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STUDY OF THE PROCESS OF PRODUCING CERAMIC GRANITE BASED ON MINERAL RAW MATERIALS AND SILICA PRODUCTION WASTE

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Abstract. Ceramic materials are widely utilized in construction and aerospace due to their mechanical strength, thermal resistance, and longevity. With increasing demand for high-quality finishing products and a global shift toward efficient resource use, it is vital to develop innovative technologies for porcelain stoneware manufacturing. This study focuses on improving the production process of porcelain stoneware in Kazakhstan by integrating microsilica into formulations based on natural raw materials from the Turkistan region. Microsilica, a by-product of ferrosilicon and metallurgical slag processing, has shown great potential in enhancing strength, durability, and water resistance in ceramic compositions. The research includes the characterization of silicon-containing minerals and other types of local geological raw materials. Several new ceramic mass formulations were developed, and the resulting porcelain stoneware samples were tested under laboratory conditions. The influence of technological parameters on the physical and mechanical properties of the final products was systematically analyzed. As a result, tile materials intended for wall and floor applications were successfully produced using natural resources from Turkistan. These tiles demonstrated improved flexural strength (up to 41 MPa), extremely low water absorption (0.023%), and enhanced frost resistance (up to 107 freeze–thaw cycles). Additionally, reduced water absorption contributed to decreased shrinkage during firing and better dimensional stability. The findings confirm that local Turkistan raw materials, when combined with microsilica, provide a promising pathway for the production of high-performance porcelain stoneware. This approach supports the advancement of Kazakhstan's ceramic industry while promoting sustainable practices through the utilization of industrial by-products.

Keywords: silica fume, ceramic granite, frost resistance, water absorption, wear resistance, shrinkage, microsilica

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МИНЕРАЛДЫ ШИКІЗАТ ПЕН КРЕМНИЙ ӨНДІРІСІНІҢ ҚАЛДЫҚТАРЫ НЕГІЗІНДЕ КЕРАМОГРАНИТ АЛУ ПРОЦЕСІН ЗЕРТТЕУ

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Аннотация. Керамикалық материалдар құрылыс және аэроғарыш өнеркәсібінде кеңінен қолданылады сондықтан керамика өнеркәсібінің дамуы жақсартылған қасиеттері бар жаңа инновациялық өнімдерді жасауды талап етеді. Жоғары сапалы әрлеу материалдарына сұраныстың артуы мен дәстүрлі шикізат ресурстарының шектеулі жағдайында керамогранит өндірісінің тиімді технологияларын іздеу өзекті мәселе болып отыр. Зерттеудің мақсаты — пайдалану сипаттамалары жақсартылған керамогранит түрін әзірлеу. Ғылыми жұмыста Қазақстандағы жергілікті шикізатты пайдалана отырып микросилика қосу арқылы керамогранит өндіріс технологиясын жетілдіруге бағытталған зерттеу нәтижелері ұсынылды. Металлургиялық шлактарды өңдеудің өнімі болып табылатын микросилика керамограниттің физика-механикалық қасиеттерін жақсартуда жоғары әлеует көрсетті. Зерттеу нысандары ретінде кремнийқұрамды материалдар және осы технологияда қолданылатын басқа да тау-кен шикізаттары, жасалған жаңа шикізат композицияларының рецептуралары мен алынған синтезделген керамогранит үлгілері алынды. Шикізат материалдарының керамогранит өндірісіне жарамдылығы зерттеліп, технологиялық параметрлердің оның қасиеттеріне әсері қарастырылды. Түркістан облысының табиғи шикізаттары негізінде қабырға мен еденге арналған жаңа плиталық материалдар алынды, олардың беріктік қасиеттері жақсарған және су сіңіргіштігі нөлге тең. Зерттеу барысында микросилика мөлшері әртүрлі болатын жаңа керамикалық масса рецептуралары әзірленді. Эксперименттік мәліметтер микросилика қосу керамограниттің иілуге беріктігін 41 МПа-ға дейін (стандарттан жоғары) арттыруға, су сіңіргіштігін 0,023%-ға дейін төмендетуге және аязға төзімділігін 107 циклге дейін ұлғайтуға мүмкіндік беретінін көрсетті. Сонымен қатар, су сіңіргіштіктің төмендеуі керамограниттің шөгуін арттырады. Алынған нәтижелер отандық керамика өнеркәсібін дамытуға, өндірілетін өнім түрлерін кеңейтуге және экологиялық мәселелерді шешуге жаңа мүмкіндіктер ашады.

