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Synthesis of cordieritic materials using raw kaolin, bauxite, serpentinite/olivinite and magnesite

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Abstract

In this work it was investigated whether it is attainable to create cordieritic materials for possible uses in ceramic applications using combinations of bauxite, kaolin, serpentinite/olivinite and magnesite. For this reason various mixtures of selected samples for the synthesis of ceramic materials consisting mainly of cordierite, among other phases, were used. After appropriate processing, specimens prepared from the mixtures were fired at various temperatures up to 1350 °C. The ceramic materials resulted after firing, were investigated regarding their phases composition and physical properties of technological interest. On this way the creation of materials having interesting combinations of properties such as shrinkage (varied from 0.11% to 9.87%), porosity (varied from 0.6% to 38.5%), density (varied from 1.43 to 2.59 g/cm^3), sufficient compressive strength (range of 13.1–31.0 MPa) and low coefficient of expansion (varied from 2.2 to 4.5*10^{-6}/C) at high temperatures is achieved.

Keywords: Cordieritic material; Ceramics; Bauxite; Kaolin; Olivinite; Magnesite

1. Introduction

Cordierite $(Mg,Fe^{2+})_2$ $(Al_2Si)^{[4]}$ $[Al_2Si_4O_{18}]$ ceramics are used in many industrial applications such as refractory products, heat exchanger or gas turbines, thermal shock-resistance tableware, catalyst supports, porous ceramics integrated circuit boards, membranes and others, mainly because of their thermal shock resistance, low thermal expansion coefficient, low dielectric constant, high mechanical strength and relative high refractoriness [1–6]. Cordierite ceramic materials were investigated in the past and several methods of their synthesis were proposed [6–15]. By the synthesis of cordierite masses based on natural raw materials talc [11], vermiculite [16], kaolin [8,14,17], dolomite [17], feldspare [15], sepiolite [3] and magnesite [8] are usually used. One of the main problems of the cordierite is its small field of existence synthesis is realised in the temperature range from 1250 to 1400 °C. In addition cordierite masses have a very narrow sintering interval, which is one of the basic problems in the production of cordierite ceramics, causing deformation and influencing other properties of the products, the composition of the raw materials influence the properties of the synthesis products. Furthermore small variations with regard to the stoichiometric composition can generate secondary reactions which are not-desired. For this reason it is easy to find the cordierite with secondary phases as mullite, corundum, spinel, forsterite, clinoenstatite and cristobalite. Goren et al. [11] concluded that in any process of cordierite synthesis it is difficult to predict the compounds that is obtained, since the relations among phases depends on temperature, the time and chemical activation as well [5,7,12,15,18–21]. Thus, for the synthesis of cordierite masses following component combinations of raw materials are reported: i) talc, kaolin, silica, alumina [1], ii) talc, kaolin, silica, feldspar [15], iii) alkaline-earth-alumino-silicate glass, kaolin, alumina, magnesite [8], iv) kaolin, quartz, technical silica, sepiolite [3], v) kaolinite, dolomite [22], vi) calcined bauxite, talc, quartz [23], vii) gibbsite, talc, clay [10], viii) stevensite-rich clay, andalusite [12] and ix) kaolinite-rich clay, vermiculite. In the present

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work, using mixtures from combinations of Greek raw materials, namely iron rich bauxite, serpentinite/olivinite containing relatively low iron percent, kaolin and magnesite, the creation of ceramic materials consisting mainly of cordierite, suitable for technical applications, was attempted. To achieve the synthesis of the ceramic materials, the raw materials above were chemically and mineralogically analyzed and specimens prepared from diverse mixtures were fired at various temperatures. Hereafter technical relevant properties, such as shrinkage after firing, open porosity, density, compressive strength and thermal expansion coefficient as well as the phase composition of the created materials were investigated.

2. Materials and methods

2.1. Materials

In Greece exist, among others, considerable deposits of bauxite, magnesite, serpentinite, olivinite and some smaller deposits of kaolin [24,25]. For the synthesis of the ceramic bodies in the present work bauxite of metallurgical type from the Parnass–Giona area (Central Greece), containing high content of iron oxides is used. Three different kaolins of low quality were also used, one from the Drama district (Chrysokefalo area), Macedonia and two from the Milos island (Kastriani area). Olivinite and serpentinite, containing relative low iron content, were taken from the Vourinos area (Kozani district, West Macedonian). Magnesite of high quality, used mainly for the production of magnesia refractories, was taken from the Mantoudi area (Euboea island) [26].

