This paper proposes an economical thermal cycle of the production of ceramic articles from submicronic powders of aluminum oxide, titanium oxide, and manganese oxide. The implementation of a given cycle involves the introduction of a special aluminophosphate bond into the charge in order to reduce the temperature of firing. The optimal composition of the material for a foam-ceramic filter with the highest physical and mechanical properties has been determined; the optimal method for preparing the original charge and the baking mode have been selected.

According to the results of tests under industrial conditions, the manufactured alumina filters became a decent alternative to known analogs used in aluminum metallurgy for the purification of liquid metal. The application and rational dosage of titanium dioxides, manganese, and aluminum aluminophosphate in porous ceramic compositions on an alumina base have made it possible to significantly reduce the time and, consequently, improve the productivity, of firing. The results obtained were evaluated by the level of maximum temperature in the cycle of heat treatment according to known technologies. Compared to those technologies, the developed technology ensures the growth of firing productivity when implementing the proposed solution by about 220 %.

It was found that the high true density of ceramic powder requires large dispersion as the relatively large powder particles are significantly worse retained in foam films and settle.

At medium (intermediate) temperatures, a large weight loss occurs at a heating rate of 10 °C/h. In this case, the decomposition progress changes in proportion to the heating speed. Changing the heating speed with temperature is the most effective technique for deparaffinization in the air. The heating time from the ambient temperature to 200 °C significantly decreases. At a certain temperature, prior to the thermal decomposition, the bond would transfer from a strongly viscous state to a liquid state

Keywords: silicon carbide, ceramic filter, permeability coefficient, aluminum oxide, polymer, porous structure

EXAMINATION OF PATTERNS IN OBTAINING POROUS STRUCTURES FROM SUBMICRON ALUMINUM OXIDE POWDER AND ITS MIXTURES

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1. Introduction

In metallurgy, ceramic filters are a tool for refining refractory metals and alloys. Advanced structures that employ filtration subsystems to participate in the life cycle of a resulting integrated article (products, manufacturing systems, etc.) from the early stages of its formation have always attracted interest [1]. The technical and economic interest of the consumer in such structures is confirmed by laboratory tests, pilot factory operations, and the practice of relevant studies. Equipping technical systems with the subsystems that filter working environments significantly contributes to their more efficient functional implementation in many cases.

Over the past decades, alumina ceramics have been increasingly utilized in the diesel engine industry related to the matrix base of combined exhaust gas filters [2]. There is also great interest from the metallurgy of aluminum in the technically and economically competitive tool for refining a liquid product, currently represented by corundum filters.

In line with Holland's early patent, any oxides can be used as ceramic components in the starting mixture. Characteristic examples are the oxides of zirconium, silicon, aluminum, magnesium, titanium, reported in works [4–6]. Preliminary choice of the composition and quantity of additives was considered on the basis of an analysis of world best practices. Underlying it was the consideration of forecasting the achievement of possibly better energy-saving technologies, primarily with a lower level of firing temperature than in the conventional process of obtaining alumina ceramics. The added oxides of TiO_2, SiO_2, MnO_2 (up to 5 % of total weight) were investigated in experimental research. These additives are recommended to be introduced into the charge to reduce the baking temperature of corundum ceramics. The SiO_2 additive is used for baking to form a liquid phase; the TiO_2 and MnO_2 additives intensified the solid-phase baking of corundum [7, 8]. This necessitates devising a new technology that would make it possible to obtain porous permeable materials, in particular foamy filters. At the same time, it should ensure the use of special binding materials. This would make it possible to execute the baking process at lower temperatures while ensuring the high mechanical strength of filters and the required permeability.

2. Literature review and problem statement

Globally, the issue under consideration is resolved by different approaches. Papers [9, 10] proposes a solution according to which a decrease in the firing temperature of a porous alumina structure is achieved mainly due to the interaction between coarse alumina particles and ultra-fine silicon oxide particles. This process was considered as one of the main analogs for the technology of alumina filtering ceramics, based on the use of additives whose presence is temporary, that is, to a certain stage in the formation of the resulting ceramic article.

Study [11] considers mullite-aluminum filters, characterized by low strength. Although they are effective enough for hot gases, they are completely unsuitable for molten liquids because the pressure of a molten metal flow is quite high, the temperature reaches 1,300–1,400 °C. Naturally, at such high temperatures and pressures of molten metal, their service life is very limited.

In work [12], polystyrene is used as a binder for the formation of a foamy filter. It has a long enough burnout cycle and is characterized by a caustic smell when burned out, requiring additional equipment to protect the environment.

Paper [13] reports the scientific aspects of making foamy filters using corundum and silicon carbide. Even though the authors use powders of submicron sizes, the most optimal baking temperature, which provides the required bending strength, reaches 1,700 °C. This requires the use of special high-temperature furnaces that make the process highly costly. In addition, for samples of large sizes, such high temperatures form an additional temperature gradient, which increases the heterogeneity of mechanical properties, in particular the cross-section strength. The spread of the size of the binding pores is much different from each other.

