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PROCEEDINGS

Editor
Prof. dr Ivica Ristic

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POROUS CERAMICS BASED ON NATURAL MINERAL SOURCES

Maja Kokunešoski¹, Aleksandra Šaponjić¹, Miroslav Stanković², Marina Vuković³,
Jelena Majstorović⁴, Dragana Jordanov¹, Milica Marčeta Kaninski¹

¹University of Belgrade- Vinča Institute of Nuclear Sciences, Belgrade, Serbia, majako@vin.bg.ac.rs;
acavuc@vin.bg.ac.rs; djordano@vin.bg.ac.rs; milica@vin.bg.ac.rs

²University of Belgrade - Institute of Chemistry, Technology and Metallurgy, Belgrade, Serbia,
mikastan@nanosys.ihtm.bg.ac.rs

³University of Belgrade - Institute for Multidisciplinary Research, Belgrade, Serbia,
marina.vukovic@imsi.bg.ac.rs

Abstract: Starting raw materials, clay and diatomite, from coal mine Kolubara, Serbia were purified using heat and chemical treatment. Porous silica ceramics were obtained at low forming pressure (40-80 MPa) and low sintering temperature (1000-1300 °C) in air. Boric acid as a low-cost additive was used. Sintered samples have average pore size diameters ranging of macroporous for clay 0.1-10 μm and for diatomite 0.05-5 μm. As-received and the obtained samples were characterized by XRD, SEM and mercury porosimetry measurements. Relations between mechanical characteristics of samples formed at different temperature were studied.

Key words: Sintering, Macroporosity, Clay, Diatomite, Boric Acid

1. INTRODUCTION

Manufacturing of porous materials from sediments materials, such as clay or diatomite, 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. 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 [1-11].

Herein, we report the utilization of the clay and diatomite as raw materials for the fabrication of porous SiO₂ based material. We have employed a facile, low cost, and green strategy to fabricate these materials by using the fused additive method with boric acid. In contrast to the processing of mono-fractional starting materials by the foaming method, and chemical method of pore formation [12], involving complicated processes and our process has demonstrated improved performance and efficiency.

Aqueous solution of boric acid was chosen to provide as sintering aid for grains of different mineral origin. 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 [13-15]. The present work is devoted to comparison of various specific properties (Young modulus and Poisson ratio) of porous monoliths having a macropore size based on clay and diatomite.

The materials made of the modified clay and diatomite opens the possibility of obtaining composite materials with desired properties, which will be the subject of future research.

2. MATERIALS AND CHARACTERISATIONS

2.1. Purification procedure of natural materials, clay and diatomite

Clay and diatomite 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.

2.1.1 Preparation of starting mixtures

Starting mixtures were prepared by homogenization of the purified clay or purified diatomite and boric acid in the amount of 1wt%. The saturated aqueous solution of boric acid was prepared by dissolving boric acid in distilled water at 25 °C, aided by a magnetic stirrer [16]. The prepared saturated aqueous solution of boric acid was used in a quantity measured out to the solid weight of 1 wt%. The prepared samples were denoted by C_{a-b} and D_{a-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 = 1000, 1150 and 1300 °C for 4 h in air.

2.2. Characterization

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

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

Element, wt.%	Al ₂ O ₃	Fe ₂ O ₃	TiO ₂	MgO	CaO	Na ₂ O	K ₂ O	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

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 10-60° 2 θ 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.

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

The morphology of clay and diatomite samples was investigated by using the Scanning Electron Microscopy (SEM) - VEGA TS 5130 MM, Tescan. Poisson's ratio (μ_{din}) and Young's modulus (E_{din}) are determined on the basis of measuring ultrasonic velocity.

The measurements were performed by using the equipment OYO model 5210, according to the standard testing procedure (SRPS B.B8.12).

3. RESULTS AND DISCUSSION

3.1. X-ray diffraction (XRD)

The XRD patterns of the as-received and treated clayey material powder or diatomite and samples with boric acid, sintered at 1150 and 1300 °C are shown in Figure 1.

In the X-ray pattern of the as-received and treated clayey material, were identified quartz (PDF No.33-1161) followed by the appearance of clay minerals of the kaolinite group, mica/illite (PDF No. 89-6538). Cristoballite (PDF No. 82-1410) is formed by recrystallization of quartz and is present at 1150 and 1300 °C, in samples C₆₀₋₁₁₅₀ and C₆₀₋₁₃₀₀.

