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PREPARATION OF RADIOTRANSPARENT CERAMIC MATERIALS BASED ON COMPOSITIONS OF THE BaO–ZnO–Al_2O_3–SiO_2 SYSTEM

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INTRODUCTION

Radiotransparent materials (RTM) are widely used in the antenna fairings of aircraft and missiles to protect antenna systems for various purposes from external factors, to equip hidden radio surveillance facilities, as well as in accelerators and electronic devices to ensure the transmission of electromagnetic energy between instrument compartments. It is known that radiotransparent materials (RTM) have low dielectric losses ($\varepsilon = 1 \div 10$; $tg\delta \leq 10^{-2}$) in the operating temperature range, which provides minimal electromagnetic field distortion in a given operating frequency range[1].

The unique capabilities of new materials created for the production of aircraft are the key to the rapid development of aircraft and rocketry. Thus, the controllability and reliability of aircraft (AC) significantly depend on the properties of the protective structures of external electronic equipment. During their maneuvering, high mechanical and thermal stresses arise in the structure of the antenna fairing that protects the antenna equipment. Increasing the speed and maneuverability of the AC, as well as increasing the target engagement range require increased protection efficiency of external antenna equipment and improving the functional characteristics of the fairings[2].

Suitable materials for such purposes must have specified dielectric characteristics in a wide range of operating temperatures, resistance to thermal and aerodynamic loads, erosion resistance to dust flows, snow and rain. Therefore, extremely strict requirements are imposed on the materials from which the fairings are made: the range of operating temperatures from

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– 60°C to + 1 500°C, the duration of the maximum operating temperature of at least 5 minutes, the flexural strength $\sigma_{fl} \geq 150$ MPa, dielectric constant $\varepsilon = 1–10$, tangent of the dielectric loss angle $tg\delta \leq 0{,}01$, TLEC $\leq 5.0 \cdot 10^{-6}$ deg^{-1}, thermal conductivity $tg\delta \leq 3.0$ W/(m°C), the degree of sintering by water absorption W ≤ 1%, and most importantly – transparency in the radio frequency range (reflection coefficient of radio waves ≤ 1%). These requirements for the functional properties of RTM, in particular their radiophysical characteristics exclude the possibility of using for the manufacture of fairings of most structural materials, including metals and fiberglass[3,4].

1. Analysis of literature data and problem statement

The problem of creating radiotransparent materials (RTM), which must possess the above set of properties is relevant, which causes great attention to it by scientists from different countries, including Japan, USA, South Korea, France, Czech Republic, China, Russia, Belarus[5,6,7,8,9,10,11,12].

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A review of modern developments in this direction has shown that today the most promising way to solve this problem is the creation of RTM based on glass-crystalline and ceramic materials. Due to the operating conditions, the advantages of refractory non-metallic RTM are heat resistance, strength and constancy of dielectric characteristics in a wide range of operating temperatures[13].

Among glass-crystalline materials, the most widespread are sitalls of spodumene and cordierite compositions, which, in addition to the desired dielectric characteristics, have high chemical resistance, sufficiently high mechanical strength, low TLEC[14], but the thermal stability of most of them is in the range of 550–600°C[15]. However, the main disadvantage of sitalls as materials for the manufacture of fairings for rocket and space technology is the low rate of high-temperature deformation (1 000°C for spodumene and 1 200°C for cordierite sitalls), which causes restrictions on their operating temperature (respectively up to 900°C and 1 100°C)[16].

Recently, high-temperature glass-crystalline materials based on $SrO–Al_2O_3–TiO_2–SiO_2$ systems, the dominant crystalline phases of which are barium aluminosilicates ($BaAl_2Si_2O_8$) and strontium ($CrAl_2Si_2O_8$) or their solid solutions, have been developed. They have a temperature of the beginning of deformation of 1 350–1 450°C, are characterized by TLEC in the range $(30–55)\cdot10^{-7}$ K^{-1} and relatively high heat resistance (up to 900°C)[17]. Refractory sitalls have also been developed[18], the phase composition of which predominantly contains monoclinic strontium anorthite ($CaAl_2Si_2O_8$) and thialite (Al_2TiO_5), which provides high thermal

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stability (not lower than 1200°C), strength (σ_{fl} = 130 MPa) and thermal stability of mechanical, thermal and dielectric properties in the operating temperature range of 20–1 200°C. However, the main disadvantage of all radiotransparent sitalls is the technological complexity and high energy consumption of production. The technology includes several high-temperature operations, including glassmaking at 1 600–1 650°C, pouring the melt into molds (700°C) and multi-stage heat treatment to ensure crystallization of the target phases (750°C and 1 250°C), which inhibits its widespread use. In addition, obtaining sitalls by powder technology is complicated by the narrow range of dispersion of the original glass powders, which is a necessary condition for obtaining densely sintered material[19].

Currently, there are a large number of developments in the field of ceramic RTM, but most of them do not meet the requirements for heat resistance, resistance to oxidation in the flow of gases containing oxygen, resulting in degradation of these materials and instability of their dielectric characteristics in the operating temperature range[20].

For example, quartz ceramics is characterized by high heat resistance, stability of dielectric characteristics in a wide temperature range, but has low mechanical strength (only σ_{fl} =45–50 MPa), low resistance to dust and rain erosion and insufficient heat protection properties (the upper limit of the operating temperature range does not exceed 1000°C)[21].

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On the other hand, although high-alumina ceramics are characterized by high strength (σ_{fl} = 300 MPa) and resistance to aggressive media, they have low resistance to thermal shock (no higher than 200°C), and their dielectric characteristics change significantly depending on the operating temperature[22]. In addition, such ceramics require high temperatures for sintering (~ 1 700°C)[23].

Radiotransparent ceramics based on nitrides of silicon, boron, aluminum, as well as oxynitride ceramics have stable dielectric characteristics at temperatures up to 2 000°C, high strength and abrasion resistance[24]. But these materials are obtained by complex and energy-intensive technology (sintering temperature above 1 800°C). In addition, most of them are prone to high-temperature oxidation, which causes their destruction and loss of functionality[25].

The authors of[26] established the possibility of obtaining a radiotransparent ceramic of spodumene-cordierite composition with a compressive strength of 165.8–202.6 MPa, a thermal resistance of not less than 1 050°C and satisfactory dielectric characteristics (ε = 3.8; $tg\delta$ = 0.0014 at a frequency of 10^{10} Hz). To obtain a complex of target phases, Li_2O–Al_2O_3–B_2O_3–SiO_2 glass was introduced as a mineralizer, which ensured the crystallization of the β-spodumene and, as a consequence, the reduction of TLEC to the level $(16.6–17.8)\cdot10^{-7}$ deg^{-1}, and also contributed to the formation of α-cordierite and sintering of ceramic materials. However, this technology requires an additional operation of glass melting at a temperature of 1 250°C, which, given the relatively high firing temperature of the products (1 300–1 350°C), significantly increases the energy consumption of production.

The results of own developments and studies of radiotransparent ceramics[27,28,29] indicate the possibility of eliminating heat-resistant materials,

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the main crystalline phases of the stable monoclinic forms $SrAl_2Si_2O_8$[30], $BaAl_2Si_2O_8$[31] and also of their solid solution[32]. Materials obtained at a temperature of 1 300–1 350°C with the main crystalline phases monoclinic $BaAl_2Si_2O_8$ and $CrAl_2Si_2O_8$, as well as their solid solutions, provides a reflection coefficient of radio waves at the level of 0.198–0.263 in the range of operating temperatures up to 1 400°C.

Thus, there is no doubt that the development of new ceramic RTMs with specified dielectric characteristics, thermophysical and physical-mechanical properties will contribute to scientific and technological progress in the fields of radio electronics, electronic and aerospace technology. At the same time, a promising direction is research aimed at reducing the energy consumption of production and ensuring high-temperature stability and reproducibility of functional properties in a wide frequency range.