In work [14], to reduce the baking temperature, the authors use powders of aluminum oxide, clad with different metals, which makes it possible to slightly reduce the temperature of baking. However, the application of coatings onto ceramic powders is a rather costly process; although it is used for powders of different fractions, it, nevertheless, does not provide for the high mechanical strength of filters.

An important condition for the effective operation of ceramic products is that they are defect-free, both as a result of the implementation of particular manufacturing technology and after repeated use by the consumer. The issues of multicyclic operation of filters in the predefined throughput range and filtration quality, as well as their recovery, are relevant given the various applications of filters with a porous permeability of ceramics [15–18]. From this point of view, the heat resistance of filters is one of the principal characteristics that ultimately determine the economic efficiency of a porous ceramic technology.

The above limitations in the considered works indicate that it is necessary to find, in the manufacture of foamy ceramic filters, an effective intermediate link, which could maintain the filter when baking it at relatively high temperatures, an order of 800–900 °C. In addition, it must have relatively low volatility and possess the capacity to ensure a decrease in the baking temperature while maintaining the required mechanical properties and the predefined permeability [19].

Thus, it is a relevant issue to establish the optimal composition for a foam ceramic filter based on aluminum oxide, which would demonstrate the highest physical and mechanical properties, and to determine the most optimal method for preparing the starting charge, as well as a baking mode. Also relevant is to devise a technology and to define the composition of a ceramic material that could become an alternative to widely used analogs [20–23], which are used in aluminum metallurgy for cleaning liquid metal. The rational dosage of titanium dioxide, manganese, and aluminum aluminophosphate in porous ceramic compositions based on alumina could reduce the time and increase the productivity of firing in a heat processing cycle.

3. The aim and objectives of the study

The aim of this study is to identify patterns in obtaining porous structures from submicron powders of aluminum oxide with activating additives, which would enable the development of a filter forming technology using foamed polymeric materials and organic binders.

To accomplish the aim, the following tasks have been set:
– to determine special features in the technology of obtaining ceramic porous structures using granulated water-soluble salts and polymeric materials;
– to select the optimal composition and baking modes of ceramic filters.

4. The study methods and materials

This work has explored techniques of obtaining porous structures by using a method of granulated water-soluble salts involving special polymeric materials. To implement the method of granulated water-soluble salts, we have selected refractory enough ($T_{pl}>900$ °C) water-soluble non-toxic salts whose parameters are given in Table 1.

Table 1

Properties of salts used to obtain porous ceramics

Salt	T_{pl}, °C	Solubility, g/100 ml
$K_2B_2O_4$	950	71
K_2SO_4	1,065	24.1
K_2PO_4	1,240	178.5
K_2CrO_4	960	79.2
$MgSO_4$	1,127	50
$NaSiO_3$	1,089	92.3

When choosing substances used in this method, we considered that at temperatures of 900...1,200 °C there is noticeable baking of the aluminum oxide with additives, which is confirmed by the shrinkage of samples [24, 25]. When melting salts in the consolidated powdered environment, there is the formation of bridges (necks), which, when dissolving salt, transform into channels connecting pores. Good solubility of salt in water is also needed, especially when boiling.

The technological factors that make it possible to change the porosity parameters of the obtained materials include the following:

– the starting granulometric salt composition;

– the amount of salt in a mixture;

– a melting point of salt.

The manufacturing sequence of obtaining porous ceramics using water-soluble salts includes the following stages:

– mixing Al_2O_3 with salt;

– vibration pressing of the mixture under a load of 1 kg/cm^2;

– baking in the air at the salt temperature $T<T_{pl}$;

– multiple rinsing in water at boiling at 100–120 °C;

– final baking at a temperature of 1,400 °C.

The electric furnace Nabertherm LH148PN was used to bake filters.

Differential thermal analysis (DTA), differentiated scanning calorimetry (DSC), and thermal gravimetric analysis (TGA) were used to collect information on the speed, extent, and products of decomposition.

5. Special features of the technology for obtaining ceramic porous structures involving the use of granulated water-soluble salts and polymeric materials

Fig. 1 shows the porous ceramics obtained by using water-soluble salts.

×50
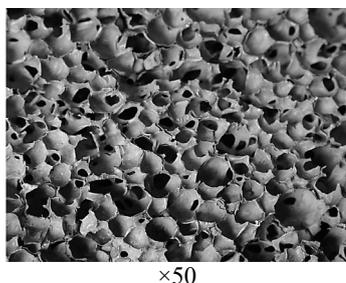
Fig. 1. A porous filter obtained by using water-soluble salts baked at T=1,400 °C in Nabertherm LH148PN2 furnace, aging duration – 1 hour

Polyurethane foam, brand PPU-10 PPI 8–13, was used to obtain a foamy structure with binding pores. These materials (foam rubber) with different parameters of porosity and density are industrially produced at a relatively low cost.

