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Multilayer High-Alumina Ceramic Materials for Disperse Systems Microfiltration with Active Layer Received in $\text{Al}_2\text{O}_3\text{-CuO}$, $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-MnO}_2$ Systems

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Abstract

Designed composition of ceramic mass for synthesis of the high-alumina ceramic substrates for production multilayer microfiltration membranes. Electrocorundum (fraction 100–250 microns) was used as filler for producing of the high-alumina substrates, as a binder – kaolinite-hydromica clay and aluminoborosilicate glass and chalk. Formation of material carried by dry pressing at the pressure of 60 MPa, the temperature of synthesis was 1200–1300 °C. The effect of the sintering temperature of the material, the amount and composition of binder on the porosity, mechanical strength, permeability and porous structure of high-alumina permeable porous substrate was investigated. The structure of the substrate is represented by an extensive network of slit-shape pore channels, an average equivalent pore diameter – 10–40 μm. The material has the following set of physicochemical properties: mechanical compressive strength is 27.41 MPa, open porosity – 36.49 %, permeability coefficient – $2.07 \cdot 10^{-7} \text{ m}^2$. The possibility of application of permeable high-alumina porous substrates as macro- and microfiltration elements in the dairy industry was researched. Designed multilayer high-alumina ceramic materials for disperse systems microfiltration with active layer received in $\text{Al}_2\text{O}_3\text{-CuO}$, $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-MnO}_2$ systems. The average pore diameter of the microfiltration layers is 1–10 μm, the open porosity – 38.90–48.42 %, the permeability coefficient of the multilayer membranes (thickness 6.15–6.25 mm) – $(1.566\text{--}1.669) \cdot 10^{-7} \text{ m}^2$.

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Keywords: ceramic substrates, membrane, electrocorundum, microfiltration, porosity, permeability, multilayer structure.

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1. Introduction

Currently, membrane processes are widely used in many industries, including the processing of raw materials in the food industry. Application of microfiltration allows purifying and concentrating of solutions without heating and evaporation. That significantly reduces power consumption of dewatering processes of fruit and vegetable juices production, milk protein concentration compared with the evaporation or freezing processes. Microfiltration are used for water treatment process, stabilization of soft drinks and wines, natural juices concentration, pasteurization, separation and recovery of valuable components from waste and process streams.

Macromolecules, proteins, colloids and bacteria during the separation and concentration of biological media often act as a dispersed phase. The particle size of the dispersed phase involves the use of microfiltration materials with pore sizes of 0.1–10 μm . Microfiltration membranes due to the high density have a large hydraulic resistance. To improve the performance of the filtration process the thickness of the microfiltration membrane should be minimal. Preparation of the microfiltration ceramic materials is possible by the creation of multilayer ceramic compositions consisting of a macrofiltration ceramic substrate and one or more microfiltration layers [1]. The macrofiltration ceramic substrate has a low flow resistance and provides high mechanical strength of the multilayer microfiltration membrane [2,3].

Requirements for microfiltration ceramic membranes for separation and concentration of biological media: high chemical resistance, mechanical strength, bio-inertness, high degree structure homogeneity and defect-free structure.

One of the most promising materials for multilayer ceramic membrane is a high-alumina ceramics [4]. It has a complex of high physical and chemical properties, however, the synthesis of high-alumina ceramics requires high temperatures. The paper considers the possibility of multilayer high-alumina membranes produced at low synthesis temperatures, due to the addition of binders and chemical reactive components. The features of the multilayer structure formation of high-alumina permeable materials for microfiltration of biological media have been studied.

2. Materials and methods

2.1. Materials synthesis

Electrocorundum (fraction 100–250 microns) was used as filler for producing of the high-alumina substrates, as a binder – kaolinite-hydromica clay and aluminoborosilicate glass. Chalk was used as an additional pore-forming agent.