2. The purpose and objectives of the study

The purpose of the study is to develop prescription-technological parameters for radiotransparent ceramic materials based on $BaO–ZnO–Al_2O_3–SiO_2$ system, as well as to study the influence of mass composition on sintering characteristics, microstructure and phase composition, which determine the main functional properties of the material and ensure reliable operation of fairings and protection of the antenna equipment of aircraft.

Research objectives included:

– substantiatiation of the content of oxide compositions of the $BaO–ZnO–Al_2O_3–SiO_2$ system, the use of which will provide simultaneous synthesis of the target phases (Zn_2SiO_4 and $BaAl_2Si_2O_8$);

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[28] Development of new compositions of ceramic masses in SrO–Al2O3–SiO2 system / G.V. Lisachuk, R.V. Kryvobok, A.V. Zakharov et al. *Functional Materials*. 2017. № 24 (1). P. 162–167.

[29] Influence of complex activators of sintering on creating radiotransparent ceramics in SrO–Al2O3–SiO2 / G. Lisachuk, R. Kryvobok, A. Zakharov et al. *Eastern-European Journal of Enterprise Technologies*. 2017. № 1 (6–85). P. 10–15.

[30] Optimization of the compositions area of radiotransparent ceramic in the $SrO-Al_2O_3-SiO_2$ system / G.V. Lisachuk, R.V. Kryvobok, K.B. Dajneko et al. *Przeglad Elektrotechniczny*. 2017. № 93 (3). P. 79–82; Development of new compositions of ceramic masses in $SrO–Al_2O_3–SiO_2$ system / G.V. Lisachuk, R.V. Kryvobok, A.V. Zakharov et al. *Functional Materials*. 2017. № 24 (1). P. 162–167.

[31] Influence of complex activators of sintering on creating radiotransparent ceramics in $SrO–Al_2O_3–SiO_2$ / G. Lisachuk, R. Kryvobok, A. Zakharov et al. *Eastern-European Journal of Enterprise Technologies*. 2017. № 1 (6–85). P. 10–15.

[32] Ceramic radiotransparent materials on the basis of BaO–Al2O3–SiO2 and SrO–Al2O3–SiO2 systems / G.V. Lisachuk, R.V. Kryvobok, O.Yu. Fedorenko, A.V. Zakharov. *Èpitöanyag – Journal of Silicate Based and Composite Materials*. 2015. № 67 (1). P. 20–23.

– development of a series of ceramic masses to study the influence of different types of aluminum-containing raw materials on the processes of sintering and phase formation of ceramics, its electrophysical and physical-mechanical properties;

– study of the possibility of intensifying the processes of radiotransparent ceramics formation by modifying the masses using small additives;

– determination of structural and phase features of the obtained materials in relation to their composition and properties.

3. Materials for the development of ceramic masses and methods for studying the phase composition and properties of the obtained materials

As the main raw materials for the preparation of celsian-slavsonite ceramics, following materials were used: metallurgical alumina (G-00), micronized alumina (CT3000SDP), aluminum hydroxide (GD-00), chemically pure barium carbonate, quartz sand of the Novoselivske deposit (Kharkiv region). The chemical composition of raw materials is given in table 1.

The developed raw material compositions differed in the type of aluminum-containing component, which allowed determining its effect on the phase composition and properties of ceramics. As an intensifier of sintering and phase formation under conditions of energy-saving firing (temperature limit was 1 200°C) in the composition of the masses of more than 100% on dry matter additives that act as intensifiers of sintering and phase formation, in particular: 2 wt. % Li_2O (samples I_L, II_L, III_L) or 1 wt. % of additive in the form of a eutectic composition (SnO_2 – 40, Li_2O – 60 mol. %) Li_2O–SnO_2 system (samples I_E, II_E, III_E) were introduced.

Table 1

Chemical composition of raw materials

Materials	Component content by chemical analysis, wt. %								
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	ZnO	BaO	LOI
Novoselivsky sand	99.13	0.39	0.04	0.20	0.04	–	–	–	0.20
Zinc white	0.06	–	–	–	–	–	99.92	–	0.02
Barium carbonate	–	–	–	–	–	–	–	70.19	29.81
Metallurgical alumina G-00	0.03	98.70	0.02	–	–	0.25	–	–	1.00
Micronized alumina CT3000SDP	0.01	99.81	0.02	–	0.10	0.06	–	–	
Aluminum hydroxide GD-00	0.02	74.18	0.02	–	–	0.25	–	25.53	

Samples were formed by semi-dry pressing and fired in an induction furnace: simultaneous synthesis of the specified compounds was carried out at a temperature of 1 200°C; the second firing provided the required level of sintering of finished products at a temperature of 1 200°C.

For the obtained samples the characteristics of sintering (apparent density ρ, water absorption W, total porosity P_t) were determined by the method of hydrostatic weighing. The main properties that determine the functionality of materials: dielectric characteristics (ε, tgδ) compressive strength σ_c, and micro-hardness (HRA, HV), were also measured. Measurements of dielectric losses of materials were performed on a "Tangent-3M" automated device in the range of 0.0001 to 1 at a range of operating voltages from 0 to 270 V. The studies were performed in the frequency range of 48–62 Hz. The hardness of the ceramic samples was determined by the depth of penetration into the material of the diamond pyramid under a smooth load of 1 MPa on the TK device (by Rockwell method).

The phase composition of the test samples was determined using the method of X-ray phase analysis (X-ray diffraction) using a DRON-3M diffractometer with CuKα radiation and a nickel filter under standard operating conditions. The study of the microstructure was performed by electron microscopic analysis using a JSM-6390LV scanning electron microscope in the secondary electrons mode.

4. Research results

4.1. Substantiation of the region of oxide compositions of the system BaO–ZnO–Al2O3–SiO2 for the synthesis of target phases

Analysis of the properties of silicates and aluminosilicates[33] showed that the synthesis of ceramic RTM should be carried out on the basis of the willemit (Zn_2SiO_4), gahnite ($ZnAl_2O_4$), celsian ($BaAl_2Si_2O_8$), spodumene ($LiAlSi_2O_6$) cordierite ($Mg_2Al_4Si_5O_{18}$) and slavsonite ($SrAl_2Si_2O_8$) phases, which have a set of necessary thermophysical, dielectric and mechanical characteristics. In particular, the compounds of willemite and celsian in the

[33] Radio-transparent ceramic materials of spodumene-cordierite composition / A.V. Zaichuk, A.A. Amelina, Y.V. Karasik et al. *Functional materials*. 2019. № 26 (1). P. 174–181; Optimization of the compositions area of radiotransparent ceramic in the $SrO-Al_2O_3-SiO_2$ system / G.V. Lisachuk, R.V. Kryvobok, K.B. Dajneko et al. *Przeglad Elektrotechniczny*. 2017. № 93 (3). P. 79–82; Development of new compositions of ceramic masses in $SrO–Al_2O_3–SiO_2$ system / G.V. Lisachuk, R.V. Kryvobok, A.V. Zakharov et al. *Functional Materials*. 2017. № 24 (1). P. 162–167; Influence of complex activators of sintering on creating radiotransparent ceramics in $SrO–Al_2O_3–SiO_2$ / G. Lisachuk, R. Kryvobok, A. Zakharov et al. *Eastern-European Journal of Enterprise Technologies.* 2017. № 1 (6–85). P. 10–15.

set of properties (table 2) meet the requirements for RTM in terms of electrophysical properties (ε, tgδ), are characterized by high melting point (1 512°C and 1 740°C, respectively) and relatively low thermal expansion (CTLE $3.2\cdot10^{-6}$ 1/K and $2.7\cdot10^{-6}$ 1/K, respectively), which creates the preconditions for obtaining heat-resistant radiotransparent ceramic materials based on them.

The presence of a complex of such properties indicates the advantages of these phases in comparison with quartz, spodumene, eucryptite and cordierite, which form the basis of existing radiotransparent sitalls and ceramic materials[34].

