Influence of aluminum-containing raw materials on the properties of radio-transparent materials

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Érkezett: 2022. 07. 04. ▪ Received: 04. 07. 2022. ▪ https://doi.org/10.14382/epitoanyag-jsbcm.2023.12

Abstract
The influence of alumina-containing raw materials on the properties and structure of radio-transparent materials (RPM) has been studied. A positive effect of metallurgical and micronized aluminum oxides on physical and technical properties was revealed, namely a significant decrease in the number of closed pores due to an increase in the number of small willemite crystals.
Keywords: celsian, willemite, radio-transparent ceramics, aluminum hydroxide, alumina, dielectric characteristics, pores
Kulcsszavak: celsian, willemite, rádiótranszparens kerámia, alumínium-hidroxid, alumínium-oxid, dielektromos jellemzők, pórusok

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1. Introduction

Radio-transparent ceramics are used as a strategically important material in aircraft and rocketry, due to the constant in a wide temperature range of operating frequencies and electrical characteristics, as well as strength, heat resistance and heat resistance.

Aircraft fairing materials support dynamic, vibrational and stationary loads: compression, bending and twisting, sudden changes in temperature (from air level to several hundred degrees per second), hypersonic flows, and in some cases high-intensity infrared, neutron, and other radiation. The structure can significantly affect the functional properties of RPM.

Among the requirements for the quality of raw materials for ceramic radio-transparent materials, the presence of impurities (chemical purity), dispersion and porosity should be highlighted. Therefore, it is necessary to study the effect of raw materials on the sintering temperature for the formation of a given phase composition and obtain the appropriate characteristics. No less promising areas of research are the study of the impact of alumina raw materials of different nature on the phase composition, sintering characteristics and functional properties of radiopaque ceramics.

2. Analysis of literature data and problem statement

In connection with the high requirements for ready-made radio-transparent materials for aircraft and a wide range of their uses, it is important to control structural features, in particular, porosity. Because strength, moisture absorption, and dielectric constant depend on the porosity index.

Minimizing its residual porosity plays a crucial role in obtaining ceramics with high dielectric constant. High values of dielectric constant are observed even for coarse-grained ceramics (with grain sizes from 1.2 to 60 μm) provided that 99% of the theoretical density is reached. At the same time, when the density of ceramics is reduced to ~ 82%, the dielectric constant of samples with an average grain size of up to 1 μm decreases significantly [1].

Fine-grained ceramics has a number of features that are clearly manifested in the field of phase transitions. For example, as the size of the crystallites (areas of coherent scattering) decreases, the microdeformations increase, which can cause suppression of the ferroelectric properties. That is, the dielectric constant and grain size are ambiguous: it is possible that the dielectric properties are suppressed in the presence of small grains in the material. This is confirmed by a study that experimentally showed that the dielectric constant decreases with decreasing grain size [1].

The results of [2] indicate that the degree of porosity of ceramics directly affects the dielectric properties. With increasing porosity, the value of the dielectric constant decreases, while the nature of its frequency dependences does not change. Therefore, by controlling the porosity of the ceramic in the manufacturing process, it is possible to obtain samples with the required dielectric constant for a particular application. The appearance of porosity is significantly influenced by aluminum-containing raw materials and the peculiarities of its sintering.

3. The purpose and objectives of the study

The aim of this work is to determine the effect of the type of alumina-containing raw materials on the phase composition, structure, and properties of radiolucent ceramic materials of celsian-willemite composition, synthesized in the temperature range 1100-1200 °C.

The main task is to characterize the influence of different in structure, the degree of purity of alumina-containing materials on the properties of X-ray contrast material, the choice of optimal raw materials to obtain the desired structure of the source product.

4. Rationale for the choice of thinning additives for research

Improving the quality of technical ceramics is determined by solving the main problem of materials science: dispersion - composition - structure - property. The relationship of these parameters is the basis of modern technologies aimed at obtaining ceramic products with specified performance properties, which is of paramount importance in increasing the competitiveness of products.

The vast majority of industrial brands of domestic alumina are characterized by a predominant aggregate size of 30-40 µm in the presence of particles with a maximum size of up to 150 µm. Such materials cannot be used in the production of densely sintered ceramics without prior grinding (brand GK - alumina non-metallurgical) or without prior heat treatment (brand G-00 - metallurgical alumina) and subsequent fine grinding. Currently, leading foreign producers of alumina-containing raw materials (Alcoa Industrial Chemical, USA; Alcan Bauxite and Alumina Aluminum Pechiney, France; Almatis GmbH, Germany) offer a wide range of ready-to-use alumina, which differ in calcination temperature, content α-Al_2O_3 and impurities, the presence or absence of mineralizers, the degree of dispersion, the specific surface area, and others [3, 4].