The characteristics of porous alumina ceramics, obtained by using refractory water-soluble salts, are given in Table 2.

Table 2

Characteristics of the porous alumina ceramics obtained by using refractory water-soluble salts

Sample group	Density γ_t, g/cm^3	Porosity P_t, %	Pore mean size R, mm	Flexural strength σ_f, MPa	Thermal stability in the air N_t=1,000 °C
1	0.3	92.4	3.5...3.8	3.5	14
2	0.34	91.4	3...3.3	4.2	14
3	0.38	90.4	3...3.2	4.8	16

The manufacturing process of obtaining porous filter ceramics includes the following operations:

– obtaining ceramic slip with a 40 % humidity of the following composition: Al_2O_3+$AlPO_4$, 10 % by weight+TiO_2, 2 % by weight+MnO_2, 2 % by weight;

– the repeated impregnation of the polymer with ceramic slip;

– the removal of excess slip from a polymeric sponge by rolling;

– control of the impregnation by weighing (if necessary, repeat the preceding operation);

– drying and subsequent baking in the air furnace at a temperature of up to 1,350 °C.

The slip was prepared by the mechanical mixing of the required dry ingredients with the subsequent addition of water to obtain the predefined rheological characteristics and humidity. The ceramic mixture was prepared from fine-dispersed powders, % by weight: aluminophosphate ($AlPO_4$), 10...20; aluminum oxide (Al_2O_3), 86...72; 2...4 (TiO_2); 2...4 (MnO_2). We next prepared a suspension in a 25...35 % aqueous solution of sodium lignosulfonate in the following ratio: a ceramic mixture, 70...90 % by weight, and sodium lignosulfonate, 10...30 % by weight. The agitation lasted over 60 minutes until a homogeneous mixture with a viscosity of 10...15 Pa·s was obtained.

The polymer was impregnated by immersing it in the slip and pressing to remove excess air. The operation was repeated 2...8 times depending on the types of the starting polymer and slip. The subsequent rolling of the polymer through the rolls eliminated the excess slip. The weight analysis of samples is necessary to control the thickness of a slip film, adhesively bound to the surface of the pore in the polymer. An increase in the mass of the polymer before drying and baking is 0.3...0.6 g/cm^3 depending on the polymer brand, the type and humidity of the slip. A sample prepared for heat treatment is placed in the furnace on a layer of the dry ceramic mixture of corundum powders and impurity oxides to ensure the most unhindered shrinkage at firing.

Fig. 2 shows the foamy structures with different porosity.

Placing samples on a rigid base leads to their adhesive sticking due to the outflow of part of the slip, disrupting the uniformity of the structure, and partial cracking. All this significantly affects the permeability and strength of an article. We fired the samples under specially selected modes:

in the first case (curve 1 in Fig. 3), heating proceeded more slowly than in the second case (curve 2 in Fig. 3). Close to optimal is the treatment under mode 2 (Fig. 3): from 0 to 150 °C – heating at a speed of 60 °C/h; aging duration is 2 hours; heating to 350 °C, at a speed of 30 °C/h; heating from 350 °C to 900 °C at a speed of 180 °C/h; heating from 900 °C to 1,350 °C at a speed of 360 °C/h, the aging duration is 1 hour – cooling with the furnace.

The rate of the increase is limited by the factor of the possible cracking of a filter during the baking process; the choice of the optimal mode is important for reducing the manufacturing cycle of making foamy filter units.

Fig. 3. Modes *1* and *2* of temperature increase (the shaded area is the optimum temperature increase rate)

Fig. 2. Foamy structures with different porosity, obtained in the furnace Nabertherm LH148PN2 (×50):
a − a porosity of 50 % at a temperature of 1,350 °C;
b − a porosity of 30 % at a temperature of 1,450 °C

The resulting samples were examined for gas permeability and mechanical strength. Gas permeability tests were conducted in accordance with GOST 11573–98 (ISO 8841-91). Bending tests were carried out in accordance with GOST 473.8–81, for compression – according to GOST 473.6–81, for thermal resistance – according to GOST 473.5–81; the average temperature drop (air-water) was 200...300 °C. Our tests have shown that the highest characteristics are demonstrated by the following composition: $AlPO_4$, 10 % by weight; TiO_2, 2 % by weight; MnO_2, 2 % by weight; Al_2O_3, 84 % by weight. A given composition possesses the following properties: permeability, $\Delta P = 5,880$ Pa; compression strength limit, $\sigma_s = 40$ MPa; bending strength limit, $\sigma_v = 40...50$ MPa; heat resistance, 1 $\sigma_s = 40$ 10 cycles of heating and cooling in the air.