Table 2

Properties of celsian and willemite phases according to[35]

Mineral	Density, g/cm³	Melting temperature, ˚C	CTLE, $\alpha\cdot10^6$ K^{-1}	Dielectric constant, ε	Dielectric losses* tgδ 10^{-4}
Willemite	3.90–4.10	1 512	3.2	5.5	–
Celsian	3.1–3.4	1 740	2.7	6.5–7.0	1.0–2.0
*at a temperature of 20 ˚C and a frequency of 1 MHz					

The $BaO–ZnO–Al_2O_3–SiO_2$ system was chosen as the basis for the synthesis of heat-resistant and strong ceramic RTMs, in some parts of which the phases of celsian $BaAl_2Si_2O_8$ and willemite Zn_2SiO_4 coexist. The subsolidus structure of this system (according to[36]), as well as the region of

[34] Саркисов П.Д., Гращенков Д.В., Орлова Л.А. и др. Современные достижения в области создания высокотемпературных радиопрозрачных материалов. *Техника и технология силикатов*. 2009. № 1. С. 2–10; Современное состояние вопроса в области технологии и производства ситаллов на основе алюмосиликатных систем. Стеклообразование, кристаллизация и формообразование при получении стронций-анортитовых и цельзиановых ситаллов / П.Д. Саркисов, Л.А. Орлова, Н.В. Попович, Н.Е. Щеголева, Ю.Е. Лебедева, Д.В. Гращенков. *Все материалы. Энциклопедический справочник*. 2011. № 8; Щеголева Н.Е., Чайникова А.С., Орлова Л.А. Исследование процесса спекания при получении стеклокерамики на оснвое стронцийалюмосиликатного стекла методом полусухого прессования. *Авиационные материалы и технологии*. 2018. № 4 (53). С. 55–62; Khomenko E.S., Zaichuk A.V., Karasik E.V., Kunitsa A.A. Quartz ceramics modified by nanodispersed silica additive. *Functional materials*. 2018. Vol. 25. №. 3. P. 613–618; Abyzov A.M. Aluminum Oxide and Alumina Ceramics (review). P. 2 : Foreign Manufacturers of Alumina Ceramics. Technologies and Research in the Field of Alumina Ceramics. *Refractories and Industrial Ceramics*. 2019. № 60. P. 33–42.

[35] Inorganic Material Database AtomWork. National Institute for Materials Science (NIMS). URL: http://crystdb.nims.go.jp.

[36] Ceramic radiotransparent materials on the basis of $BaO–Al_2O_3–SiO_2$ and $SrO–Al_2O_3–SiO_2$ systems / G.V. Lisachuk, R.V. Kryvobok, O.Yu. Fedorenko, A.V. Zakharov. *Épitöanyag – Journal of Silicate Based and Composite Materials*. 2015. № 67 (1). P. 20–23; Inorganic Material Database AtomWork. National Institute for Materials Science (NIMS). URL: http://crystdb.nims.go.jp.

oxide compositions within the $BaAl_2Si_2O_8$ – Zn_2SiO_4 – Al_2ZnO_4 – SiO_2 elementary tetrahedron is presented in fig. 1.

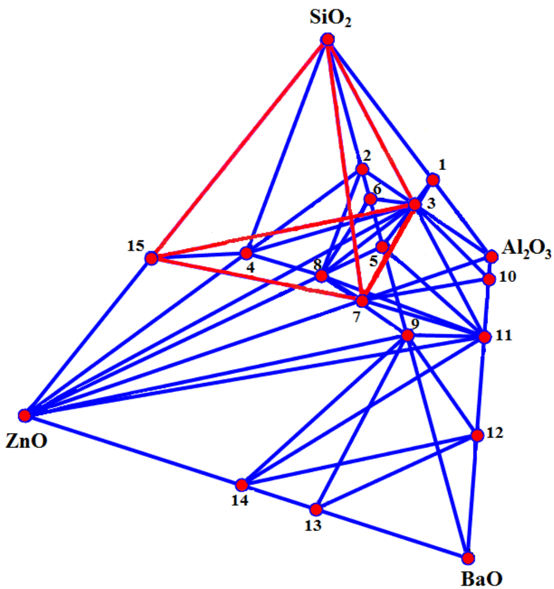


Fig. 1. State diagram of the ZnO–BaO–Al_2O_3–SiO_2 system and the region of oxide compositions within the elementary $BaAl_2Si_2O_8$–Zn_2SiO_4–Al_2ZnO_4–SiO_2; tetrahedron: 1 – $Al_6Si_2O_{13}$; 2 – $BaSi_2O_5$; 3 – $BaAl_2(SrO_4)_2$; 4 – $BaZn_2Si_2O_7$; 5 – $BaSiO_3$; 6 – $Ba_2Si_3O_8$; 7 – Al_2ZnO_4 ; 8 – $Ba_2ZnSi_2O_7$; 9 – Ba_2SiO_4; 10 – $Ba_7Al_{64}O_{103}$; 11 – $BaAl_2O_4$; 12 – $Ba_4Al_2O_7$; 13 – Ba_2ZnO_3 ; 15 – Zn_2SiO_4

The most interesting in this case are the areas of oxide compositions that allow the simultaneous synthesis of the target compounds. As can be seen from fig. 1, a given combination of phases ($BaAl_2Si_2O_8$ + Zn_2SiO_4) occurs in 4 elementary tetrahedra of the system, however, the lack of information on the dielectric characteristics of the $BaZn_2Si_2O_7$ ternary compound does not allow us to assess the suitability of oxide compositions belonging to $BaZn_2S_2$ Zn_2SiO_4–$BaZn_2Si_2O_7$–$BaAl_2Si_2O_8$ to obtain radiotransparent ceramics. In addition, according to[37], the $BaZn_2Si_2O_7$ phase is characterized by high anisotropic thermal expansion in the temperature range of 100–800°C. The low-temperature modification of this compound has a high thermal

[37] Thieme C., Schlesier, M., Oji Dike E. et al. Variable thermal expansion of glass-ceramics containing Ba1−xSrxZn2Si2O7. *Scientific Reports*. 2017. № 7. P. 33–44.

expansion (CTLE = $17.6 \cdot 10^{-6}$ K^{-1}) and shows a polymorphic transformation at 280 °C, accompanied by a sharp increase in cell volume (~ 2%)[38]. Therefore, the elementary tetrahedra $ZnO–Zn_2SiO_4–ZnAl_2O_4–BaAl_2SiO_8$ and $Zn_2SiO_4–ZnAl_2O_4–SiO_2–BaAl_2Si_2O_8$ were considered as the basis for the synthesis of radiotransparent ceramics of the willemite-celsian composition.

Using the geometro-topological analysis of the system, the method of which is described in detail in[39], for these elementary tetrahedra geometro-topological characteristics (table 3), in particular their relative volumes (ΔV), degree of asymmetry (K_a) and eutectic temperatures (T_{evt}), were calculated.

Table 3

Characteristics of elementary tetrahedra of the $BaO–ZnO–Al_2O_3–SiO_2$ system, containing the target phases

Elementary tetrahedron	ΔV, ‰	K_a	T_{evt}, K	Content of components, mol. %			
				1	2	3	4
$ZnO–Zn_2SiO_4–ZnAl_2O_4–BaAl_2Si_2O_8$	61.22	3.039	1605	44.86	45.56	5.92	3.66
$Zn_2SiO_4–ZnAl_2O_4–SiO_2–BaAl_2Si_2O_8$	165.88	1.802	1594	43.15	5.52	48.05	3.27

The obtained results showed that the $Zn_2SiO_4–ZnAl_2O_4–SiO_2–BaAl_2Si_2O_8$ tetrahedron is characterized by the largest relative volume and a much smaller degree of asymmetry, as well as a lower eutectic temperature. This is the basis for the conclusion regarding the manufacturability of model compositions belonging to the elementary tetrahedron, which contains the phases of the willemite, celsian, quartz and granite. Fig. 1 shows the visualization of the subsolidus state of the $BaO–ZnO–Al_2O_3–SiO_2$ base system and the region of oxide compositions selected for the development of ceramics of the willemite-celsian composition[40].