Kaolinite-hydromica clay, aluminoborosilicate glass, chalk were exposed to magnetic purification and grinding in ball mill SPEEDY (Italy) by combining wet milling with humidity 40–45 %, residual on sieve 0.063 was 1.0–2.0 wt. %. The ratio of grinding media to the dry weight of milled material was 1.5:1. Obtained slurry was mixed with electrocorundum and dried. Press-powder was produced from the dried mixture with addition 6–8 wt. % polyvinyl acetate emulsion. Pressing was carried out on a hydraulic press at the pressure of 60 MPa. The formed samples were sintered in an electric laboratory furnace “Nabertherm” at 1200–1300 °C held at the maximum temperature for 1 h.

Porous ceramic coatings on a porous substrate were prepared by dipping the substrate into a finely dispersed ceramic suspension and by subsequently calcining it at temperatures of 1200–1300 °C.

The fine powders were prepared by co-precipitation. Aqueous salt solutions were used for the synthesis of fine powders, ammonia solution ($\rho = 0,983 \text{ g/cm}^3$) were used as precipitant. All reagents were analytical grade purity.

2.2. The study of porous structure, physicochemical properties and filtration capacity of the materials

As methods for the study of the pore structure and filtration capacity of the porous permeable materials were used:

- equilibrium (non-transport) methods: electron and optical microscopy methods were used for the determination of open porosity. The microstructure was investigated by the scanning electron microscope JEOL 7600F (Japan), the macrostructure – optical microscope Leica DFC 280 (Germany).

- transport methods for determination of permeability coefficient of the material. Permeability coefficient of the ceramic material was calculated by the volume of fluid passing through the filter element per unit time using the formula

$$K = \frac{\mu \cdot b \cdot V}{S \cdot t \cdot (P_1 - P_2)}$$

where K – permeability coefficient, m^2 ; μ – absolute (dynamic) viscosity of the fluid, $Pa \cdot s$; b – the membrane thickness, m ; V – volume of fluid passing through the membrane, m^3 ; P_1 , P_2 – pressure at the inlet and outlet of the membrane, respectively, Pa ; S – the membrane surface area, m^2 ; t – time of fluid flow, s .

Determination of the mechanical compressive strength was carried out on hydraulic presses Walter + baiag Series LFM 100 (Switzerland). Cylindrical samples of diameter 25 mm and height 50 mm were used for determining of the compressive strength.

Thermal analysis was carried out on the DSC 404 F3 Pegasus® of firm NETZSCH at the temperature range 25–1250 °C in an inert atmosphere.

X-ray diffraction analysis (XRD) was carried out on DRON-7 with ionization registration of X-rays. Radiation – Cu-K α , detector – Geiger counter. Recording speed is 1–2 °/min in a 2 θ angles from 10 to 70°.

3. Results and discussion

Synthesis of high alumina permeable substrate was carried out at 1200–1300 °C with the ceramic masses including, wt. %: electrocorundum – 85.0–95.0, kaolinite-hydromica clay – 4.5–7.5, aluminoborosilicate glass – 1.0–2.0, chalk – 1.0–4.0.

The structure of the permeable high-alumina substrate is represented by an extensive network of slit-shape pore channels (Fig. 1). Electrocorundum particles have an irregular shape, an average particle diameter is 100–150 μm , an average equivalent pore diameter – 10–40 μm . Pores of this size allow using the material for macrofiltration of the disperse systems affecting the region of microfiltration processes.