6. Determining the optimal composition and baking modes of ceramic filters

Table 3 gives the comparative characteristics of filters obtained by using different methods: from porous alumina ceramics, obtained using refractory water-soluble salts (sample groups 1.1...1.3) and burnout impurities (sample groups 2.1...2.3). Overall dimensions of alumina filters with a throughput capacity of 2 m^3/h are 380×380×450 mm^3.

The DTA curve of the mixture based on aluminum oxide has several peaks that correspond to the registered changes. The mixture underwent a series of transformations, including a moisture loss, softening of the bond, and the decomposition of components (Fig. 4).

Our study has shown that the critical temperature interval for the deparaffinization of mixtures is between 350 °C and 420 °C. Changes within this temperature interval depend on the ceramic powder-filler. The nature of bond metal-oxygen in ceramics is the main factor determining the extent of interaction between the ceramics and polymeric bond during thermal decomposition. For example, in the aluminum oxide Al_2O_3, where the metal-oxygen bond is more ionic than covalent, there is a surface reaction. The mass spectrometry analysis determined the evaporation rate of volatile products. In this case, the DWT furnace was used. The heating mode was as follows: up to 350 °C, at a speed of 100 °C per hour; up to 800 °C, at a speed of 400 °C per hour; aging duration at a given temperature is 30 minutes; increasing the temperature from 800 °C to 1,400 °C over 2 hours.

Table 4 gives the volatile components of several different mixtures that were registered after heating over 30 minutes to 150, 300, and 600 °C. For tests, we used a mullite tube and linings made of zirconium oxide; the submicron powders of aluminum oxide or silicon carbide were used as reference materials.

Table 3

The physical and geometric characteristics of filter sample groups

Sample group	Porosity P_t, %	Pore mean size D, mm	$K_p=T/D$	Mean size of interpore distances T, mm	Recycling factor F, mm^{-1}	Constant at a regular porous structure a, mm	$K_a=D/a$	Pore quantity per area unit N_s, 1/m^2·10^{-3}	$K_y=D^2 \cdot N_s$
1.1	2.4	3.5...3.8	0.106	0.37...0.4	2.7	3.9...4.2	0.9	56.6...65.5	0.81
1.2	1.4	3...3.3	0.119	0.36...0.39	2.8	3.4...3.7	0.89	72.9...86.4	0.79
1.3	0.4	3...3.2	0.132	0.4...0.42	2.5	3.4...3.6	0.88	76.7...86.4	0.78
2.1	4.4	0.9...1.1	0.079	0.07...0.09	14.3	1.0...1.2	0.92	694...1,000	0.83
2.2	2.7	2.8...3.1	0.102	0.29...0.32	3.4	3.1...3.4	0.91	86.4...104	0.82
2.3	2.7	3.8...4	0.102	0.39...0.41	2.6	4.2...4.4	0.9	51.5...56.6	0.82
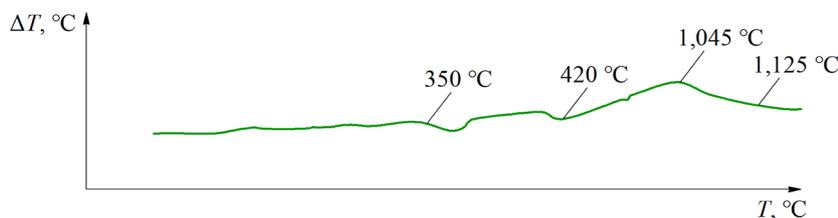
Fig. 4. DTA curve when the amount of paraffin and bond is 12 % by weight

Table 4

Volatile products of oxidation at different temperatures of firing in the air, % by weight

