

PROCESSES OF TRANSFER IN POROUS MEDIA

DEVELOPMENT OF THE POROUS SUBSTRATES OF CERAMIC MEMBRANE FILTERS

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Results of studying the processes of manufacture of the porous substrates of ceramic membrane filters have been presented. Specimens of ceramic porous substrates suitable for the manufacture of membrane filters have been obtained in the porosity interval 30–60% and the pore-size interval 0.4–100 μm based on the investigations carried out.

In filtration of liquid and gaseous media, one must use special bioinert and corrosion-resistant filter elements with a high fineness and efficiency of filtration for removal of harmful microorganisms (bacteria and viruses), dust, and other impurities, including nanosize particles. Already the membrane methods of separation of liquid and gaseous media occupy a firm place in the arsenal of industrial technological processes [1].

Oxide ceramic is one of the most promising filter materials owing to its high bioinertness and corrosion and heat resistance. Better properties are possessed by ceramic membrane filters characterized by a gradient pore structure and consisting of a microporous substrate and one or a few membrane layers. The use of the multilayer structure enables one to decrease hydrodynamic resistance and thus to increase the capacity of a membrane filter. The microporous substrate ensures mechanical strength, and the membrane bed ensures filtering capacity (fineness of filtration). Furthermore, part of the contaminants are trapped by the substrate, as a result of which the contaminant capacity of the system increases [2].

This work seeks to study the influence of the dispersity and morphology of aluminum-oxide powders, dopants, and technological binders and the conditions of obtaining ceramic substrates on their properties.

Investigation Procedure. In the work, we have used aluminum-oxide powders of different morphologies and dispersities of particles: GN alumina (average particle size $D_{av} \approx 5 \mu\text{m}$), G-00 alumina ($D_{av} \approx 75 \mu\text{m}$), M1 electrocorundum ($D_{av} \approx 1 \mu\text{m}$), M20 electrocorundum ($D_{av} \approx 20 \mu\text{m}$), and M200 electrocorundum ($D_{av} \approx 200 \mu\text{m}$).

Dopants in the form of the powders of four-component glass (FCG) of the composition $\text{CaO-B}_2\text{O}_3\text{-SiO}_2\text{-BaO}$ and the compound MnTiO_4 were added to the aluminum-oxide powders to reduce the sintering temperature. Aluminum hydroxide (Al(OH)_3) was used to increase the porosity and the degree of strengthening. As a porogen we used ammonium bicarbonate (NH_2CONH_2) which was added to the powder mixture above 100% in an amount of 20 and 40%. The compositions of the mixtures used are given in Table 1.

To determine the mechanical properties and size of the specimens we molded them in steel molds at a pressure of 50 MPa under the conditions of uniaxial compression. The molded specimens were sintered in the temperature interval 1200–1700°C. The microstructure of the materials sintered was studied with a CamScan scanning electron microscope (England). The pore size (by the bubble method) was measured with a POROMER-1 device.

Investigation Results. Table 2 gives data on the influence of temperature on the porosity of the sintered specimens; for convenience of the work, we arranged the specimens not in order of specimen number. As is clear from the table, the porosity of the specimens depends on a number of factors: the sintering temperature, the origin and granulometric composition of Al_2O_3 powders, the composition of dopants, and the amount of the porogen.

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TABLE 1. Compositions of Ceramic Mixtures

No. of composition	Composition, wt%	No. of composition	Composition, wt%
1	85% GN + 5% FCG + 10% Al(OH) ₃	11	[85% M20 + 5% FCG + 10% Al(OH) ₃] + NH ₂ CONH ₂
2	85% GN + 5% MnTiO ₄ + 10% Al(OH) ₃	12	[85% M20 + 5% MnTiO ₄ + 10% Al(OH) ₃] + 40% NH ₂ CONH ₂
3	85% M20 + 5% FCG + 10% Al(OH) ₃	13	100% M1
4	85% M20 + 5% MnTiO ₄ + 10% Al(OH) ₃	14	[95% GN + 5% FCG] + 20% NH ₂ CONH ₂
5	[85% GN + 5% FCG + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂	15	[95% GN + 5% MnTiO ₄] + 20% NH ₂ CONH ₂
6	[85% GN + 5% MnTiO ₄ + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂	16	85% G-00 + 5% FCG + 10% Al(OH) ₃
7	[85% M20 + 5% FCG + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂	17	[85% G-00 + 5% FCG + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂
8	[85% M20 + 5% MnTiO ₄ + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂	18	[95% G-00 + 5% FCG] + 20% NH ₂ CONH ₂
9	[85% GN + 5% FCG + 10% Al(OH) ₃] + 40% NH ₂ CONH ₂	19	[85% G-00 + 5% MnTiO ₄ + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂
10	[85% GN + 5% MnTiO ₄ + 10% Al(OH) ₃] + 40% NH ₂ CONH ₂	20	[85% M200 + 5% FCG + 10% Al(OH) ₃] + 20% NH ₂ CONH ₂

