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Preparation and characterization of clay-based porous ceramics with boric acid as additive

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Abstract

Intention of this work was to obtain porous silicon dioxide ceramics by using boric acid as an inexpensive additive at low forming pressure and low sintering temperature. Starting raw material, smectite clay from surface coal mine Kolubara, Serbia, was purified from organic and inorganic impurities by using heat and chemical treatment. Boric acid was used as binding and sintering aid in amount of 0.5, 1 and 2 wt%. Powder was compacted by using different pressures: 40, 60 and 80 MPa. Pressed samples were sintered at 850, 1000, 1150, and 1300 °C for 4 h in air. A relatively high porosity of nearly 40% is obtained for the samples pressed at 40, 60 and 80 MPa and sintered at 1000 °C. Median pore size diameters are in the range of macroporous up to 0.2 μm and 10 μm in the samples sintered at 1150 and 1300 °C, respectively. X-ray diffraction (XRD), scaning electron microscopy (SEM), and porosimetry measurements were employed to characterize the phases and microstructure of the obtained ceramics. The relations between mechanical characteristics of samples (Young modulus and Poisson ratio) and content of boric acid were studied.

Keywords: A. Sintering; B. Porosity; D. Clays; Boric acid

1. Introduction

Porous ceramics materials are extensively used as filters, heat insulators, absorbers, catalyst supports etc. in different fields of engineering. Application of porous ceramics strongly depends on the pore size, permeability, and specific surface area [1–4]. At present, the most extensively used are the following manufacturing methods of porous permeable ceramics: processing of mono-fractional starting materials, foaming method, method of burning-out of additives, and chemical method of pore formation [5]. Each manufacturing method of porous permeable ceramics has both advantages and essential disadvantages compared to other methods. Specifically, ceramics prepared by the foaming method or by the chemical method of pore formation are characterized by low permeability due to predominantly closed porosity. Ceramics obtained by the method of burning-out of additives have inhomogeneous porous structure, due to the fact that obtaining a homogeneous distribution of components in the volume of the mixture is difficult. For this reason the search for new technologies of manufacturing porous ceramics is being continuously pursued [6].

Clays are used as liner materials in drug delivery system and agrochemical delivery agents, and as catalytic materials [7–13]. They also play a vital role in biogeochemical processes by retaining or releasing metal nutrients in the soil. Clays consist of negatively charged aluminosilicate layers kept

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together by cations. The most characteristic property is their ability to take up water between the layers, resulting in strong repulsive forces and expansion of clay [12].

Clay generally consists of a mixture of different clay minerals and associated minerals. The most abundant clays are minerals from smectite group, with 2:1 layer structure comprised of sheets linked by weak van der Waals forces [13]. Smectite is the name used for a group of phyllosilicate mineral species, the most important being montmorillonite, beidellite, nontronite, saponite, and hectorite. The most common mineral from smectite group is montmorillonite, with a general chemical formula $(1/2Ca,Na)(Al,Mg,Fe)_4(Si,Al)_8O_{20}(OH)_4 \cdot nH_2O$. Montmorillonite is the main constituent of bentonite, derived by weathering of volcanic ash [14].

The structure, chemical composition, exchangeable ion type, and small crystal size of smectite clays are responsible for several unique properties, including: large chemically active surface area, high cation exchange capacity, interlamellar surfaces having unusual hydration characteristics, and sometimes the ability of modifying strongly the flow of liquids. The relatively low price and high abundance mean that this material can also be used in agricultural industries and for filtering and decolorizing various types of oils [15].

The present work is devoted to performing low-temperature synthesis of montmorillonite-based porous ceramics having a macropore size by applying the method of burning-out of additive. Influence of the content of boric acid on mechanical characteristics of clay, like Young modulus and Poisson ratio, has also been studied.