Oxidation product	Atmo-sphere without samples	Composition			
150 °C		Al_2O_3	Mixture 1	Mixture 2	Mixture 3
B_2	20.9	21	20.8	20.9	20.9
N_2	78	77.9	78	78.1	78.0
Ar	0.9	0.96	0.94	0.95	0.95
CO_2	0.1	0.2	0.1	0.1	0.1
H_2O	<0.l	0.1	0.1	<0.1	<0.1
150 °C		Si_3N_4	Mixture 4	Mixture 5	Mixture 6
B_2	–	20.8	21	20.7	20.8
N_2	–	78	77.9	78.3	78.1
Ar	–	0.95	0.96	0.94	0.94
CO_2	–	0.1	0.1	0.1	0.1
H_2O	–	0.1	–	<0.l	<0.1
300 °C		Al_2O_3	Mixture 1	Mixture 2	Mixture 33
B_2	20.9	21.2	9.6	14.6	11.8
N_2	77.9	77.6	82.7	82.4	82.2
Ar	0.96	0.98	1.0	0.99	0.99
CO_2	0.2	0.2	2.8	1.7	2.4
H_2O	<0.1	<0.1	0.2	<0.1	<0.1
CO	<0.l	<0.1	3.2	0.1	2.3
Methane	–	–	0.02	–	0.03
Ethan	–	–	0.13	0.13	–
Ethylene	–	–	–	–	0.04
Propylene	–	–	0.03	0.03	0.04
Methanol, ethanol	–	–	0.07	0.03	0.06
Various hydrocar-bons	–	–	0.2	–	0.1
Total quantity of organic substances	–	–	0.45	0.19	0.27
600 °C		Si_3N_4	Mixture 4	Mixture 5	Mixture 6
B_2	20.8	8.6	11.3	7.9	
N_2	78.0	84.1	82.8	84.1	
Ar	0.94	1.01	1	1	
CO_2	0.1	2.7	2.1	3	
H_2O	0.1	0.2	0.1	0.2	
CO	–	2.9	2.3	3.1	
Methane	–	<0.1	–	0.01	
Ethan	–	–	0.1	0.13	
Ethylene	–	0.06	–	0.01	
Propylene	–	0.06	0.04	0.08	
Methanol, ethanol	–	0.09	0.08	0.2	
Various hydrocarbons	–	0.2	0.1	0.2	
Total quantity of organic substances	–	0.44	0.32	0.63	

Mixtures in Table 4 differ in the volumetric content of a paraffin binding material. Thus, mixture 1 contains it in the amount of 15 % by weight, mixture 2 – in the amount of 10 % by weight, mixture 3 – in the amount of 5 % by weight; the basic material is Al_2O_3. In mixtures 4, 5, and 6, Si_3N_4 was the basic material.

Table 4 shows that at 150 °C the composition of the evaporated gas is very close to that of the air. It is likely that when these mixtures are heated to 1,500 °C there is slight oxidation of the bond's components.

Starting from 300 °C, all mixtures are oxidized. The main decomposition products CO_2 and CO form both by directly oxidizing the bond's components and by oxidizing the products of their pyrolysis. At 600 °C, the oxidation almost ends. Important is the concept of the relative degree of the mixture decomposition. That implies subtracting the volume of gas released by the reference samples of aluminum oxide or silicon nitride from the total volume of gas produced by the corresponding mixtures and comparing this difference to the total amount of organic matter in the starting samples.

The emergence of light hydrocarbons is the result of both pyrolytic decomposition of large polymer molecules and the transfer of hydrogen by radicals. This explains the formation of methane (CH_4), ethane (C_2H_6), propane (C_3H_8), drying of ethylene compounds (C_2H_4), propylene (C_3H_6), and hydrogen. Benzene and toluene can be synthesized by ring formation and dehydrating hexane and heptane aliphatic carbohydrates, which contain 6 and 7 carbon atoms, respectively. Organic acids (propionic and acetic) can be obtained by the incomplete oxidation of small hydrocarbon molecules or by chopping large molecules during oxidation. However, if the oxygen supply is quite large, pyrolytic fractions can transform into CO_2 and water. Results of the mass-spectrometry analysis of silicon nitride mixtures at firing in the atmosphere of nitrogen at 600 °C are given in Table 5.

Table 5

The difference in the decomposition degree of mixtures treated at 600 °C in the air

Mixture	Gas volume (cm^3)	paraffin, %	water, %
Al_2O_3/1	29	9.1	57.1
Al_2O_3/2	12	5.9	71
Al_2O_3/3	12	6.1	74
SiC/4	33	9.8	54.4
SiC/5	17	8.1	65
SiC/6	28	7.8	61

Table 5 shows that the pyrolytic fractions of various mixtures of silicon carbide of different compositions produce almost the same amount of total gas. The application of DTA, TGA, DSC, and mass-spectrometry analysis helped determine some output control lines in the decomposition reaction, the maximum temperature of deparaffinization, as well as the rate and products of evaporation. The above procedures typically employed a small sample of the composition of the examined mixture. Therefore, the results of those studies require adjustment when investigating actual compressed articles. Experiments with real products are necessary to determine the heating rate based on the data on enthalpies obtained by using DTA, the temperature profiles of TGA, and the mass-spectrometry data on decomposition products. The process of removing the bond from actual products was investigated at heating rates of 5 °C/h and 10 °C/h. At a rate of 10 °C/h in the interval from 300 °C to 400 °C, the weight of the samples decreases intensively enough; at temperatures about 500 °C, the process slows down. Data on the aluminum oxide mixture with a butyl stearate plasticizer show that relatively rapid weight loss occurs at 10 °C/h. At a higher heating rate, a large amount of volatile substances is formed in a short period of time. During the period over which the greatest weight loss occurs, the local partial oxygen pressure is significantly reduced. This is due to the lack of time to evaporate volatile substances and for oxygen from the surrounding space to penetrate the sample. Changing the partial pressure around the sample changes the decomposition behavior. If decomposition did not depend on the heating rate, the curve of total weight loss would shift towards a higher temperature interval while increasing the heating rate. At medium (intermediate) temperatures, a large weight loss occurs at a heating rate of 10 °C/h. This is possible if the decomposition course changes in proportion to the heating rate. These results demonstrate that changing the heating rate with temperature is the most effective means of deparaffinization in the air. The low rate of deparaffinization, the TGA and mass spectrometry results show that there is a relatively small thermal decomposition below 200 °C. That is, it is possible to significantly reduce the heating time from the ambient temperature to 200 °C. At a certain temperature, prior to the thermal decomposition, the bond would transfer from a strongly viscous state to a liquid state.