TABLE 2. Influence of Temperature on the Porosity (%) of the Sintered Specimens

No. of specimen	Sintering temperature, °C									
	1200	1250	1275	1300	1350	1400	1450	1500	1600	1700
1	48	46		43	38	30				
5				55	49	44	40	32		
14				53	50	43	39	33		
9				63		54		44	35	22
2	36	20		6						
6	52	38	34	21						
15	49	40	32	25						
10	59	47	40	32	20					
3				47	45	43		38	34	
7				54	51	45		45	40	
11				62		54		52	47	26
4	45	40	37	32	27					
8	54	50		43	36	31				
12				52	43	40	37		31	
16				62		55	50			
17				66		59	55			
18				66		60	56			
19		51	45	38						
20				58		55	56			
13	47	45	40	39	27					

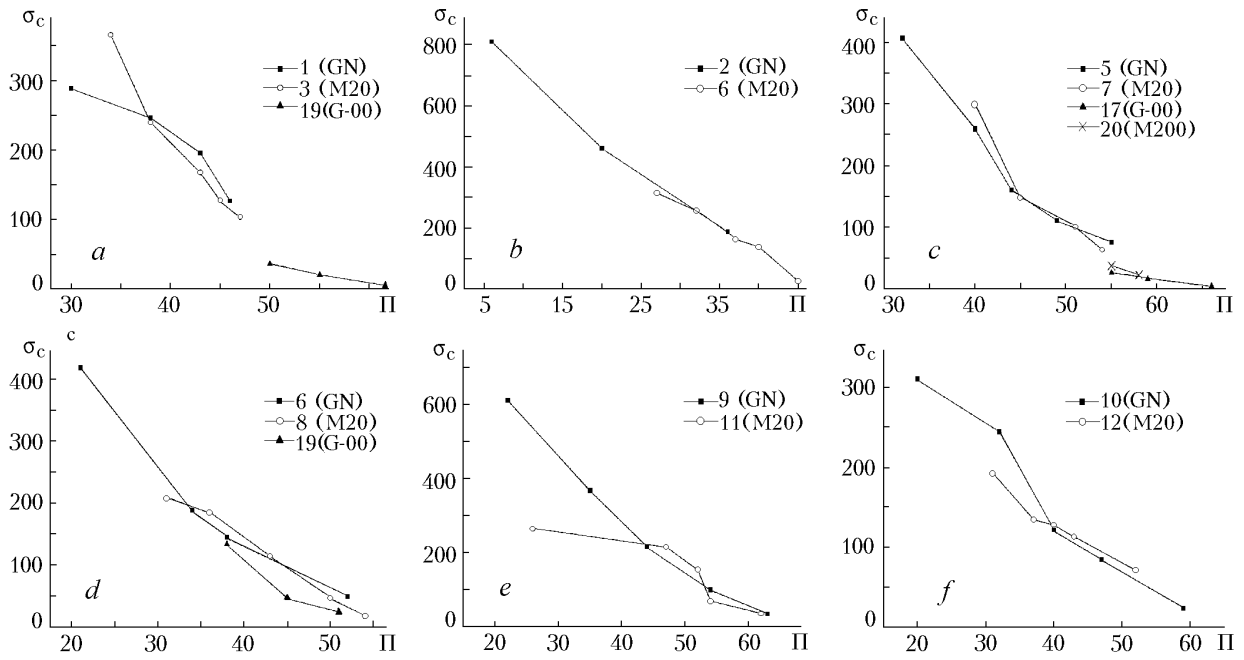


Fig. 1. Dependence of the compressive strength on the porosity of the ceramic specimens under study: a and b) without a porogen; c and d) 20% NH_2CONH_2 ; e and f) 40% NH_2CONH_2 ; a, c, and e) the activator of sintering is FCG; b, d, and f) the activator of sintering is MnTiO_2 (we have indicated the numbers of specimens and the compositions).