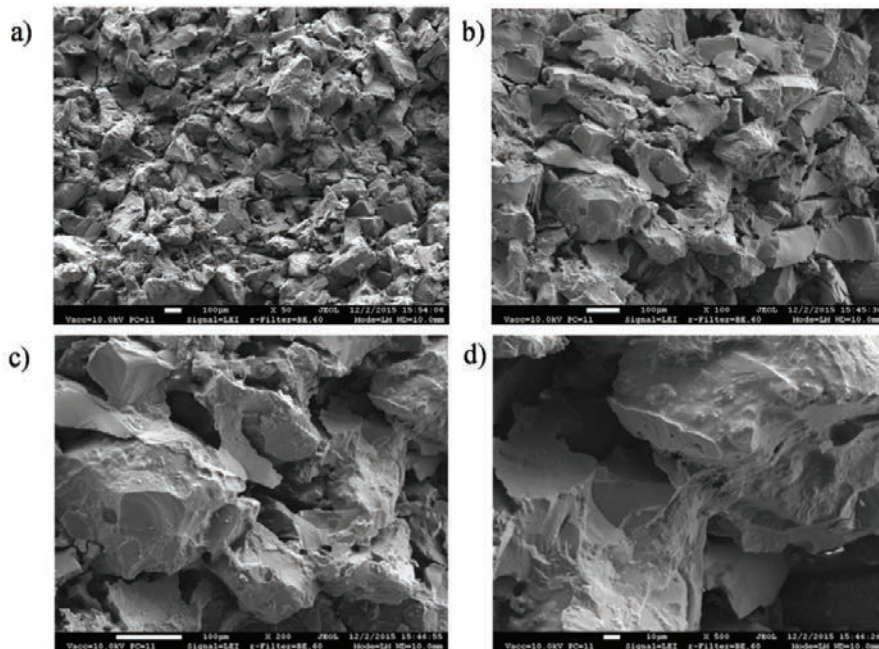


Fig. 1. Structure of the substrate obtained at 1250 °C. Magnification $\times 50$ (a); $\times 100$ (b); $\times 200$ (c); $\times 500$ (d).

The open porosity of the high-alumina permeable substrate is 34.50–37.06 %, the mechanical compression strength – 8,38–37,26 MPa depending on the synthesis temperature, quantity and composition of the binder.

It was established that aluminoborosilicate glass intensifies the sintering processes of the high-alumina materials and provides strong cohesion of electrocorundum particles after sintering at 1250 °C. Addition of chalk in the ceramic composition leads to crystallization of the binder. The degree of crystallinity determines the level of physical and chemical properties of the high-alumina permeable substrate.

The investigation of the permeability coefficient of the high-alumina substrate shows that the increase of the open porosity of the material to 33–35 % followed by a linear increase of the permeability coefficient. For values of open porosity in excess of 35 % the permeability coefficient remains practically unchanged (Fig. 2).

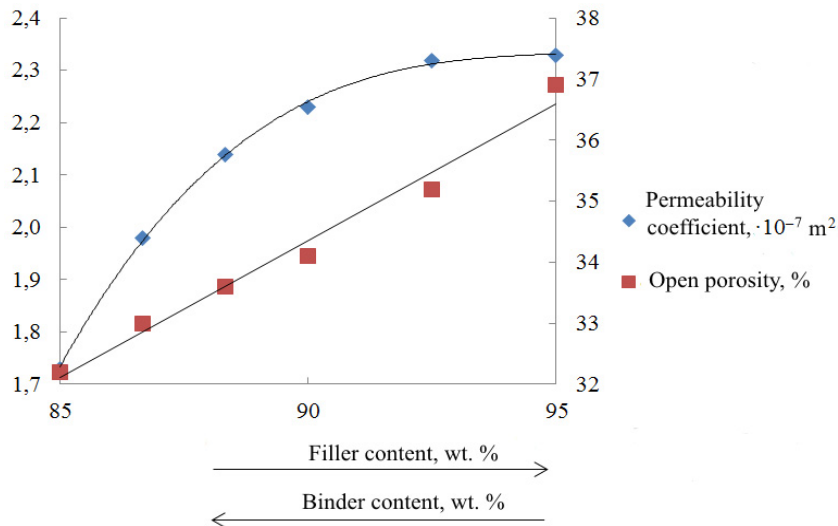


Fig. 2. Relationship between open porosity and permeability coefficient of the high-alumina ceramic substrate.