In view of the above, it is of interest to study the effectiveness of the use of micronized alumina and aluminum hydroxide as alternative aluminum-containing materials.

5. Materials and methods

During the research, aluminum-containing materials were used to obtain celsian-willemite ceramics: alumina grade G-00, alumina ST3000SDP, aluminum hydroxide (Alcoa Industrial Chemical, USA; Alcan Bauxite and Alumina Aluminum Pechiney, France; Almatis GmbH, Germany).

The most widely used method for obtaining alumina is Bayer's method [5], which consists in obtaining a solution of sodium aluminate by the interaction of natural bauxite with a solution of sodium hydroxide. The resulting sodium aluminate solution is purified from impurities, and after appropriate treatment, pure aluminum hydroxide is isolated, from which alumina is obtained by calcination in rotary kilns at a temperature of 1150 - 1200 °C. As aluminum hydroxide is an intermediate in the production of alumina, it is the same raw material available in Ukraine as alumina and is produced by the same manufacturers.

Alumina ST3000 SDP is a new development of the company Alcoa Industrial Chemicals (now Almatis GmbH). It is made of alumina ST3000 SG (ground in a ball mill with the addition of 0.06 - 0.12 wt% MgO in a spray dryer), especially for parts with a polished surface, such as pump valves, pistons, shut-off valves for hot and cold water mixers, etc. The sintering temperature recommended by the manufacturer is 1600 °C.

According to petrographic analysis, aluminum hydroxide brand GD00 consists of colorless, transparent aggregates of spherulites, consisting of lamellar crystals. Aggregates are represented by hydrargillite, have a complex round, round-polygonal, rectangular shape. Unit size: maximum - 130 µm, single - up to 190 µm, which prevails 40 ÷ 80 µm [7].

Determination of the apparent density, water absorption and open porosity of the experimental samples was performed by hydrostatic weighing in water on samples of ceramic materials weighing from 50 to 80 g.

Samples in the form of tablets with a diameter of 20 mm and a height of 3 mm were used to determine the dielectric constant and the tangent of the dielectric loss angle. The measurements were performed on an automated device (Tangent-3M), designed to measure the characteristics of the dielectric loss in the range 0.0001 to 1 at a range of operating voltages between 0 and 270 V.

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 CuKβ radiation and a nickel filter under standard operating conditions. The American ASTM 1527 21 file was used to identify phases [6].

Studies of the morphology of the developed ceramic materials were performed by scanning electron microscopy on a microscope JSM-6390LV (Jeol, Japan) in the mode of secondary electrons. The study was subjected to chipping of materials, which allowed to assess the features of its structure more objectively (because the fault reveals defective areas of the sample).

Total shrinkage is determined by changes in linear dimensions after firing. Shrinkage is determined on tiles measuring 100×100×10 mm.

Hardness was tested using the Rockwell method. According to this method of hardness measurement, the depth of penetration into the test material of the diamond pyramid is found.

6. Results and discussion

Using the method of X-ray analysis, it was determined that the main contribution to the formation of micropores is made by aluminum hydroxide of a hydrargillite structure as a result of the removal of constitutional water and the rearrangement of the crystal lattice under the influence of heat treatment with the formation of porous fine-grained aggregates with a highly developed surface, consisting of single-crystal particles of corundum.

Thus, this study confirm the feasibility of using aluminum hydroxide to intensify the solid-phase synthesis of aluminosilicates, in particular $SrAl_2Si_2O_8$ $BaAl_2Si_2O_8$ and sintering ceramics, which are of considerable interest for the technology of ceramic RPM.

The paper investigates metallurgical alumina brand G-00, as well as alternative aluminum-containing raw materials (micronized alumina brand ST3000 SDP, and aluminum hydroxide brand GD-00), which are of interest in terms of intensification of structure and phase formation of ceramic RPM based on barium anornurite), and other aluminosilicates.