Using thermodynamic analysis, the probability of formation of target crystalline phases was determined by the value of Gibbs free energy ($\Delta G^0_T < 0$) in the temperature range 298–1 698 K. The results of calculations showed a high probability of formation of Zn_2SiO_4 zinc and $BaCO_3$ barium metasilicates from the mixture of SiO_2 and $BaCO_3$. Due to this, it becomes

[38] Thieme C., de Souza G.B., Rüssel C. Glass-ceramics in the system BaO-SrO-ZnO-SiO2 with adjustable coefficients of thermal expansion. *C. J. Am. Ceram. Soc*. 2016. № 99. P. 3097–3103.

[39] Subsolidus conceptual design of CaO–Al2O3–TiO2–SiO2 system and its significance for manufacturing advanced ceramics / M.I. Ryschenko, Y.N. Pitak, E.Yu. Fedorenko et al. *China's Refractories*. 2016. № 25 (1). P. 44–52.

[40] The Material Project. URL: https://materialsproject.org/#apps/phasediagram.

possible to simultaneously form a given combination of ($BaAl_2Si_2O_8$ and Zn_2SiO_4) phases in the temperature range 1 150–1 250 C by the reaction: $Zn_2SiO_4 + Ba_2Si_3O_8 + 2Al_2O_3 + SiO_2 = 2BaAl_2Si_2O_8 + Zn_2SiO_4$.

4.2. Development of raw material compositions and research of influence of aluminum-containing raw materials on properties of ceramics

Based on the information on the structure of the basic oxide system, the oxide composition was chosen as the basic one, the content of which corresponds to the ratio of the given phases ($BaAl_2Si_2O_8 : Zn_2SiO_4 = 1 : 1$) taking into account their stoichiometric composition of compounds. In accordance with the research objectives, on the basis of the specified model composition, ceramic masses have been developed using various types of aluminum-containing raw materials: metallurgical alumina G–00, micronized alumina CT3000SDP and aluminum hydroxide GD–00 (samples I_0, II_0, III_0, respectively).

The results of studies of the properties of ceramic samples are presented in table. 4. Studies have shown that the firing products are characterized by a high level of sintering (water absorption W = 0–0.6%, total porosity P_t = 0.45–1.74%, apparent density ρ = 2 800–3 000 kg/m^3). It is established that when a two-component eutectic additive is introduced into the masses, intensive melt formation occurs. As a result, the samples undergo high-temperature deformation (with the exception of those that included metallurgical alumina in the mass).

By electrophysical properties (ε = 2.08–3.61; $tg\delta=(0.91\div8.14)\cdot10^{-2}$), the obtained materials meet the requirements for RTM in terms of the level of dielectric characteristics. It was found that when using aluminum hydroxide, the values of ε and tgδ are the lowest. Determination of physical and mechanical properties of the samples showed that the highest level of compressive strength and hardness (HV = 471 and σ_c = 1 529 MPa) is observed for samples of ceramics obtained using metallurgical alumina G-00.

The positive effect of sintering intensifier additives (2 wt. % Li_2O) affects only the samples obtained using aluminum hydroxide GD-00, for which the Vickers hardness and compressive strength increase by 24% to 403 HV and 1 368 MPa, respectively.

It is also established that when introduced into the composition of the masses of 1 wt. % of the eutectic mixture of the SnO_2–Li_2O system there is an intensive formation of a melt, which causes high-temperature deformation of the samples.

Table 4

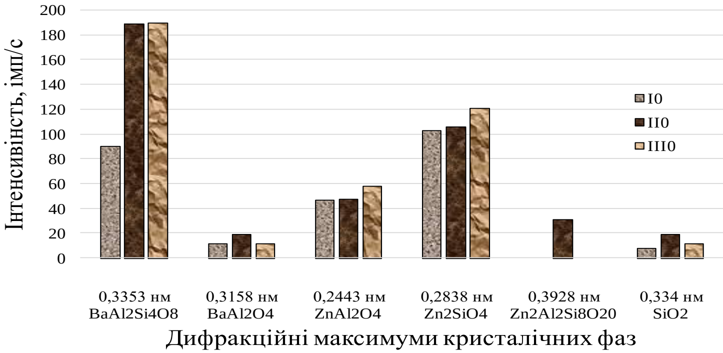
Properties of radiotransparent ceramic samples

Properties	Sample code								
	I_0	I_L	I_E	II_0	II_L	II_E	III_0	III_L	III_E
Apparent density *ρ*, kg/cm^3	2 990	2 990	2 850	2 990	3 000	2 850	2 880	2 860	2 660
Water absorption W, %	0.05	0.31	0.17	0.18	0.46	0	0.6	0.51	0.35
Total porosity P_t, %	0.15	0.94	0.45	0.54	1.39	0	1.74	1.47	0.93
Dielectric constant, ε	2.85	2.41	3.34	3.11	2.33	3.61	2.46	2.08	3.85
Dielectric loss tangent, tgδ	0.0755	0.0242	0.0394	0.0438	0.0599	0.0814	0.0091	0.0744	0.0634
Rockwell hardness, HRA	74	63	–*	72	71	–*	56	71	–*
Vickers hardness, HV	471	261	–*	435	403	–*	180	403	–*
Compressive strength σ_c, MPa	1 529	831	–*	1 405	1 368	–*	610	1 368	–*
*samples exposed high temperature deformation									

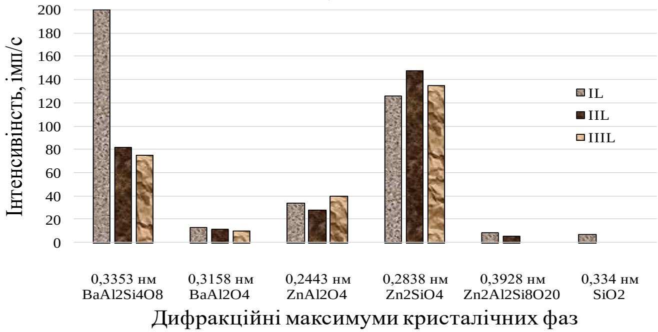
4.3 Research of structural-phase features of the received materials

X-ray phase analysis of the obtained ceramic RTM showed that the main crystalline phases obtained are willemit and celsian (fig. 2).

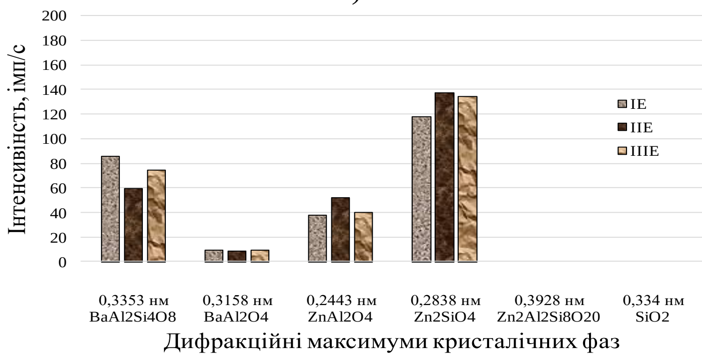
Analysis of the intensities of the diffraction maxima of the crystalline phases made it possible to trace the effect of aluminum-containing raw materials, as well as the additives of sintering and phase-forming intensifiers on the phase composition of the obtained materials. Thus, according to the intensity of the impact on the formation processes of these phases, aluminum-containing materials can be arranged in a row: metallurgical alumina G-00 < micronized alumina (CT3000SDP) < aluminum hydroxide GD-00. In addition, there are concomitant phases of gahnite, zinc petalite, barium aluminate, the amount of which depends on the type of aluminum-containing raw materials. The lowest content of accompanying phases was recorded in the samples obtained using aluminum hydroxide. Analysis of radiographs showed that when using alternative aluminum-containing raw materials (micronized alumina and aluminum hydroxide), the intensity of the $BaAl_2Si_2O_8$ and Zn_2SiO_4 reflexes increases even in the absence of additives intensifiers of sintering and phase formation. The positive effect of the Li_2O addition affects the increase in the intensity of the reflexes of the main phases and the decrease of the reflexes of zinc petalite and quartz, and with the introduction of the $Li_2O–SnO_2$ eutectic additive the number of concomitant phases is minimal.