If the heating rate is very high (approximately 25 °C/h), then, near the transition temperature, there would occur such harmful effects as swelling and deformation (distortion). The tests at heating rates of 25, 50, and 100 °C/h, from ambient temperature to 200 °C, established that there is a heating rate limit (25...50 °C/h) at which there are no harmful effects at the onset of deparaffinization cycle. In a temperature interval of 200...500 °C, the safe rates are 5...10 °C/h depending on the size and shape of components. A weight loss by the mixture containing aluminum oxide at a heating rate of 5 °C/h is moderate in the interval 200...375 °C and becomes quite large when heated to 500 °C. Silicon carbide performs similarly: a weight loss becomes large at a temperature above 400 °C. For both mixtures heated from 200 °C to the maximum temperature at a rate of 10 °C/h, there is a gradual weight loss. Hence, it follows that the cycle of deparaffinization can be reduced from 100 hours to 30...60 hours. This can be achieved by active heating at a rate of 25 to 50 °C/h, followed by heating to a threshold temperature of 500 °C at a rate of 5 to 10 °C/h. When designing the cycle of deparaffinization, it is necessary to take into consideration both the shape and size of components. In large parts, the bond disintegrates slower than in small ones due to that the volatile substances evaporate worse from the inside of large components while oxygen penetrates it worse. Local partial oxygen pressure in a large sample during decomposition is smaller than that in a small one.

As shown in Fig. 5, the rate of aerial diffusion increases if the articles become porous. Experimental data revealed that the mean pore diameter D of those appeared after the release of the bond is proportional to the mean diameter of ceramic particles R: $D=(0.3...0.4) \cdot R$ for aluminum oxide; $D=(0.2...0.3) \cdot R$ for silicon carbide. The numerical value of constants depends on the ratio of ceramic powder volume to the volume of the bond and the sized-based distribution of particles of ceramic powder.

Fig. 6 shows the weight loss curves by aluminum oxide and silicon carbide.
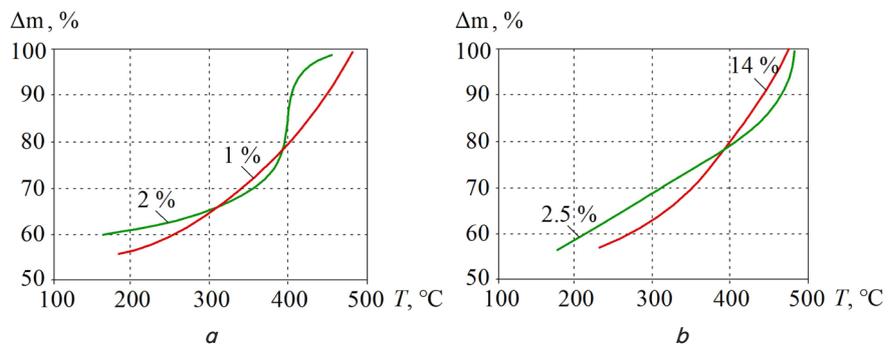
Fig. 5. Loss of mass by the bond as a function of temperature for different compositions of silicon carbide mixtures with different concentrations of the bond's components at two heating rates: a — paraffin — 1 %, sodium lignosulfonate — 2 %; b — paraffin — 14 %, sodium lignosulfonate — 2.5 %
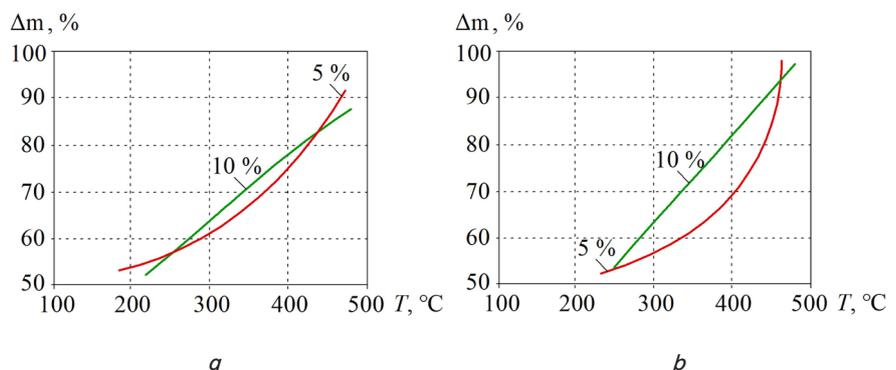
Fig. 6. A weight loss by the bond as a function of temperature for two different mixtures at two heating rates: a — aluminum oxide with a three-component bond and butyl stearate; b — silicon carbide with a four-component bond; the heating rate to 200 °C is 25 °C/h