The XRD-analysis revealed that the sample of the as-received diatomite had a typical opal structure [17,18]. The XRD pattern shows broadening of the diffraction lines in the regions around 15–25 of 2θ, which is associated with presence of an amorphous silica phase. Cristoballite (PDF No. 82-1410) is the major crystalline phase in the samples sintered at 1150 and 1300 °C, followed by peaks of quartz (PDF No. 33-1161).

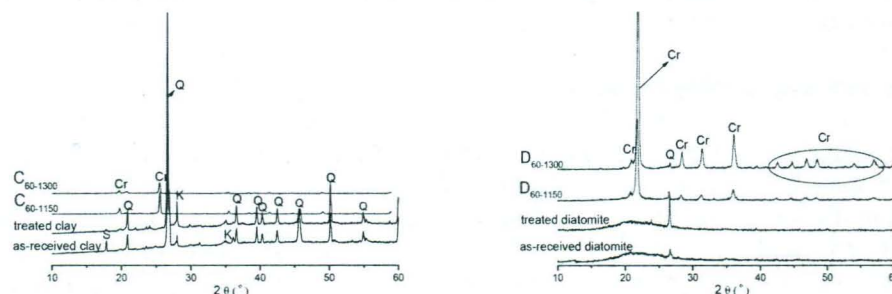


Figure 1. XRD patterns C / D_{60-1150, 1300}: S smectite PDF: 29-1490, K kaolinite PDF: 89-6538,

Q quartz PDF: 33-1161, Cr cristobalite PDF: 89-3606.

3.1 Mercury intrusion

Samples with 1 wt% of boric acid, obtained at the low forming pressures from 40 to 80 MPa and sintering temperatures at 1150 and 1300 °C, were observed (Figures 2 and 3). The sample sintered at 1000 °C, were damaged and disabled for use in further analyses because of their friable nature.

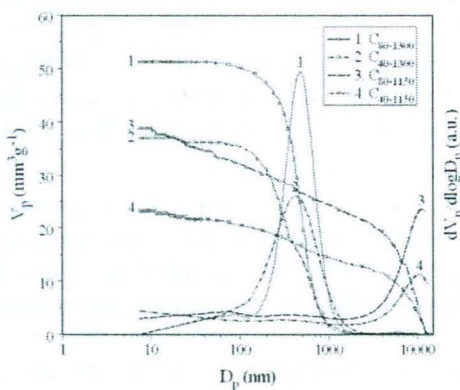


Figure 2. Pore size distribution versus pore diameter of samples: C_{40,80-1150}, and C_{40,80-1300}.

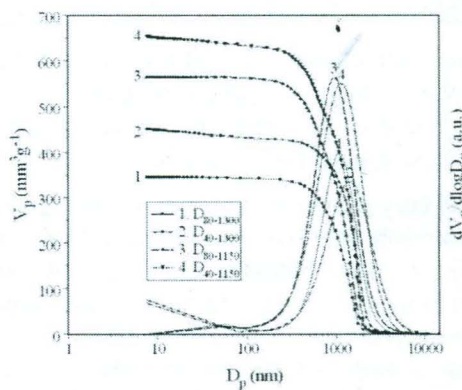


Figure 3. Pore size distribution versus pore Diameter of samples: D_{40,80-1150}, and D_{40,80-1300}.

For the clay samples by increasing the sintering temperature from 1150 to 1300 °C, average pore size diameter significantly decrease (Figure 2). For the clay samples sintered at 1150 °C the pore size distribution curves over the entire range of diameters are situated from 2,5 to over 10 μm which is substantially higher in comparison to the sample obtained at 1300 °C (0.15-1 μm). The samples sintered at 1150 °C have two peaks within the range from 0.1 to 1 μm, which indicates presence of group of smaller diameter pores. The samples sintered at 1300 °C have a shoulder around 0.15 μm which also