a)



b)

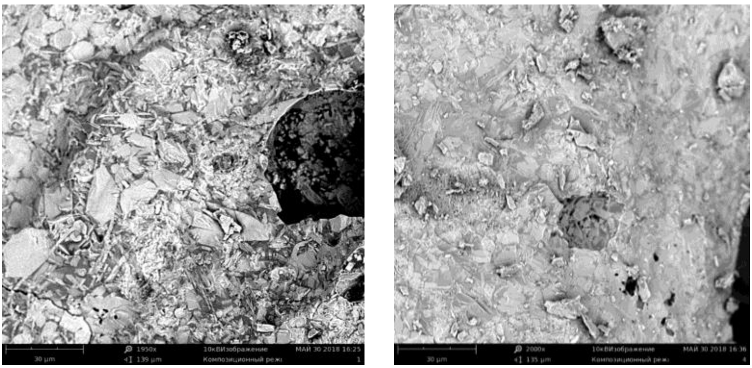


c)

Fig. 2. The intensity of the main reflexes of the crystalline phases in the samples: a) without additives; b) with 2 wt. % Li_2O; c) with 1 wt. % $Li_2O–SnO_2$

Studies of the microstructure of the obtained radiotransparent ceramics (SEM-images of the samples are presented in figs. 3, 4) showed that in comparison with sample I_0, the structure of sample II_0 containing micronized alumina is fine-crystalline. The difference in the shape and size of the crystals is also noticeable. The inner surface of the pores is covered with small crystalline formations. In both samples there are elongated prismatic and lamellar crystals of willemite with an average size of 22.4×11.4 μm and needle crystals of celsian with an average size of 15.75×0.55 μm.

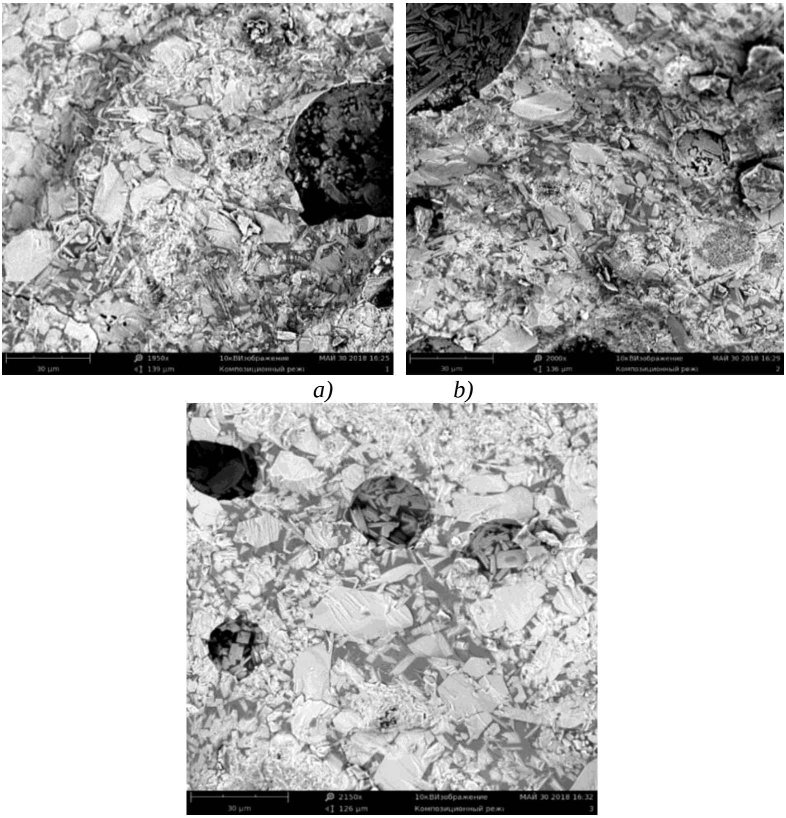
There are also fine crystals of willemite with an average size of 1.70×1.15 μm, which form clusters between larger crystals, which contributes to the compaction of the material. In samples I_0 and II_0, which do not contain additives of sintering and phase formation intensifiers, there are spherical pores with a predominant size of ~ 25 μm. Comparative analysis of microphotographs indicates that the use of micronized alumina (sample II_0) can reduce the closed porosity of the material by reducing the pore size.



a) *b)*

Fig. 3. SEM-images of radiotransparent ceramics samples:
a) sample I_0, obtained using metallurgical alumina G-00;
b) sample II0 obtained using micronized alumina CT3000SDP

The data obtained indicate that the introduction of small additives, in particular 2 wt. % Li_2O helps to reduce the pore size by almost half (up to ~ 17.6 μm in the I_L sample and up to ~ 13.2 μm in the I_E sample) and a denser arrangement of celsian and willemite crystals due to changes in their quantitative ratio (fig. 4).



a) *b)* *c)*

Fig. 4. SEM-images (2000) of samples of radiotransparent ceramics, obtained using metallurgical alumina G-00: a) sample I_0 (without additives); b) sample I_L (with 2 wt. % Li_2O); c) sample I_E (with 1 wt. % Li_2O–SnO_2 eutectic composition)

Samples of ceramics, which include a eutectic additive (1 wt. % Li_2O–SnO_2) have a larger number of glass phases. At the same time, the size of formations increases due to the intensive growth of faces in the melt (maximum size of willemite crystals – 34.5×16.1 μm, celsian crystals – 18.3×1.1 μm). Finely dispersed crystalline formations also slightly increase in size (on average up to 1.65×1.65 μm).

4.4. Substantiation of the choice of method and optimization of technological parameters of fairing formation

The specificity of the technology of fairings manufacturing is that the method of forming must implement their design features and specific requirements for functional characteristics and operating conditions, and also take into account the manufacturability of materials from which thin-walled products of complex configuration are made[41].

The choice of the method of fairing formation is based on the analysis of the advantages and disadvantages of each of them, taking into account manufacturability and economic feasibility. Thus, for the formation of the main fairings methods of hot casting of thermoplastic suspensions and thermoplastic pressing with a temporary bond can be used. The advantage of this method is a decrease in shrinkage during firing and a high strength of the semi-finished product in a dry state, which allows mechanical processing of semi-finished products before firing. However, this method is in the stage of laboratory research and requires industrial development.

Highly concentrated suspensions are used for electrophoretic molding, which allows obtaining a higher density of castings than in conventional slip casting. The use of the electrophoresis method significantly accelerates the molding process at a small casting thickness (up to 10 mm), while for thick-walled products this method is not effective. The disadvantage of this method is the impossibility of forming large complex products, because the electrophoretic molding is quite fast mass gain at the anode (core). In this case, from the layer of mass gained towards a cathode there is intensive water drainage; casting, losing moisture gives shrinkage, which leads to the formation of cracks on the outer surface of the semi-finished product. An increase in the current density leads to a thixotropic effect, which also leads to a casting defect. In addition, when forming large-sized products, it is extremely difficult to ensure a uniform distribution of moisture in the mold, and therefore its uniform electrical conductivity. As a result, there is an uneven mass gain, and the formed casting with walls of different thickness is rejected[42].

The most technological and relatively easy to implement method of forming thin-walled shells of the fairing is casting from water slips, which occurs by mass gain on the surface of the gypsum mold. There are free casting of slip and injection molding. Casting of semi-finished products under pressure allows obtaining a strictly defined thickness, the same for all parts of the semi-finished

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[41] Khatavkar N., Balasubramanian K. Composite materials for supersonic aircraft radomes with amelio-rated radio frequency transmission. *A review*. 2016. № 6 (8). P. 6709–6718.