2.2. Methods

The chemical analysis of the raw materials was realised using a XRF-spectrometer (EDS, Bruker S2-Ranger). Measurements were carried out at 40 kV with an Al filter (500 μm) for the heavier elements (Fe, Mn, Ti, Ca, K) and at 20 kV for the lighter elements (P, Si, Al, Mg, Na) without using filter. For the mineralogical analysis an x-ray diffractometer system (Bruker Advance D8, Bragg–Brentano geometry) was used. For the collection of the x-ray data, the diffractometer was operated with a copper x-ray tube at 35 kV/35 mA, Ni-filter and LinxEye detector. Data were collected over a range from 7° to 70° 2θ. The x-ray powder data collected for the quantitative estimation of the crystalline phases were refined by the Rietveld method [27,28] using the Rayflex Autoquan program [29]. In order to include the Roentgen-amorphous in the quantitative phase analysis a crystalline internal standard (corundum) was added (15–20%) to the specimens, whereas the homogenization of the samples was performed by hand in a mortar.

After chemical and mineralogical analysis bauxite, kaolin and serpentinite or olivine mixtures were milled (with Fritsch-Bico pulverizer), and test specimens in the shape of tablets of 40 mm diameter and 10 mm thickness were prepared, using uniaxial pressing at 130 bar. The maximum grain size of the raw material powder mixtures was less than 20 μm. For the mixtures of bauxite, kaolin and magnesite 6% w/w water was added. Specimens of the mixtures were fired in an electrical furnace (Nabertherm LHT 08/17) at 1250, 1275, 1300, 1350 or 1400 °C for one, two, four and eight hours, in order to find out the minimum of the time which was necessary to produce ceramic mass of satisfying cohesiveness and stability, as well to observe the initial temperature of their melting. Their porosity and density was measured using the Archimedes method (DIN EN 993-1). To define the compressive strength at room temperature, average value from 6 specimens are measured, uniaxial compression according to ASTM C109 was used. The thermal expansion of the ceramic bodies was measured using a Netzsch DIL 402 dilatometer. The microstructure of the firing products was investigated using a scanning microscope (Philips XL 30).

3. Results and discussion

3.1. Chemical and mineralogical analysis

The chemical composition of the bauxite, kaolin I (kaolin I of Milos), kaolin II (kaolin II of Milos), kaolin III (kaolin from Drama), serpentinite/olivinite and the magnesite samples is shown in Table 1 and their mineralogical composition in Table 2. The bauxite was composed mainly of diaspore (64%) and lower amounts of boehmite (13%), hematite (11%), goethite (3%), anatase (2%), calcite (about 2%), traces of rutile, and amorphous phase (3%). The iron content of the bauxite was high (18.07% Fe_2O_3) and the TiO_2-content considerable (3.24%).

The composition of the kaolin varied essentially in the three different samples. The kaolin I had a relative low aluminum content (21.19% Al_2O_3) and high silicium content (63.39% SiO_2), while it had also a relatively high content of amorphous phases (27%). Its kaolinite content was 42%, the sum of its crystalline SiO_2 modifications (cristobalite, tridymite and quartz) was 30%. Approximately similar was the composition of the kaolin II. The kaolin III, in the opposite, had no

Table 1
Chemical composition of the raw materials (wt%).

	Bauxite	Kaolin			Serpentinite	Olivinite	Magnesite
		I	II	III			
SiO_2	6.67	63.39	67.90	55.19	40.18	39.10	6.63
Al_2O_3	55.16	21.19	12.70	29.07	0.58	1.81	0.31
Fe_2O_3	18.07	0.14	0.07	0.01	3.19	9.28	0.96
CaO	1.67	0.05	0.02	0.22	0.10	0.10	2.40
MgO	0.00	0.00	n.a.	0.07	41.74	42.05	40.44
SO_3	0.53	0.20	1.63	n.a.	0.14	0.10	0.38
Na_2O	n.a.	n.a.	n.a.	n.a.	0.10	0.10	n.a.
K_2O	0,00	n.a.	0.03	2.25	0.04	0.09	0.28
TiO_2	3.24	0.43	0.32	0.48	0.02	0.08	0.07
MnO	n.a.	0.01	0.01	n.a.	0.16	0.11	0.01
P_2O_5	n.a.	0.09	0.08	0.01	0.04	1.10	n.a.
LOI	13.86	14.51	17.19	11.25	13.50	6.59	48.15
Sum	99.20	100.01	99.95	98.54	99.79	99.50	99.63

n.a = not analyzed.