength (Shimadzu Autograph AG-X 50 kN universal testing machine, operating at 0.5 mm/min speed of applied force).

3. Results and discussion

Fig. 1 shows the XRD spectra of the kaolin and alumina waste after the refining process.

The analysis of the XRD pattern of the kaolin sample revealed that it consists predominantly of the clay mineral kaolinite (JCPDS card no. 14-0081), and also showed peaks corresponding to mica (JCPDS card no. 83-1808) and quartz (JCPDS card no. 46-1045). The alumina waste presented peaks characteristic of alumina (JCPDS card no. 46-1212) and of other phases (impurities) such as sulfur oxide (JCPDS card no. 73-2169) and sodium oxide (JCPDS card no. 3-1074).

Fig. 2 shows the particle size distribution of the samples of kaolin and alumina waste.

The particle size distribution of kaolin and waste alumina showed a bimodal behavior. The kaolin presented an average diameter of 7.1 μm and D_{50}=3.4 μm. On the other hand, the alumina waste exhibited a broader distribution, with an average diameter of 11.4 μm and D_{50}=9.6 μm. The average diameter takes in account whole mass of the sample and D50 is related to the value of diameter to 50% of accumulated mass. A correlation of these values clearly indicates that the average diameter and accumulated fraction (D_{50}) of kaolin relative to alumina waste were smaller by approximately 38% and 65%, respectively.

Table 1 describes the chemical compositions of the kaolin, alumina waste, and formulations M1, M2 and M3. The composition of kaolin contained about 56% silica and 35% Al_2O_3. The alumina/silica ratio was lower than the desired level for the synthesis of mullite, which would be approximately 2.6. From the formulations, it can be seen that the addition of alumina waste significantly increased the percentages of Al_2O_3, as expected, since this waste has a high Al_2O_3 content (90.9%). This addition increased the Al_2O_3/SiO_2 ratio of the three formulations, and the formulation that came closest to the solid solution of mullite 3:2