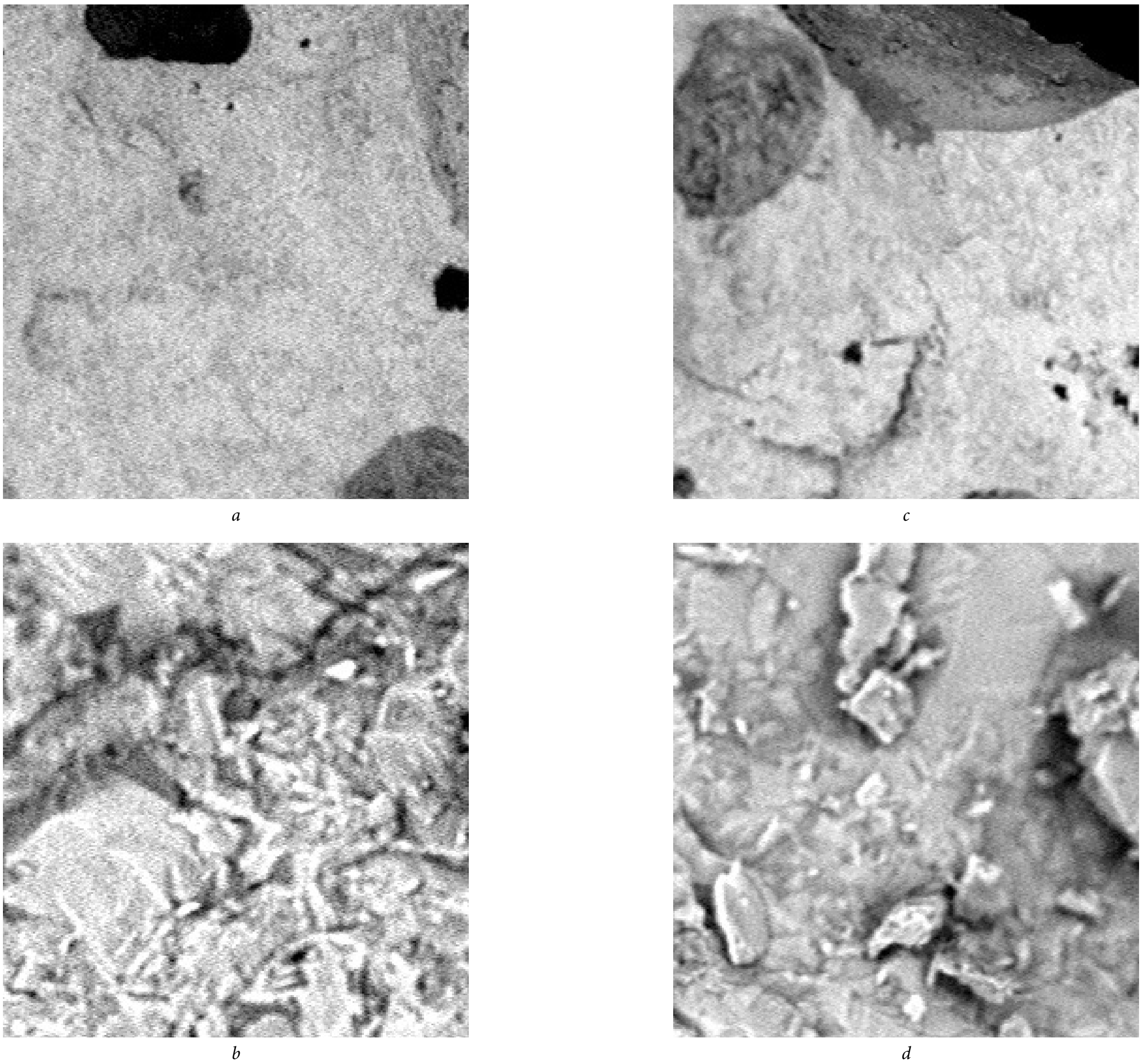

Fig. 1 *SEM images of test samples with magnification of ×250 Sample I (a), Sample II (c), and magnification of ×2000 Sample I (b), Sample II (d)*
1. ábra *A próbatestek SEM felvételei 250-szeres nagyítással I. minta (a), II. minta (c), 2000-szeres nagyítással I. minta (b), II. minta (d)*

Material	The content of components, wt. %		
	Sample I	Sample II	Sample III
Novoselivsky sand	30.05	30.10	28.66
Zinc whitewash	34.11	34.17	32.54
Barium carbonate	21.16	21.19	20.18
Alumina metallurgical G-00	14.67	-	-
Alumina micronized ST3000SDP	-	14.54	-
Aluminum hydroxide GD-00	-	-	18.62

Table 1 *Batch composition of the samples*
1. táblázat *A minták összetétele*

The data obtained as a result of differential thermal and petrographic analysis indicate the feasibility of using alternative aluminum-containing materials to intensify low-temperature synthesis of celsian.