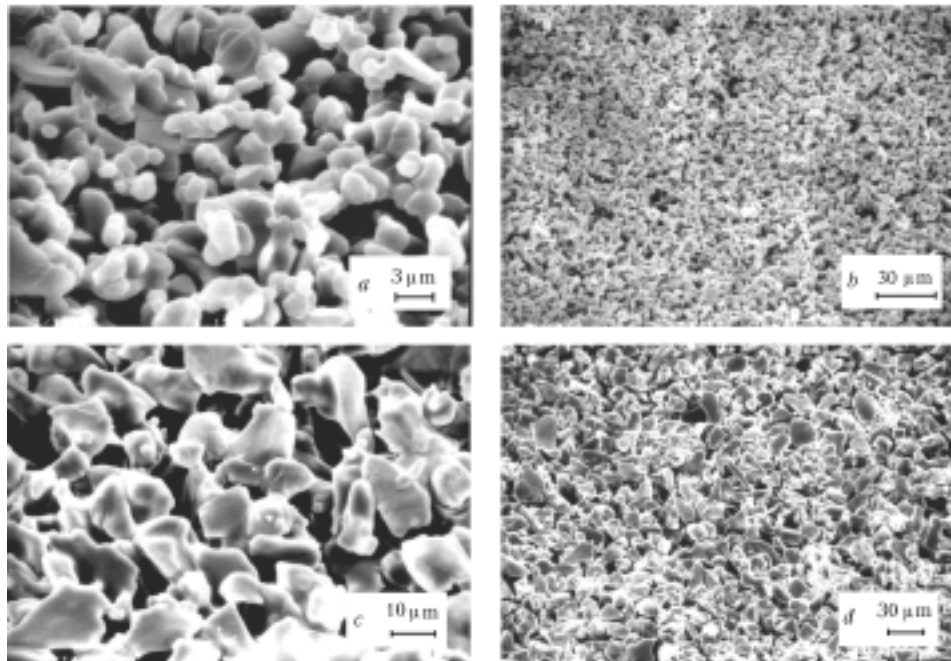


Fig. 2. Microstructure of sintered specimens with different magnifications: a and b) composition No. 3, sintering temperature 1300°C ; c and d) composition No. 5, sintering temperature 1400°C .

TABLE 3. Influence of the Sintering Temperature on the Pore Diameter

No. of specimen	Sintering temperature, °C	Porosity, %	Pore diameter, μm	
			maximum	average
1	1250	46	1.5	1.3
	1300	43	1.8	1.1
5	1350	49	3.4	2.6
	1400	47	3.7	3.0
14	1350	52	3.7	2.2
9	1400	57	5.6	4.0
2	1200	36	0.66	0.64
6	1250	37	2.6	1.8
15	1250	40	2.7	1.8
10	1275	40	4.0	2.5
3	1300	46	5.6	4.5
	1400	46	5.6	4.2
7	1350	51	7.4	6.2
11	1600	46	9.7	8.6
4	1250	39	4.9	2.8
8	1300	42	5.6	4.7
	1350	44	7.4	6.0
12	1400	43	7.4	5.3
	1275	38	0.36>	
16	1300	61	7.4	6.5
	1400	54	7.7	6.4
	1450	50	7.0	4.9
17	1300	66	12	9.3
	1400	59	11	8.9
	1450	56	12	9.7
18	1300	66	12	10
	1400	60	12	10
	1450	56	12	9.3
19	1250	50	9.3	7.9
	1275	45	8.2	6.5
	1300	38	8.9	6.4
20	1300	60	97	81
	1400	56	99	83
	1450	58	100	89

Besides the sintering temperature, a large influence on the porosity is exerted by activators of sintering contributing to the process of compaction. At the same sintering temperature, the specimens with MnTiO₄ have a lower porosity than the compositions doped with four-component glass. The addition of Al(OH)₃ does not exert a substantial influence on the process of sintering. The introduction of a porogen leads to an increase in the specimens' porosity, all other things being equal.

As is clear from Fig. 1, the compressive strength of the specimens mainly depends on their porosity and the sintering activator. The size and nature of the starting powders do not exert a substantial influence on this dependence. For the same porosity, the specimens with additions of four-component glass exhibited a larger strength than the specimens with MnTiO₄.

Table 3 gives data on the influence of the sintering temperature on the pore size in the specimens under study. As the sintering temperature increases, the porosity of the specimens decreases, whereas the pore size changes only slightly.

The introduction of a porogen contributes to the increase in the pore size. The specimens with additions of MnTiO_4 have a lower permeability than the specimens with additions of four-component glass, all other things being equal.

For the specimens under study, the values of the maximum and average pore size are fairly close. The pores are uniformly distributed over the structure, which is confirmed by the results of studying the microstructure with the scanning microscope (Fig. 2) and in the process of measurement of the maximum and average pore size by the bubble method. The microscopic measurements of the average pore size have shown a substantially larger (1.5–2 times) size than that measured by the bubble method.

Conclusions. Thus, based on the investigations carried out, we have obtained specimens of ceramic porous substrates, suitable for manufacture of membrane filters, in the porosity interval 30–60% and the pore interval 0.4–100 μm .

NOTATION

D_{av} , average particle size, μm ; Π , porosity, %; σ_c , compressive strength, MPa. Subscripts: av, average; c, compression.

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