indicates presence of another group of smaller diameter pores. A diminution of total pore volume and porosity of the samples obtained at 1150 °C in compared to samples obtained at 1300 °C (Figure 2). Due to pores merging, the average pore size diameters are higher for the samples sintered at 1150 °C (9.4 μm) in compared to samples obtained at 1300 °C (0.4 μm). Sintering of B₂O₃ and SiO₂ [19] in the presence of impurities in clay [13] leads to melting processes [20–25] which leads to pore merging. Figure 3 shows the pore size distribution curves for the diatomite samples with boric acid, pressed at all applied pressure and sintered at 1150 and 1300 °C, determined by mercury porosimetry. The pore size distribution from 0.25 to 5 μm for the samples 1150 °C and 1300 °C are observed. The samples sintered at 1150 °C have peak within the range from 0.05 to 1 μm, which indicates presence of group of smaller diameter pores. Total pore volumes were lower for the samples sintered at 1300 °C compared to the samples sintered at 1150 °C (Figure 3). A diminution of average pore size versus the applied pressure is observed at the samples obtained at the same temperature. Measurements confirm the well-known macropore character of the clay and diatomite.

3.2. Scanning electron microscope (SEM)

Figure 4 shows the microstructure of as received clayey and diatomite materials and unpolished samples with boric acid formed at 40 MPa and sintered at 1150 and 1300 °C, respectively.

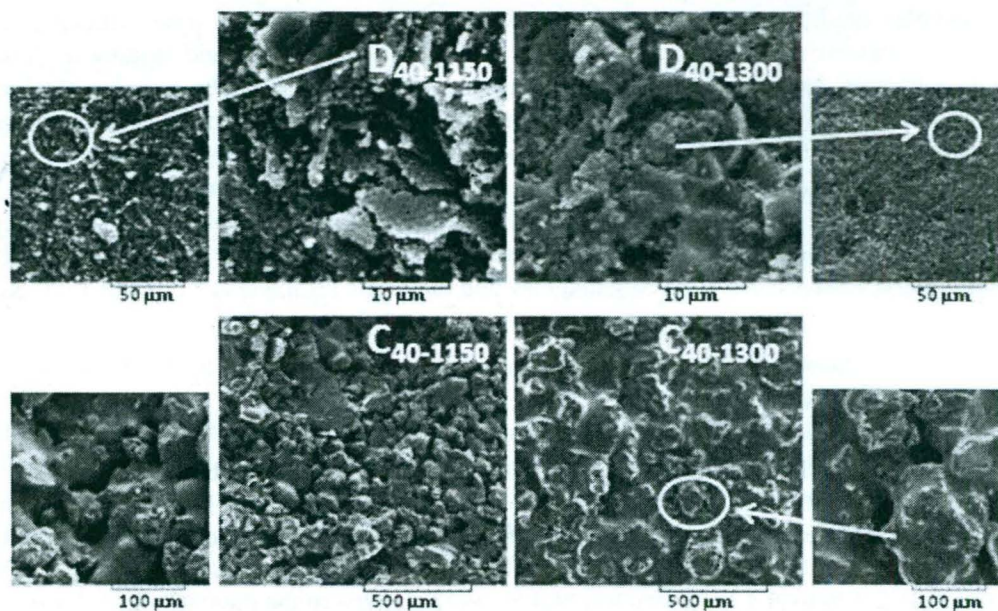


Figure 4. Images of samples C / D_{40-1150, 1300}.

Due to different microstructures of these starting materials, boric acid had different effects on the formation of pores [13-15]. During the preparation of these as-received materials the reduction of impurities by the acid and heat treatments, introduced changes in the structure and made both of the materials, more porous. In the SEM image of the clayey investigated materials, grains mostly agglomerated, are visible (Figure 4). The surface morphology of the clay sample with boric acid has a large numbers of irregular connected pores and voids between particles for all investigated samples.

The SEM image of the as received diatomite shows frustules which have disk, capsule-shaped with middle circular opening. Regularly spaced rows of fine pores run circularly along the disk walls in a form of honeycomb with fine pores of dimensions ranging from micro to nanometer scale [17]. On the other side, bimodal distribution of pores is easily noticed in the diatomite sample with boric acid, resulting from the combination of the inherent fine porosity of the diatomite grains and larger intra-grain pores (Figure 4). The investigated diatomite samples have a significantly smaller pore diameter in comparison with the samples of clay sintered at 1150 °C, which are also modified with boric acid [13-15]. All these observations are in good agreement with the results obtained by mercury porosimetry.