Fig. 7 shows the process of removing the bond; it demonstrates that the extent of the bond removal depends on oxygen diffusion.

Fig. 8 shows that the heating rate of components with a large surface to volume ratio may be higher than that for components with a small surface to volume ratio. It is important that there is no internal cracking in this case.
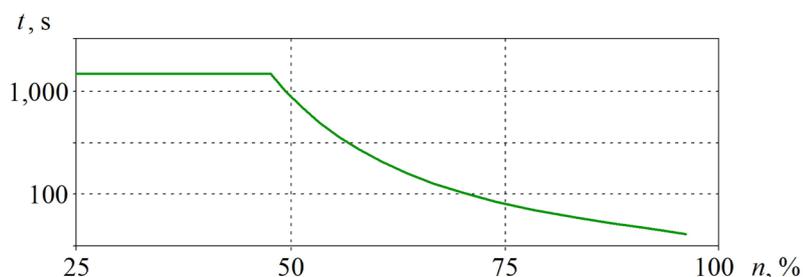
Fig. 7. Air diffusion time as a function of the extent of bond removal
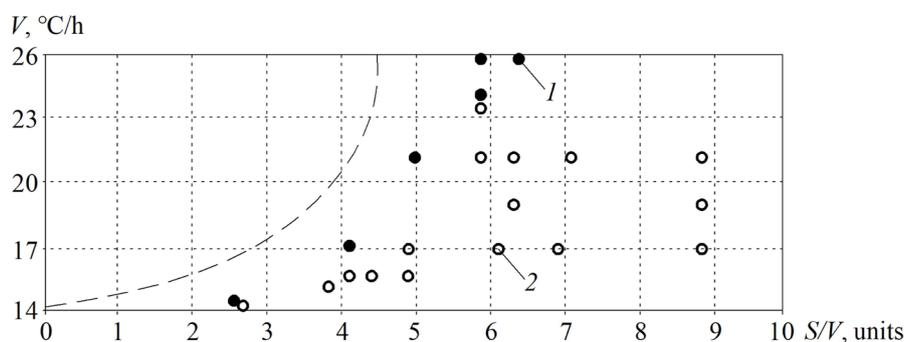
Fig. 8. Evolution of defects as a function of the surface to volume ratio depending on heating rate: *1* — with defects; *2* — defect-free

Cracks in parts with a small surface to volume ratio emerge as a result of high gas pressure. To improve the structure formation in polymeric bonds, a variety of additives is used.

Most electrolytes, similar to substances such as sucrose and glycerin, are very similar to water, thereby reducing the temperature of structure formation as they dehydrate the polymer.

Other compounds, such as ethyl alcohol and propylene glycol, increase the temperature of structure formation. Any substance that reduces the temperature of structure formation can also enhance the gel density. Methylcellulose can form complexes with hydroxybenzene compounds and can interact with surface-active mycelium, increasing their viscosity and gel strength. The cellulose-derived bonds of agar and agarose (derived from agar obtained by additional purification) belong to the chemical family of carbohydrates. Cellulose consists of carbohydrate glucose. Agar is typically obtained from red seaweed by repeated extraction and purification. It consists of a chain of two forms of carbohydrate galactose. Its polymer chains form bundles of swirling spirals.

Methylcellulose is soluble in cold water and transforms into a gel in hot water. Structure formation is due to the hydrophobic processes of self-association. Agar and agarose dissolve in hot water and turn into a gel when cooled. In agar gels, connecting double spiral chains forms a cell spatial structure. Hydroxyl groups along polymer chains interact strongly with water molecules through a hydrogen bond that keeps water molecules inside a gel structure's cells. Conditions of pressing water suspensions of ceramic powder, which contains, as a bond, a cellulose polymer such as agar or agarose, depend both on the rheology of the polymer and the temperature dependence of structure formation. When agar dissolves, the aqueous solution has a small viscosity when cooled until there is a moment of transformation into a gel. At this temperature, the solution turns into a stiff mass. The characteristic strength of gels derived from a variety of substances varies greatly. Bonds from agar are well suited for the injecting pressing of ceramics as they combine two main properties: suitable rheology and high gel strength.