[42] Additive Manufacturing of Ceramics: Issues, Potentialities, and Opportunities / A. Zocca, P. Colombo, C.M. Gomes, J. Günster. *Journal of the American Ceramic Society*. 2015. № 98 (7). P. 1983–2001.

product, which eliminates the appearance of defects. The obtained semi-finished product has a dense package of particles of the dispersed solid phase, and therefore high flexural strength. Injection molding is carried out from slips with a density of ρ = 1 860–1 920 kg/m^3. It should be noted that the method of injection molding from water slips is acceptable only for the formation of only equal in thickness thin-walled shells[43].

The mechanism of casting formation is as follows. The liquid phase of the slip under the action of capillary forces penetrates into the pores of the mold, transferring the solid phase, which is deposited on the walls of the mold, forming a casting. The driving force of the process at this stage is the difference between the moisture content of the gypsum form and the suspension (slip). The formed dense layer of material has low moisture conductivity and slows down the process of mass gain, with increasing thickness of the mass layer to 60 mm, the process almost stops[44].

The casting quality largely depends on how accurately the technological parameters of slip casting correspond to the properties of the slip, which depend on the composition of the technological mixture. For this reason, the key problem of technology is the optimization of technological parameters in each case of production. Therefore, the study of the rheological properties of non-plastic slip used in the production of ceramic fairings and the determination of optimal technological parameters for the formation of semi-finished products is an important technological task.

The main characteristics of aqueous ceramic slip include density, moisture, fluidity, viscosity, thickening factor, rate of mass gain. The slip must meet the following requirements: be free of foam and gas inclusions, have satisfactory fluidity under low viscosity; be aggregatively stable (characterized by the absence of aggregation, coagulation and sedimentation of solid phase particles); have a high filtering capacity to ensure fast and defect-free mass gain; be chemically inert, provide sufficient strength and low shrinkage of semi-finished products, as well as the possibility of their easy release from the mold[45].

The following factors for obtaining stable rheological properties of clay less slips and optimizing the casting process are of great importance: the degree of purity of the material (no foreign ions in the suspension), the

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[43] Aqueous injection moulding of porcelains / I. Santacruz, M. I. Nieto, R. Moreno et al. *Journal of the European Ceramic Society*. 2003. № 23. P. 2053–2060.

[44] Mangels J.A. Injection Molding Ceramics. *Proceedings of the 6th Annual Conference on Composites and Advanced Ceramic Materials: Ceramic Engineering and Science Proceedings*. 2008. Vol. 3. Issue 9/10.

[45] Klimoshl Yu.A., Levitskii I.A. Rheological properties of slips based on polymineral clays with electrolyte additives. *Glass and Ceramics*. 2004. Vol. 61. № 11–12. P. 375–378.

conditions of material preparation (preliminary thermal treatment, the method and degree of grinding), the presence or absence of slip evacuation and its storage duration; selection of thinning additives to reduce the moisture content of the slip while maintaining high fluidity, selection of adhesive additives that strengthen the casting.

Usually, when using slip casting in the technology of traditional types of fine ceramics to improve the rheology of the slip and reduce their moisture at the stage of wet grinding of the raw material mixture, electrolyte diluents and surfactants are added. The use of electrolytes typical of clay-containing slippers does not give the desired result in the formation of semi-finished products from non-plastic slippers. It should also be noted that the introduction of diluents of inorganic nature makes its adjustments in the process of forming the phase composition of radiotransparent ceramic materials, which may negatively affect their properties.

Despite significant progress in the field of controlling the properties of ceramic suspensions upon the introduction of surfactants, information on the conditions of their use is very limited, and further studies are required to determine the mechanisms of their action. In addition, the surfactants used in ceramic production are provided by a fairly narrow spectrum. Many questions concern the stability of dispersed systems (absence of their separation during long-term storage), and the influence of the composition of solid phase particles on the rheological properties (pH, fluidity, density, rate of mass gain, etc.). The information available in the scientific literature on these issues is often limited to certain mass compositions and investigated surfactants and is often contradictory[46]. This can be explained by the fact that complex polymineral dispersions are most often studied, and the properties of solutions of polyelectrolytes and surfactants associated with the state of their macromolecules in solution are extremely unstable and change with the concentration of additives and the degree of ionization of functional groups. In this regard, it is not always possible to definitely interpret the results of studies of systems that combine the properties of complex, both chemically and phase wise, constituents of ceramic slips and multifunctional polyelectrolytes and surfactants, which necessitates their further study.

The efficiency of stabilization and dilution of clay-free slip is determined primarily by the magnitude of the generated ξ-potential. The most common method of dilution of such suspensions is to adjust the value of their hydrogen pH. Changes in ξ-potential and viscosity in individual pH intervals

[46] Effect of dispersant on the rheological properties and slip casting of concentrated sialon precursor suspensions / X. Xin, I.L.L. Marta, R. Fu Oliveira, J.M.F. Ferreira. *J. Eur. Ceram. Soc*. 2003. № 23. P. 1525–1530.

are determined by the adsorption charge of the particles, compression or expansion of the electric double layer.

Based on the analysis of recommendations for the use of diluents manufactured by Zschimmer & Schwarz[47] for further research aimed at optimizing the rheological parameters of the slip of willemite-celsian ceramics, the Dolapix PC 67 was selected. This additive, which by its composition is a sodium salt of polycarboxylic acid, makes it possible to prepare slips with a high concentration of the solid phase, has a wide deflocculation interval, counteracts thixotropy and does not foam, which is also important. Since the product is liquid and completely dissociates in aqueous solution, the deflocculation effect begins immediately after adding to the slip. Thus, the Dolapix PC 67 additive makes it possible at any time to adjust the viscosity of the slip directly on the casting line. The deflocculation effect of Dolapix PC 67 is the result, on the one hand, of the ion exchange of the additive and the solid particles of the slip and the effect on their electrical double layer. On the other hand, the polymer chains are attached to the mineral particles and thus carry out steric repulsion. This helps to stabilize the suspension, as the solid particles remain highly dispersed due to the lack of aggregation. The recommended amount of additive varies between 0.1–0.5% of the solid content in the slip. Since the effect of the additive on the rheology of the slip depends on the composition of the solid part of the suspension, it is necessary to experimentally test and determine the optimal amount of additive in each case[48].

To improve the adhesion properties of the slip polyvinyl alcohol (PVA 1788) was used, which is a high-molecular chemically inert polymer, easily soluble in water, has film-forming properties. PVA is an excellent emulsifying, adhesive and film-forming polymer, which is used as an adhesive additive in the manufacture of building mixtures to prevent cracking. The study of the rheological properties of the ceramic slip was performed on a suspension containing 70 wt. % of fine solid phase (willemit-celsian composition). Diluents and adhesives were added to the suspension dissolved in water. The limits of variation of diluents and adhesives in the study of technological parameters of the slip are given in table 5.

[47] Milias A., Tsetsekou A., Agrafiotis C. Optimization of the rheological properties of alumina slurries for ceramic processing applications. Part I: Slip-casting. *Journal of the European Ceramic Society*. 2001. № 21. P. 363–373.

[48] Evcin A. Investigation of the effects of different deflocculants on the viscosity of slips. *Scientific Research and Essays*. 2011. № 6 (11). P. 2302–2305.

Table 5

The content of the slip components with a moisture content of 30%

Raw materials	Component content, wt. %							
	P_1	P_2	P_3	P_4	D_1	D_2	D_3	D_4
Mixture of celsian and willemite in a ratio of 1:1	70	70	70	70	70	70	70	70
Polyvinyl alcohol (PVA 1788)	0.35	0.58	0.82	1.05	–	–	–	–
Sodium salt of polycarboxylic acid (Dolapix PC 67)	–	–	–	–	0.2	0.3	0.4	0.5
**P series – slips with PVA 1788 **D series – slips with Dolapix PC 67*								

Determination of the moisture of ceramic slips was performed after drying a portion of the slip in a drying cabinet at a temperature of 120ºC to constant weight. The moisture content of the slip was calculated by the formula:

$$W = \frac{m_{sl} - m_{d.m.}}{P_{sl}} \cdot 100\%,$$

where m_{sl} is the slip mass, g; $m_{d.m.}$ is the mass of dry matter after drying of the slip, g.

