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Effect of boric acid on the porosity of clay and diatomite monoliths

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Received 21 October 2015; received in revised form 14 December 2015; accepted 5 January 2016

Abstract

Porous silica ceramics were obtained at low forming pressure (40–80 MPa) and low sintering temperature (850–1300 °C) for 4 h in air. Boric acid was used as a low-cost additive, in the amount of 2 wt%. Relatively high porosities of nearly 40% and 65% are obtained for the samples of clay and diatomite pressed at 40 MPa, and sintered at 1000 °C, respectively. The samples sintered at 1150 °C and 1300 °C have the average pore size diameters in the range of macroporous for clay 0.2–10 μm and for diatomite 0.2–5 μm. X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy, and mercury porosimetry measurements were employed to characterize of the obtained samples. Measurements of densities and open porosities by immersion technique were used, according to the Archimedes principle. The relations between mechanical characteristics of the samples formed by using different pressures and sintered at different temperature, were discussed.

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

1. Introduction

Porous ceramics provide an opportunity for combining important properties of materials, such as high porosity with high strength and high thermal and chemical stability. This combination of properties is very important for various industrial applications such as filters, heat insulators, absorbents, catalyst supports and advanced environmental applications, such as membranes or chromatography columns [1–12]. Also, these materials have traditionally been used as building materials and thermal insulation.

Manufacturing of porous materials from sediments materials, such as natural clayey material powder (clay) or diatomite (diatomaceous earth), has become a matter of increased interest because of the possibility of employing an easy, low cost, and green manufacturing strategy while retaining characteristic features of the original material. Deposit areas of clay and diatomite have a high economic potential.

The sediments materials represent attractive materials for synthesis of porous ceramics due to their low price, natural porosity (diatomite) and high abundance. In this work we will show how a low cost clay and diatomite can be used to fabricate porous materials by dry pressing and conventional sintering at a relatively low temperature. Clay and diatomite were used as raw materials from surface coal mine Kolubara, Serbia. This basin has distinctly separate layers of clay and diatomite. During coal exploitation a huge amount of clay and diatomaceous earth is deposited.

Diatomaceous earth is typically soft, friable and fine grained, characterized by a relatively low density, chemically inert in most liquids and gases and sparingly soluble in water with a low thermal conductivity. It is an attractive material for fabrication of porous ceramics due to its low cost, natural porosity and versatile appealing properties.

The structure, chemical composition, exchangeable ion type and small crystal size of clay minerals are responsible for

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http://dx.doi.org/10.1016/j.ceramint.2016.01.034
0272-8842/

several unique properties, including: large chemically active surface area, high cationic exchange capacity, interlamellar surfaces having unusual hydration characteristics and sometimes the ability of modifying the flow of liquids.

Aqueous solution of boric acid was chosen to provide as sintering aid for grains of different mineral origin. When heated boric acid, it forms boron trioxide (B_2O_3). The effect of boric acid, pressure forming, sintering temperature on the microstructure, porosity parameters and mechanical properties of clay and diatomite monoliths have been studied [13,14]. The present work is devoted to comparison of various specific properties of porous monoliths having a macropore size based on clay and diatomaceous earth.

2. Experimental

2.1. Material

Natural clayey material powder, clay and diatomaceous earth were used as raw materials from the surface coal mine Kolubara, Serbia. Boric acid (Alkaloid AD, Skopje, Macedonia) was used as sintering aid.

These materials were purified by using thermal and chemical treatments before processing. Organic impurities have been removed from the materials by heat treatment (600 °C, 2 h) in air. Afterwards, the materials were chemically treated in aqueous solution of 0.5 M HCl (p.a. 37%, BDH Prolabo) (wt% 1:10). The suspensions were stirred for 6 h at 60 °C. After decanting the liquid phase, the residual sediments were dried at 120 °C until they achieved their constant weight. The schematic illustration of the experimental procedure is summarized in Fig. 1.