Fusible aqueous solution of boric acid was used as the binder and sintering aid for grains of different mineral origin. Aqueous solution of boric acid was chosen also to provide porous microstructure. When heated above 170 °C, boric acid dehydrates and forms metaboric acid (HBO_2). Further heating leads to boron trioxide (B_2O_3). It is expected that sintering temperature of silicon dioxide ceramics in the presence of boric acid will be lowered.

As far as the authors of this work are aware, there are no information about the influence of B_2O_3 on the properties of a thermally treated clay. However, the effects of "boron wastes" having high content of B_2O_3 have been investigated especially in the area of thermal behavior and microstructural development of clay. Small additions of B_2O_3 in the clay will result in a significant boost of its utilization. In nature B_2O_3 is found in sediments and sedimentary rocks. The effect of "boron wastes" on clay depends on the borates production route in different geographical regions. Content of B_2O_3 in chemical and mineralogical compositions of "boron sintering additives" is from 3.5 to 26 wt% [16–18].

2. Experimental

2.1. Materials

Smectite clay from surface coal mine Kolubara, Serbia, was used as the raw material. Boric acid (Alkaloid AD, Skopje, Macedonia) was used as the binding and sintering aid.

The as-received clay was purified using thermal and chemical treatments before processing. Organic impurities have been removed from the clay by heat treatment (600 °C, 2 h) in air. Then, the clay was treated in aqueous solution of 0.5 M HCl (p.a. 37%, BDH Prolabo) (wt% 1:10) in order to reduce the content of iron oxide. The suspension was stirred for 6 h at 60 °C. After decanting the liquid phase, the residual sediment was dried at 120 °C till constant weight.

2.1.1. Preparation of starting mixtures

Three starting mixtures were prepared by homogenization of purified clay and boric acid in amounts of: x=0.5, 1.0, and 2.0 wt%. The aqueous solution of boric acid was prepared by dissolving boric acid powder in destiled water at 25 °C, aided by a magnetic stirrer [19]. The powders were pressed into pellets under different uniaxial pressures: y=40, 60, and 80 MPa. The pressed samples were sintered at: z=850, 1000, 1150, and 1300 °C for 4 h in air. The prepared samples were denoted by $C_{x\text{-}y\text{-}z}$, in accordance with the processing conditions: x, content of boric acid; y, applied pressure; and z, sintering temperature.

2.2. Characterization

Chemical compositions of the starting and treated materials, obtained by the inductively coupled plasma (ICP) spectrometry (Spectro-Flame, Spectro-Analytical Instruments), are listed in Table 1. Chemical compositions show that the starting and treated clays are mainly composed of SiO_2. Also, impurities such as Al_2O_3, Na_2O, and K_2O are present (Table 1). The treated material has a distinctly lower content of Fe_2O_3.

Samples were characterized at room temperature by X-ray powder diffraction (XRD) by using Ultima IV Rigaku diffractometer, equipped by Cu $K\alpha_{1,2}$ radiation, with generator voltage 40.0 kV and generator current 40.0 mA. The range of 15–70° 2θ was used for all powders in a continuous scan mode with a scanning step size of 0.02° at scan rate of 10°/min.

The morphology of clay samples was investigated by using Scanning Electron Microscopy (SEM) – JEOL JCM-5800 LV.

The mercury intrusion porosimetry was applied for the measurements of pore size distribution and total intrusion volume. Measurements were performed by the automatic porosimeters Fisons – 2000 series (the limiting pressure 200 MPa and pore diameters from 7.5 to 15000 nm) and Carlo Erba – 120 macropore unit (the limiting pressure 0.1 MPa and pore diameter from 100,000 to 15,000 nm) and applying data processing program Milestone 200.

The total porosity (ε_t) of the samples was calculated according to equation $\varepsilon_t = (1-\rho/\rho_t)100$, where ρ and ρ_t are

Table 1
Chemical composition (percentage weight: wt%) of the starting and treated materials.

Element	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	SiO_2
As-received clay, wt%	6.05	2.06	0.48	0.35	0.18	1.05	1.76	88
Treated material, wt%	5.10	0.96	0.52	0.25	0.21	1.21	1.53	90