3.2. Young modulus and Poisson ratio

Figure 5 shows a variation of Young's modulus versus forming pressure (40, 60 and 80 MPa) in samples of clay and diatomite with boric acid sintered at 1150 and 1300 °C.

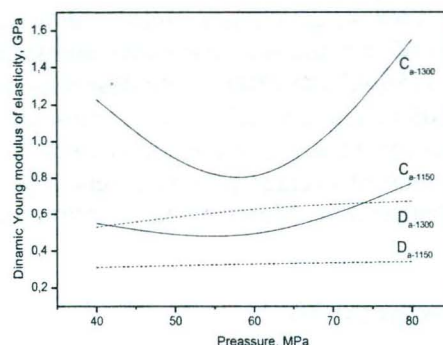


Figure 5. Young's modulus of samples C / D_{40, 60, 80-1150, 1300} versus the applied pressure.

Clay samples modified by boric acid, sintered at 1150 and 1300 °C, have generally higher Young's modulus in comparison to diatomite samples, also modified by boric acid (Figure 5). Young's modulus slightly increases, as a function of the forming pressure (Figure 5). The samples of clay pressed at 60 MPa and sintered at 1150 and 1300 °C have lower Young's modulus in comparison to the samples obtained at 40 and 80 MPa (Figure 5). Sintering of B₂O₃ and SiO₂ [19] in the presence of impurities in the clay (Table 1) leads to low temperature eutectic reactions and melting processes [20-24]. The consequences of the melting processes are the appearance of liquid phase, which produces glassy phase upon cooling and therefore deteriorates the mechanical properties, like Young modulus [25]. Poisson's ratio ranging 0.35-0.37 for all investigated clay and diatomite samples, at 1150 and 1300 °C.

4. CONCLUSION

Porous SiO₂ ceramics based on the clay and diatomite were synthesized by using inexpensive method and starting raw materials. Boric acid in amount of 1 wt% was used as the powerful flux and low cost additive. The samples were pressed at 40, 60 and 80 MPa and sintered from 1000 to 1300 °C. For the clay samples sintered at 1150 °C the pore size distribution curves over the entire range of diameters are situated from 2,5 to over 10 μm which is higher in comparison to the diatomite samples (0.25 to 5 μm). Young's modulus slightly increases, as a function of the forming pressure. Clay samples generally have higher Young's modulus in comparison to diatomite samples, also modified.

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REFERENCES

1. Akhtar, F.; Rehman, Y.; Bergström, L. A study of the sintering of diatomaceous earth to produce porous ceramic monoliths with bimodal porosity and high strength. *Powder Technol.* 2010, 201, 253-257.
2. Akhtar, F.; Andersson, L.; Ogunwumi, S.; Hedin, N.; Bergström, L. Structuring adsorbents and catalysts by processing of porous powders. *J. Eur. Ceram. Soc.* 2014, 34, 1643-1666.
3. Greil, P. Advanced engineering ceramics. *Adv. Mater.* 2002, 14, 709-716.