Apparently, the linear increase of the permeability coefficient up to 35 % of open porosity was caused by the increase number of open pores channels involved in filtration processes. For values of open porosity in excess of 35 % new pore channels in the structure of the material are not formed, the material structure is represented by an extensive network of pore channels. The further increase of open porosity associated with growth of interstitial pore space by reducing the contact area between the electrocorundum particles.

The possibility of application of porous ceramic substrates as a filter element for cleaning the milk and milk products were studied. Tests of physical and chemical (in accordance with GOST 5867–90, p. 2) and the microbiological criteria (GOST 10444.15–94) were carried out on the basis of production and testing laboratory (accreditation certificate № BY / 112 02.2.0.4339) RUE "Institute of Meat and Dairy Industry". The results showed that the filter element separates about 10 % fat and 90 % of the number of mesophilic aerobic and facultative anaerobic microorganisms (QMAFAnM). To increase the efficiency of microfiltration it is required to apply microfiltrating membrane layer on the surface of the ceramic substrate in order to reduce the pore size of the material to a value of 1–10 μm .

It may be noted that the size of the bacteria in the milk is 0.6–7 μm , the pore size of the substrate is several times greater than the size of the filtered bacteria. It indicates physicochemical interactions between the components of the disperse system and the substrate surface.

Materials including $\alpha\text{-Al}_2\text{O}_3$ – 96–98 wt. %, MnO_2 – 1–2 wt. %, TiO_2 – 1–2 wt. % were studied to obtain the microfiltration membrane layer. Gibbsite (fraction 10–20 μm) was used as $\alpha\text{-Al}_2\text{O}_3$ component.

A feature of the system $\text{Al}_2\text{O}_3\text{-MnO}_2\text{-TiO}_2$ is the formation of solid solution enabling sintering materials at temperatures less than $1500\text{ }^\circ\text{C}$ [5, 6]. It is known [7] that the nano-sized crystals of MnO_2 and TiO_2 have biocidal properties, directional crystallization of which would impart the unique properties for the filtration material.

The structure of the membrane coating is homogeneous and is characterized by high porosity (Fig. 3). Electrocorundum particles have rounded shape, the average diameter of the particles is $10\text{--}20\text{ }\mu\text{m}$. The coating thickness is $250\text{ }\mu\text{m}$, penetration of membrane layer particles into pores of the substrate is observed to the depth of $40\text{--}50\text{ }\mu\text{m}$. The membrane layer has higher porosity in comparison with the substrate, the pore size allows to apply the multilayer membrane for microfiltration processes.

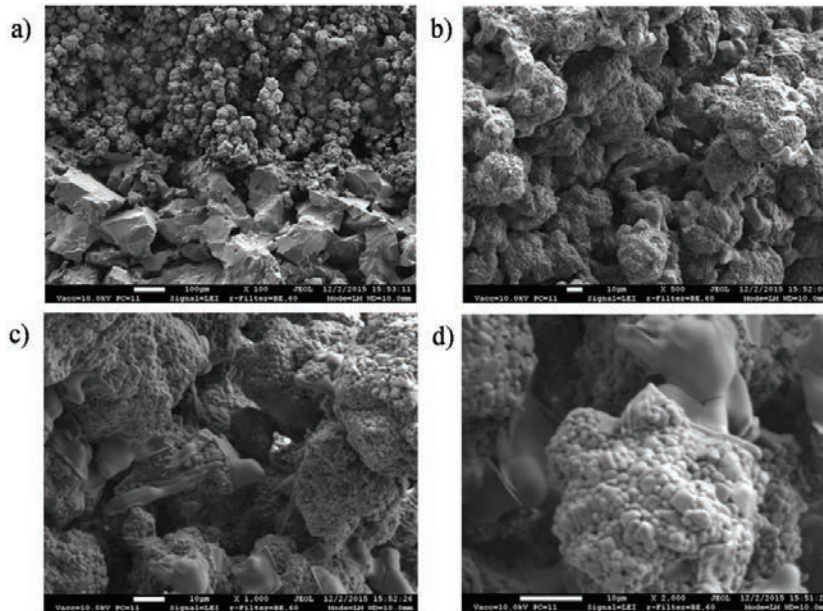


Fig. 3. The structure of the membrane layer prepared in $\text{Al}_2\text{O}_3\text{-MnO}_2\text{-TiO}_2$ system. Magnification $\times 100$ (a); $\times 500$ (b); $\times 1000$ (c); $\times 2000$ (d).