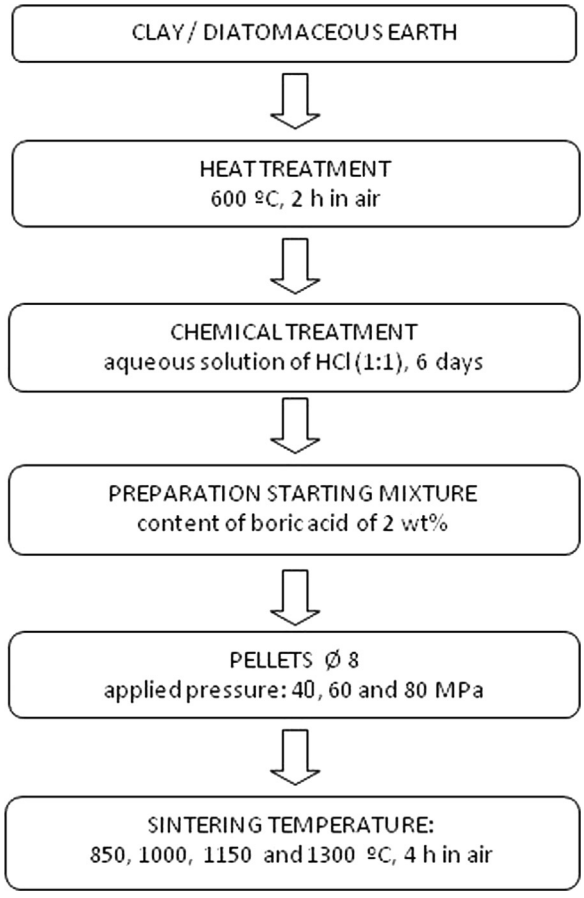

Fig. 1. Schematic overview of the experimental procedure.

2.1.1. Preparation of starting mixtures

Starting mixtures were prepared by homogenization of the purified clay or purified diatomaceous earth and boric acid in the amount of 2.0 wt%. The saturated aqueous solution of boric acid was prepared by dissolving boric acid powder in distilled water at 25 °C, aided by a magnetic stirrer [15]. The prepared saturated aqueous solution of boric acid was used in a quantity measured out to the solid weight of 2.0 wt%. The prepared samples were denoted by $C_{a\text{-}b}$ and $D_{a\text{-}b}$ in accordance with the processing conditions: a- applied pressure, and b- sintering temperature while labels for C and D represent clay and diatomite, respectively. The powders were pressed into pellets under different uniaxial pressures: a=40, 60, and 80 MPa. The pressed samples were sintered at: b=850, 1000, 1150 and 1300 °C for 4 h in air (Fig. 1).

2.1.2. Characterization

The complete chemical compositions of the as-receved materials, clay and diatomite are listed in Table 1 [13,14].

The clay fraction from the natural clayey material was collected in the following way: the clayey material collected in situ was dried, grounded and passed through a sequence of sieves yielding a homogeneous powder with particle size smaller than 63 μm, corresponding to 37.82 % of the original mass. This method is applied in order to characterize clay sample with X-ray powder diffraction (2–60° 2θ, continuous scan mode with a scanning step size of 0.02° at a scan rate of 2°/min). Samples were characterized at room temperature applying X-ray powder diffraction (XRD) technique by using the Ultima IV Rigaku diffractometer, equipped by Cu K$\alpha_{1,2}$ radiation, generator voltage 40.0 kV and current 40.0 mA. The range of 5–60° 2θ was used for all powders in a continuous scan mode with a scanning step size of 0.02° at a scan rate of 5°/min.

Table 1
Chemical composition (wt%) of the as-receved materials clay and diatomite.

Element, wt.%	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	Na_2O	K_2O	SiO_2
Clay [13]	6.05	2.06	0.48	0.35	0.18	1.05	1.76	88.00
Diatomite [14]	12.28	3.29	–	0.44	0.70	0.12	1.01	73.68

Functional groups of clay and diatomaceous earth and the synthesized samples were studied by using the Fourier transform infrared (FTIR) spectroscopy. The powder samples with small amount of KBr were pressed in a mold and then introduced into a Perkin Elmer FT-IR spectrometer, Spectrum Two. Spectral data of the samples were collected between 1200 and 450 1/cm.

Please cite this article as: M. Kokunešoski, et al., Effect of boric acid on the porosity of clay and diatomite monoliths, Ceramics International (2016), http://dx.doi.org/10.1016/j.ceramint.2016.01.034