The compositions of raw material mixtures (*Table 1)* are calculated, in which the aluminum-containing component is represented by different raw materials: metallurgical alumina G – 00 (I), micronized alumina CT3000SDP (II) and aluminum hydroxide GD – 00 (III).

Properties are shown in *Table 2*, all samples fully comply with the norms of dielectric properties for radiolucent ceramics (dielectric loss tangent $tg\delta$ = 10-2 ... 10-5, dielectric constant ε <10). Sample I has zero total porosity and water absorption, but has the highest total shrinkage (6.05%). According to the obtained data, it is expedient to use both G-00 metallurgical alumina and CT3000SDP micronized alumina for further research.

As can be seen from the microphotographs of *Figs. 1a, 1c* taken at a magnification of 250×, ceramic samples I and II, have a crystalline homogeneous structure without visible defects (cracks) and foreign inclusions. Both materials are characterized by the presence of closed pores, mostly spherical in shape. The pore size varies in a wide range: from 4 μm to 207 μm. The preferred pore size is ~25 μm.

Sample	Properties								
	General shrinkage L_{gen}, %	Imaginary density ρ, g/cm³	Water absorption W, %	Total porosity Pt, %	Dielectric constant, ε	Tangent of the dielectric loss angle, tgδ	Rockwell hardness, HRA	Vickers Hardness, HV	Strength limit of compression $\sigma_{ст}$, MPa
I	6.05	2.99	0	0	2.85	0.0076	74	471	1520
II	2.35	2.99	0.18	0.54	3.11	0.0044	72	435	1405
III	5.83	2.88	0.6	1.74	2.46	0.0091	56	180	610

Table 2 Properties of samples fired 1200 °C
2. táblázat 1200 °C-on égetett minták tulajdonságai

The compared microphotographs indicate that the use of micronized alumina (sample II) can reduce the closed porosity of the material by reducing the pore size. Photographs of the microstructure of the samples at high magnification (× 2000) are more informative. The obtained data indicate that in comparison with sample I obtained using metallurgical alumina, the structure of sample II containing micronized alumina is fine-crystalline. In *Fig. 1b* and *1d*, it can be seen that the inner surface of the pores is covered with small crystalline neoplasms. The difference in the shape and size of the crystals is also noticeable. In both samples there are lamellar crystals with a size of 22.4×11.4 μm (for example, barium aluminate) and needle crystals of 15.75×0.55 μm (celsian). Finely divided willemite crystals up to 1.70×1.14 μm in size form clusters between larger crystals, which contributes to the compaction of the material.

The effect of different types of aluminum-containing raw materials on the main properties of radiotransparent ceramic materials based on the BaO - ZnO - Al_2O_3 - SiO_2 system was studied.

It is established that all samples obtained using the developed masses meet the requirements for RPM on electrophysical characteristics. Due to the maximum level of sintering at a firing temperature of 1200 °C (water absorption W = 0 - 0.5%, open porosity Pv = 0 - 1.74%) the received materials belonging to densely sintered ceramics are characterized by high indicators of durability and hardness.

Microscopic studies showed the presence of closed porosity. The positive effect of using CT3000SDP micronized alumina is noted by the reduction in the number of pores due to the increase in the number of small willemite crystals. In general, the work solves the problem of obtaining ceramic radiopaque materials and studying their properties depending on the phase composition and structure.

7. Conclusions

Raw material compositions containing different types of aluminum-containing raw materials were developed: metallurgical alumina brand G-00, micronized alumina brand ST3000 SDP and aluminum hydroxide brand GD-00.

It is established that the materials fired at a temperature of 1200 °C are characterized by the maximum level of sintering (W = 0-0.5%, P = 0-1.74%) and completely satisfy requirements to radio-transparent materials on electrophysical characteristics. ε = 2.08 - 3.85, $tg\delta$ = (0.0091-0.0755) · 10^{-2}. Samples of ceramics obtained using metallurgical alumina G – 00 predominate in terms of the level of physical and mechanical properties and σ_{st} = 1529 MPa).

The microstructure of the samples has a high density, but in the materials obtained in the laboratory there are closed pores, mostly spherical in shape with an average size of ~25 μm, the number of which decreases when using micronized alumina.

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Ref.:
Bilohubkina, K. V. – **Fedorenko**, O. Yu. – **Lisachuk**, G. V. – **Kryvobok**, R. V., – **Zakharov**, A.V.: *Influence of aluminum-containing raw materials on the properties of radio-transparent materials*
Építőanyag – Journal of Silicate Based and Composite Materials, Vol. 75, No. 3 (2023), 84–87. p.
https://doi.org/10.14382/epitoanyag-jsbcm.2023.12