The structure-forming particles of the membrane layer, shown in Fig. 3, are represented by porous aggregates composed of $0.5\text{--}1\text{ }\mu\text{m}$ crystals. It is assumed that the formation of the crystal structures represented in Fig. 3 was caused by the decomposition of $\text{Al}(\text{OH})_3$ during the calcination of gibbsite, which is accompanied by the release of large amounts of H_2O and decrease of particles volume by $13\text{--}15\%$. Gibbsite loses two molecules of chemically bound water at heating of $200\text{--}300\text{ }^\circ\text{C}$ and converts into boehmite. Further heating of boehmite to a temperature of $500\text{ }^\circ\text{C}$ leads to conversion of boehmite into $\gamma\text{-Al}_2\text{O}_3$. Conversion of $\gamma\text{-Al}_2\text{O}_3$ to $\alpha\text{-Al}_2\text{O}_3$ takes a place at temperatures of $850\text{--}1200\text{ }^\circ\text{C}$ and is accompanied by 14.3% volume decrease.

The obtained structure of the structure-forming particles should provide the adsorption properties of the particles and unique filtration properties due to physicochemical interaction between dispersed system and membrane layer. The open porosity of the membrane layer is $42.88\text{--}48.42\%$, the permeability coefficient of the multilayer membrane (thickness 6.25 mm) – $(1.573\text{--}1.669) \cdot 10^{-7}\text{ m}^2$, the original substrate (thickness 6.00 mm) – $2.322 \cdot 10^{-7}\text{ m}^2$.

Currently, the system $\text{Al}_2\text{O}_3\text{-CuO}$ is interesting for producing permeable membranes due to eutectic at temperatures $1260\text{ }^\circ\text{C}$, which makes it possible to reduce the synthesis of the high-alumina materials. High biocidal activity of CuO nanocrystals (size 100 nm) results in their wide use as additives to increase resistance of the materials and structures to biochemical corrosion [7, 8]. Materials including $\text{Al}_2\text{O}_3\text{--}90\text{--}95\text{ wt. \%}$, $\text{CuO}\text{--}5\text{--}10\text{ wt. \%}$ were studied to obtain the microfiltration membrane layer.

The membrane layer is represented by porous material (Fig. 4). The structure of the layer is formed by platelet shaped crystal agglomerates. The aggregates of crystals are $\text{Cu}_2\text{Al}_2\text{O}_4$ compound which is characterized by the

formation of twin crystals (Fig. 4d). The material structure is represented by an extensive network of slit-shape pore channels of average diameter of 1–10 μm which allows application of the membrane for microfiltration processes.