7. Discussion of results of studying the devised alternative energy-saving technology of alumina filter production

Based on the results of our industrial tests of the alumina filter (Fig. 1), fabricated according to the above technology (Table 2), we made an alternative to known analogs used in aluminum metallurgy for the purification of liquid metal. Due to the use and rational dosage of the dioxides of titanium, manganese, and aluminum aluminophosphate in porous ceramic compositions based on alumina (Fig. 2), we managed to significantly reduce the time and, consequently, improve the productivity of firing (Fig. 3). The results obtained (Table 3) were estimated on the basis of the level of maximum temperature in a heat treatment cycle for known technologies with chromium oxide additive and the conventional technology of corundum ceramics without metal oxide additives. In comparison with these technologies, the energy-saving technology that we devised ensures a 220 % increase in productivity.

Our study has shown that the critical temperature interval for the deparaffinization of mixtures lies between 350 °C and 420 °C (Fig. 4). Changes within this temperature interval depend on a ceramic powder-filler.

The rate of air diffusion increases if articles become porous (Fig. 5). The experimental data revealed that the mean diameter of pores that appeared after the release of the bond is proportional to the mean diameter of ceramic particles.

The heating rate of components with a large surface to volume ratio may be higher than that for parts with a small surface to volume ratio (Fig. 8). It is important that there is no internal cracking in this case.

The limitation of this paper is that the full thermogravimetric studies were not carried out at baking involving various additives. In addition, not all samples were tested for the mechanical strength of filters; no comparison of mechanical properties to known world manufacturers of such filters was performed.

In further studies, it would be advisable to conduct operational experiments of the designed filters and compare their characteristics.

8. Conclusions

1. It has been established that the high true density of ceramic powder requires large dispersity as the larger particles of powder are worse kept in foam films and settle. Starting from 300 °C, all mixtures are oxidized. The basic products of CO_2 and CO decomposition form both through the direct oxidizing of the bond's components and by oxidizing the products of their pyrolysis. At 600 °C, the oxidation almost ends.

2. Our tests on obtaining porous structures have demonstrated that the highest characteristics were demonstrated by the following composition: $AlPO_4$, 10 % by weight; TiO_2, 2 % by weight; MnO_2, 2 % by weight; Al_2O_3, 84 % by weight. A given composition possesses the following properties: permeability, ΔP=5,880 Pa; compression strength limit, σ_s=40 MPa; bending strength limit, σ_v=40...50 MPa; heat resistance, 110 cycles of heating and cooling in the air. The samples were fired according to a specially selected mode. We have proposed the optimal composition for a foam ceramic filter, obtained from a ceramic mixture composed of finely dispersed powders, % by weight: aluminophosphate ($AlPO_4$), 10...20; aluminum oxide (Al_2O_3), 86...72; 2...4 (TiO_2); 2...4 (MnO_2). The mixture was prepared in a 25...35 % aqueous solution of sodium lignosulfonate in the following ratio: ceramic mixture, 70...90 % by weight; sodium lignosulfonate, 10... 30 % by weight. Agitation was performed over 60 minutes before obtaining a homogeneous suspension with a viscosity of 10...15 Pa·s. The polymer was impregnated by immersing it in slip and pressing to remove excess air. The operation was repeated 2...8 times depending on the types of the starting polymer and slip. The subsequent rolling of the polymer through the rolls removed the excess slip. Weight analysis of samples is necessary to control the thickness of the slip film, adhesively bound to the surface of the pore in the polymer. The increase in the polymer before drying and baking is 0.3...0.6 g/cm³ depending on the polymer brand, the slip type and humidity. Close to optimal is treatment under the following mode: from 0 to 150 °C, heating at a rate of 60 °C/h, the aging duration is 2 hours; heating to 350 °C at a rate of 30 °C/h. Subsequent heating is carried out from 350 °C to 900 °C at a rate of 180 °C/h; heating from 900 °C to 1,350 °C, at a rate of 360 °C/h, the aging duration is 1 hour – cooling with the furnace. The low rate of deparaffinization, the TGA and mass-spectrometry results show that there is a relatively small thermal decomposition below 200 °C. In other words, it is possible to significantly reduce the heating time from the ambient temperature to 200 °C. At a certain temperature, prior to the thermal decomposition, the bond would move from a strongly viscous state to a liquid one. Our study has shown that the critical temperature interval for the deparaffinization of mixtures is between 350 °C and 420 °C. Changes within this temperature interval depend on a ceramic powder-filler. The nature of metal-oxygen relation in ceramics is the main factor determining the extent of interaction between the ceramics and polymeric bond during thermal decomposition. It has been established that the heating rate of components with a large surface to volume ratio can be higher than that for parts with a small surface to volume ratio. It is important that there is no internal cracking in this case.

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