The moisture of the experimental suspensions containing additives was 30%.

The slip fluidity (τ_1) was determined by the flow time of 25 ml of suspension through a pipette hole with a diameter of 4 mm. The suspension collected in the pipette should flow in a continuous stream after opening the upper hole. For a more accurate determination of the parameter, 5 parallel measurements were performed, according to which the arithmetic mean yield value was found.

Determination of the rate of mass gain was performed using gypsum rods. Before the experiment, the gypsum rods were dried to constant weight at a temperature of 70-75°C. To determine the rate of mass gain, the rod was immersed to the mark in a glass with a slip and kept for 1 min. After gaining mass on gypsum rods, they were dried to constant mass and weighed to the nearest 0.01 m. The speed of slip gaining (g/min) was determined by the mass gained per unit time:

$$g_{mass} = g_1 - g_0,$$

where g_{mass} is the weight of the dry mass gained on the gypsum rod for 1 min, g; g_1 is the weight of dry rod with mass, g; g_0 – weight of the dry gypsum rod, g.

Studies on the dilution of non-plastic ceramic slip were performed using Dolopix PC 67 additive. The degree of the material dilution was determined by the dependence of the slip fluidity on the concentration of the diluent additive $\tau_1 = f(C_{Dolapix})$.

The strength of the samples in the dry state was measured on a device for determining the strength at three-point bending, which provides (0.05–0.1) N/s loading rate. For research, 60 mm long and 8 mm in diameter samples were formed, which, after drying at 110°C, were cooled in a desiccator. Before the test, the diameter of the sample was measured with a micrometer with an error of ± 0.5 mm.

The sample was placed on support prisms and the load was gradually increased until the destruction of the sample took place. The flexural strength of the samples in the dry state was calculated by the formula:

$$\sigma_{fl} = \frac{7.46 \cdot P}{d^3},$$

where P is the destructive load, g; d is the diameter of the sample, mm.

The permissible difference between the values of parallel measurements is indicated in table 6.

Table 6

Discrepancy of parallel measurements of flexural strength in the dry state

Flexural strength, MPa	Discrepancy between measurement results, MPa
up to 1.0	0.05
1.0–2.0	0.10
2.0–3.0	0.20
over 3.0	0.30

The effect of the Dolapix PC 67 diluent additive and the PVA 1788 adhesive additive on the fluidity, mass gain and strength of the casting is illustrated in the form of graphical dependences (fig. 5). As can be seen from Fig. 5a, with the introduction of PVA 1788 within the experimental concentrations the flexural strength of castings in the dried state increases. P_4 and P_3 samples (7.22 MPa and 6.12 MPa, respectively) containing more than 0.8 wt. % PVA are characterized by the highest strength. This is a positive technological factor in terms of transportation of castings and the possibility of their machining. However, the introduction of an adhesive additive leads to deterioration in the slip fluidity: the leakage time of the slip is doubled.

When adding a Dolapix PC 67 diluent additive to the slip in an amount of up to 0.2 wt. %, a significant improvement in slip fluidity is observed: in comparison with the D_0 reference slip, which does not contain additives, the flow time of 25 cm^3 of D_1 suspension through the pipette opening decreased by 10 s. With a further increase in the concentration of the diluent additive from 0.2 wt. % to 0.6 wt. % (more than 100% on dry matter) fluidity changes increases insignificantly (slip leakage time decreases by 1 s). At the same time deterioration of mass gain is observed. It should also be noted that the use of Dolapix PC 67 slightly increases the strength of the dry casting (from 1.76 MPa to 2.53 MPa) with the introduction of the additive in the amount of 0.6 wt. %. Therefore, the introduction of more than 0.3 wt. % Dolapix PC 67 is not advisable.

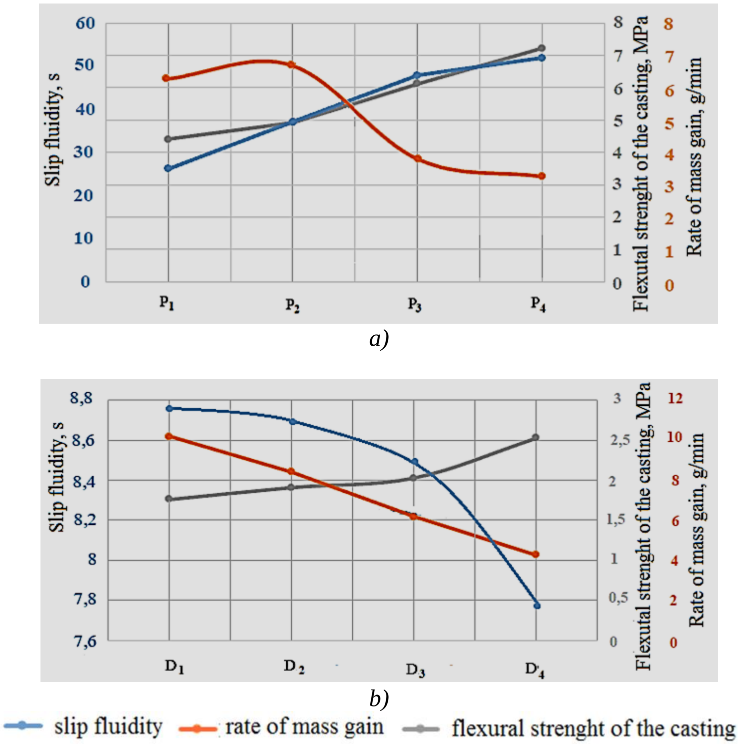

Fig. 5. Effect of additives on the slip properties and the strength of the casting: a) PVA 1788 (adhesive additive); b) Dolapix PC 67 (diluting additive)

Taking into account the obtained data, the possibility of combining diluent and adhesive additives was further investigated, which will allow optimizing the technological parameters of slip casting of willemit-celsian ceramics. The composition of the optimal complex additive was determined using FFE 2[49] experiment. The content of adhesive and diluent additives studied in the previous step, varied within the concentrations specified in table 7. The study was performed for slips with moisture of 30%.

Table 7

Planning matrix and natural plan of FFE 2^2 experiment

Experiment no.	X_1	X_2	Polyvinyl alcohol (PVA 1788)	Sodium salt of polycarboxylic acid (Dolapix PC 67)
1	+ 1	+ 1	1.05	0.42
2	– 1	+ 1	0.35	0.42
3	+ 1	– 1	1.05	0.14
4	– 1	– 1	0.35	0.14
Checkpoint			1.05	0.28

The research results are illustrated by the diagrams of dependences of the slip fluidity, the rate of mass gain and the strength of the castings in the dry state on the concentration of additives, which are shown in fig. 6. Using the obtained data, the areas of concentrations of additives were determined, the use of which (provided that they are present simultaneously) provide the required level of slip properties: fluidity – 5÷11 s; the rate of mass gain – 6÷8 g/min, as well as sufficient strength of the casting after drying 5÷8 MPa, and therefore determine the manufacturability of the formation of thin-walled shells of fairings of willemite-celsian ceramics by casting from water slips.

According to the analysis of the experimental results the range of optimal concentrations of the components of the complex additive, which allows to make a slip of high fluidity with satisfactory filtration properties and to obtain high-strength castings, was determined (fig. 6d).

Taking into account the considerations of economic feasibility, the optimal composition of the complex additive is as follows Dolapix PC 67 – 0.38 wt. % (more than 100 on dry matter); PVA 1788 – 0.7 wt. % (more than 100 on dry matter).

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[49] Ивахненко Ю.А., Варрик Н.М., Максимов В.Г. Высокотемпературные радиопрозрачные керамические композиционные материалы для обтекателей антенн и других изделий авиационной техники (обзор). *Труды ВИАМ*. 2016. № 5 (41). С. 36–43.