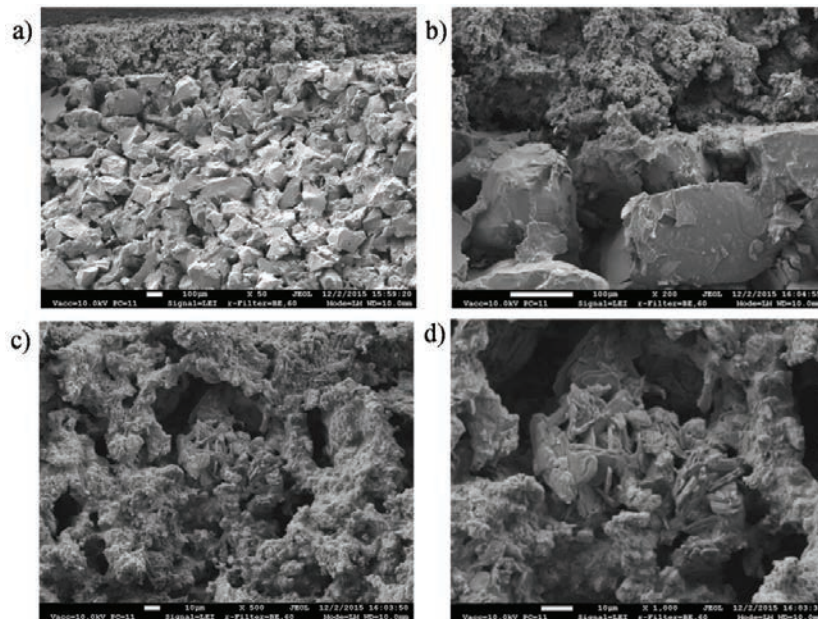


Fig. 4. The structure of the membrane layer prepared in $\text{Al}_2\text{O}_3\text{-CuO}$ system. Magnification $\times 50$ (a); $\times 200$ (b); $\times 500$ (c); $\times 1000$ (d).

Fig. 4 shows that the coating thickness is 150 μm , penetration of membrane layer particles into pores of the substrate is observed to a depth of 15–25 μm . The open porosity of the membrane layer is 38.9–41.4 %, the permeability coefficient of the multilayer membrane (thickness 6.15 mm) – $(1.566\text{--}1.657) \cdot 10^{-7} \text{ m}^2$, the original substrate (thickness 6.00 mm) – $2.322 \cdot 10^{-7} \text{ m}^2$.

4. Conclusions

Electrocorundum (fraction 100–250 microns) was used as filler for producing of the high-alumina substrates, as a binder – kaolinite-hydromica clay, aluminoborosilicate glass and chalk. The aluminoborosilicate glass intensifies the sintering processes of the high-alumina materials due to formation of low temperature aluminosilicate eutectics and makes it possible to produce permeable ceramic substrates at 1250 $^\circ\text{C}$ with high performance: mechanical compressive strength is 27.41 MPa, open porosity – 36.49 %, permeability coefficient – $2.07 \cdot 10^{-7} \text{ m}^2$. The research provided the possibility of application of permeable high-alumina porous substrates as macro- and microfiltration elements in the dairy industry.

Application of the gibbsite in the system $\text{Al}_2\text{O}_3\text{-TiO}_2\text{-MnO}_2$ for producing of microfiltration layers allows creating of permeable materials with mesoporous structure-forming particles. The obtained structure of the structure-forming particles should provide adsorption properties of the particles and unique filtration properties due to physicochemical interaction between dispersed system and membrane layer. The open porosity of the membrane layer is 42.88–48.42 %, the permeability coefficient of the multilayer membrane (thickness 6.25 mm) – $(1,573\text{--}1,669) \cdot 10^{-7} \text{ m}^2$, the original substrate (thickness 6.00 mm) – $2.322 \cdot 10^{-7} \text{ m}^2$.

Producing of porous structure in the system $\text{Al}_2\text{O}_3\text{-CuO}$ (ratio of components $\text{Al}_2\text{O}_3\text{:CuO} = 9\text{:}1$) occurs due to the formation of platelet-shaped $\text{Cu}_2\text{Al}_2\text{O}_4$ crystal agglomerates. It allows to obtain microstructured materials which are represented by an extensive network of slit-shape pore channels. The average pore diameter is 1–10 μm , the open porosity of the membrane layer is 38.9–41.4 %, the permeability coefficient of the multilayer membrane (thickness 6.15 mm) – $(1.566\text{--}1.657) \cdot 10^{-7} \text{ m}^2$, the original substrate (thickness 6.00 mm) – $2.322 \cdot 10^{-7} \text{ m}^2$.

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