4. Green, D.J.; Colombo, P. Cellular ceramics: intriguing structures, novel properties, and innovative applications, *MRS Bull*, 28 (2003) 296–300.
5. Ueno, S.; Lin, L.M.; Nakajima, H. Formation mechanism of porous alumina with oriented cylindrical pores fabricated by unidirectional solidification. *J. Am. Ceram. Soc.* 2008, 91, 223–226.
6. Van Setten, B.A.A.L.; Spitters, C.G.M.; Bremmer, J.; Mulders, A.M.M.; Makkee, M.; Moulijn, J.A. Stability of catalytic foam diesel-soot filters based on Cs₂O, MoO₃, and Cs₂SO₄ molten-salt catalysts. *Appl. Catal., B Environ.* 2003, 42, 337–347.
7. Dhar, G.M.; Snirivas, B.N.; Rana, M.S.; Kumar, M.; Maity, S.K. Mixed oxide supported
8. hydrodesulfurization catalysts: a review. *Catal. Today* 2003, 86, 45–60.
9. Nair, J.; Nair, P.; Ommen, J.G.V.; Ross, J.R.H.; Burggraaf, A.J.; Mizukami, F. Influence of
10. peptization and ethanol washing on the pore-structure evolution of sol-gel-derived alumina catalyst supports. *J. Am. Ceram. Soc.* 1998, 81, 2709–2712.
11. Falamaki, C.; Naimi, M.; Aghaie, A. Dual behavior of CaCO₃ as a porosifier and sintering aid in the manufacture of alumina membrane/catalyst supports. *J. Eur. Ceram. Soc.* 2004, 24, 3195–3201.
12. Li, S.H.; Wijn, J.R.; Layrolle, P.; Groot, K. Novel method to manufacture porous
13. hydroxyapatite by dual-phase mixing. *J. Am. Ceram. Soc.* 2003, 86, 65–72.
14. Khalil, T.; Abou El-Nour, F.; El-Gammal, B.; Boccaccini A.R. Determination of surface area and porosity of sol-gel derived ceramic powders in the system TiO₂-SiO₂-Al₂O₃. *Powder Technol.* 2001, 114, 106–111.
15. Sepulveda, P.; Bittner, J.G.P. Processing of cellular ceramics by foaming and in situ polymerisation of organic monomers. *J. Eur. Ceram. Soc.* 1999, 19, 2059–2066.
16. Kokunešoski, M.; Šaponjić, A.; Maksimović, V.; Stanković, M.; Pavlović, M.; Pantić, J.; Majstorović, J. Preparation and characterization of clay-based porous ceramics with boric acid as additive, *Ceram. Int.* 2014, 40, 14191–14196.
17. Šaponjić, A.; Stanković, M.; Majstorović, J.; Matović, B.; Ilić, S.; Egelja, A.; Kokunešoski, M. Porous ceramic monoliths based on diatomite, *Ceram. Int.* 2015, 41, 9745–9752.
18. Kokunešoski, M.; Šaponjić, A.; Stanković, M.; Maksimović, V.; Egelja, A.; Ilić, S.; Matović, B. Effect of boric acid on the porosity of clay and diatomite monoliths, *Ceram. Int.* 2016, 42, 6383–6390.
19. Hammond, C.R. Physical constants of inorganic compounds. In: *Handbook of Chemistry and Physics*, 84th ed.; Editor, Lide D.R., CRC Press, 2003–2004, pp. 39–166.
20. Matović, B.; Šaponjić, A.; Devečerski, A.; Miljković, M. Fabrication of SiC by carbothermal-reduction reactions of diatomaceous earth, *J. Mater. Sci.* 2007, 42, 5448–5451.
21. Matović, B.; Šaponjić, A.; Bošković, S. Carbonitriding reactions of diatomaceous earth: phase evolution and reaction mechanisms, *J. Serb. Chem. Soc.* 2006, 71, 677–683.
22. Rockett, T.J.; Foster W.R. Phase Relations in the System Boron Oxide-Silica, *J. Am. Ceram. Soc.* 1965, 48, 75–80.
23. Carlson, E.T. The system CaO-B₂O₃, *J. Res. Natl. Inst. Stan.* 1932, 9, 825–832.
24. Morey, G.W.; Merwin, H.E. Phase Equilibrium Relationships in the Binary System, Sodium Oxide-Boric Oxide, with Some Measurements of the Optical Properties of the Glasses, *J. Am. Ceram. Soc.* 1936, 58, 2248–2254.
25. Roller, A.P.; Sur les borates de potassium: Etude du système K₂O-B₂O₃, *Comptes Rendus Académie des Sciences de Paris* 1935, 200, 1763–1965.
26. Sosman, R.B.; Merwin, H.E. Preliminary report on the system lime-ferric oxide, *Washington Academy Science Journal* 1916, 6, 532–537.
27. Wartenberg, H.V.; Reusch, H.J.; Saran, E. Schmelzpunktdiagramme höchstfeuerfester Oxyde. VII. Systeme mit CaO und BeO, *Zeitschrift für Anorganische und Allgemeine Chemie* 1937, 230, 257–276.
28. D.deFaoite, Browne, D.J.; Chang-Dí'az, F.R.; Stanton, K.T.; A review of the processing, composition, and temperature-dependent mechanical and thermal properties of dielectric technical ceramics, *J. Mater. Sci.* 2012, 47, 4211–4235.