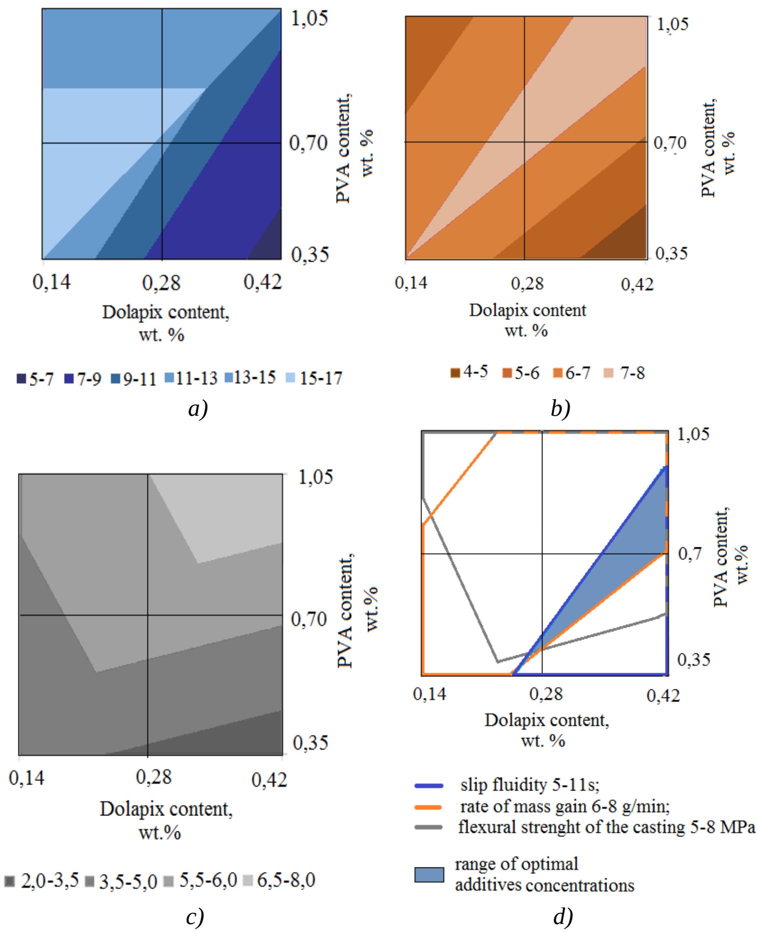

Fig. 6. Influence of additives on the properties of slip and castings: a) slip fluidity, c; b) rate of mass gain g/min; c) flexural strength of the casting, MPa; d) range of optimal concentrations of additives

Thus, as a result of the conducted researches the influence of diluting (Dolapix PC 67) and adhesive (PVA 1788) additives on the technological properties of the non-plastic slip of willemite-celsian composition was determined. The optimal composition of the complex additive (Dolapix PC 67 – 0.38 wt. % + PVA 1788 – 0.7 wt. % over 100 on dry matter) is determined, which provides a high fluidity slip (τ_1 = 9÷11 s) with sufficient rate of mass gain (6÷7 g/min), which is able to form a casting with high flexural strength (5÷6.5 MPa).

CONCLUSIONS

As a result of the research, the area of the most technologically advanced compositions of the $BaO–ZnO–Al_2O_3–SiO_2$ system for the production of Willemite-Celsian ceramics of the composition was determined. This region is localized within the concentration limits of the elementary tetrahedron Zn_2SiO_4–$ZnAl_2O_4$–SiO_2– $BaAl_2Si_2O_8$, which is characterized by insignificant asymmetry (K_a = 1.802), the largest relative volume (ΔV = 165.88 ‰) and low eutectic temperature (T_{eut} = 1594 K). The composition of the eutectic of this tetrahedron was also determined, ml. %: 43.15 Zn_2SiO_4; 5.52 $ZnAl_2O_4$; 48.05 SiO_2; 3.27 $BaAl_2Si_2O_8$. Compositions that belong to the selected region of the basic oxide system imply the simultaneous synthesis of target phases (Zn_2SiO_4, $BaAl_2Si_2O_8$). The established possibility of one-stage low-temperature (1 200°C) synthesis of willemite and celsian, makes it possible to simplify the technology of obtaining multiphase radio-transparent ceramics.

The positive effect of alternative alumina raw materials, as well as additives-intensifiers of sintering and phase formation, on the structure and phase composition of the obtained materials has been established. The intensity of the influence on the processes of the target phases (willemite and celsian) formation of the experimental aluminum-containing materials increases in a row: metallurgical alumina G-00, micronized alumina CT3000SDP, aluminum hydroxide GD-00. It is established that the use of micronized alumina (sample II_0) allows reducing the closed porosity of the material by reducing the pore size. The influence of sintering and phase formation intensifier additives on the functional properties, phase composition and microstructure of the obtained materials was determined. It is shown that the addition of 2 wt. % Li_2O or 1 wt. % SnO_2 – 40 mol. %, Li_2O – 60 mol. % eutectic composition helps to reduce the porosity of materials (reduces both the number and size of pores) and contributes to the compaction of the structure due to a more compact arrangement of the crystalline phases by increasing the proportion of fine crystals of willemit.

The optimal technological parameters of aircraft fairings molding by slip casting are determined. The aircraft fairing after firing and machining are shown in the Ffg. 7.

As a result of studying the properties of slips of willemite-celsian ceramics, the composition of a complex additive (Dolapix PC 67 – 0.38 wt. % + PVA 1788 – 0.7 wt. % over 100 on dry matter), the use of which provides an increase in slip fluidity, accelerated mass gain and an increase in the strength of the casting, was determined.

As a result of the research carried out, a densely sintered willemite-celsian ceramics, which meets the requirements for RTM in terms of functional properties, has been developed. The new material differs from the existing analogs by a lower synthesis temperature (1 200°C), low dielectric constant (ε = 2.08–3.11) and increased strength (σ_c = 831–1 529 MPa).

Fig. 7. The aircraft fairing after firing and machining

SUMMARY

The results of complex studies aimed at developing prescription-technological parameters for obtaining radiotransparent ceramic materials with specified electrophysical properties are presented. The choice of the basic oxide BaO–ZnO–Al_2O_3–SiO_2 system has been substantiated, and the areas of oxide compositions that are promising for the production of radiotransparent ceramics of the willemite-celsian composition have been determined. The possibility of one-stage low-temperature synthesis of willemite (Zn_2SiO_4) and celsian ($BaAl_2Si_2O_8$) at 1 200°C was established. Dense-sintered ceramic materials of celsian-willemite composition, the dielectric characteristics of which meet the requirements for radiotransparent materials (ε = 2.08 ... 3.11; tgδ = 0.0091...0.0755), have been obtained. The influence of various types of aluminum-containing raw materials on the sintering characteristics, phase composition and basic functional properties of the obtained radiotransparent ceramics has been investigated. It is shown that the intensity of the processes of formation of target phases (Zn_2SiO_4 and $BaAl_2Si_2O_8$) increases when using aluminum hydroxide and micronized alumina as an alternative aluminum-containing raw material, and the use of the latter makes it possible to reduce the closed porosity of the material. The

effect of sintering additives and phase formation intensifiers on the functional properties, qualitative phase composition and microstructure of the obtained ceramic materials has been studied. It was found that when using aluminum hydroxide as an aluminum-containing component of ceramic masses, the introduction of small additives: 2 wt. % Li_2O or 1 wt. % of the eutectic composition of the Li_2O-SnO_2 system (the corresponding oxides are taken in a ratio of 3 : 2) helps to reduce the dielectric losses of ceramics and significantly improves the strength indicators. The study of the microstructure of the obtained materials by scanning electron microscopy showed that the use of these additives provides not only the formation of the target crystalline phases, but also causes a decrease in the porosity of materials by reducing the number and size of pores. The positive effect of the additives is also manifested in the compaction of the structure of radiotransparent ceramics due to an increase in the proportion of finely dispersed willemite crystals and a more compact arrangement of crystalline phases.

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