Түйін сөздер: микрокремнезем, керамогранит, аязға төзімділік, су сіңіру, тозуға төзімділік, шөгу, микросилика

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ИССЛЕДОВАНИЕ ПРОЦЕССА ПОЛУЧЕНИЯ КЕРАМОГРАНИТА НА ОСНОВЕ МИНЕРАЛЬНОГО СЫРЬЯ И ОТХОДОВ КРЕМНИЕВОГО ПРОИЗВОДСТВА

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Аннотация. Керамические материалы широко применяются в строительной и авиакосмической промышленности. Развитие керамической промышленности требует создания нового инновационного изделия с улучшенными свойствами. В условиях растущего спроса на высококачественные отделочные материалы и ограниченности традиционных сырьевых ресурсов актуальной задачей является поиск новых, более эффективных технологий производства керамогранита. Цель исследования – разработка керамогранита с улучшенными эксплуатационными характеристиками. В работе представлены результаты исследования, направленные на совершенствование технологии производства керамогранита в Казахстане с использованием местного сырья путем введения в его состав микросилики. Микросилика как продукт переработки металлургических шлаков, продемонстрировала высокий потенциал для улучшения физико-механических свойств керамогранита. Объектами исследования являются кремнийсодержащие материалы, а также используемые в данной технологии другие виды горнорудного сырья, разработанные новые рецептуры сырьевых композиций и полученные синтезированные образцы керамогранита. Исследованы сырьевые материалы на предмет их пригодности для производства керамогранита, изучено влияние технологических параметров на свойства керамогранита. Получены новые плиточные материалы для стен и пола на основе природного сырья Туркестанской области с улучшенными прочностными свойствами и нулевым водопоглощением. В ходе исследования были разработаны новые рецептуры керамических масс с различным содержанием микросилики. Экспериментальные данные свидетельствуют о том, что добавление микросилики позволяет повысить прочность керамогранита при изгибе 41 МПа (выше стандарта), снижение водопоглощения до 0,023% и увеличение морозостойкости до 107 циклов, а также снижение водопоглощения повышает усадку керамогранита. Полученные результаты открыли новые перспективы для развития отечественной керамической промышленности, расширения ассортимента производимой продукции и решения экологических проблем.

Ключевые слова: микрокремнезем, керамогранит, морозостойкость, водопоглощение, износостойкость, усадка, микросилика

Introduction. Development of the construction materials industry in the Republic of Kazakhstan is aimed at the production of high-quality and durable ceramic products - specifically ceramic granite - based on locally sourced natural mineral raw materials. The quality and durability of ceramic products are influenced by their compressive strength and frost resistance. High-strength ceramics, including ceramic granite, are characterized by increased indicators of both compressive strength and frost resistance. In particular, ceramic granite composed of quartz, feldspar, and kaolin demonstrates a unique combination of mechanical strength and chemical inertness. Its microstructure, characterized by coarse quartz grains, mullite crystals, and an amorphous silicate phase, defines its exceptional properties. In the context of rising demand for thin, large-format tiles, understanding these interrelations becomes crucial for the development of new generations of ceramic granite that maintain high-performance characteristics.

The manufacturing process of ceramic granite includes several stages, typically using tunnel roller kilns with designated zones: preheating (or drying), preliminary heating, firing, rapid cooling, slow cooling, and final cooling. The resulting products demonstrate high mechanical properties and near-zero water absorption. In some cases, the firing process results in surface defects known as pinholes or craters (Bayandina, 2011:80; Moshnyakova, 2017:100).

According to E.V. Vdovina's research (Vdovina, 2007: 102), during sintering of raw materials in the presence of a liquid phase, carbon-containing components act as reducing agents at high temperatures. It was established that at firing temperatures starting from 700°C, new crystalline phases begin to form, including SiO_2, silicates, and complex aluminosilicates. At 800-950°C, decomposition of limestone and dolomite carbonates occurs with the release of CO_2, alongside the thermal breakdown of sulfates and fluorides. At high temperatures of 1150-1200°C, a liquid phase forms due to the presence of feldspars rich in alkali metals. These feldspars act as fluxes, and the liquid phase fills pores and dissolves clay mineral oxides, leading to significant shrinkage and densification of the body. The ceramic phase composition includes a broad array of minerals formed during sintering of clay, sand, and feldspar-based raw materials.

In nature, feldspars represent a large and widely distributed group of rock-forming minerals in the silicate class, while kaolin is a clay primarily composed of the mineral kaolinite - $Al_4[Si_4O_{10}](OH)_8$. Its main composition includes approximately 47% silicon dioxide (SiO_2), 39% aluminum oxide (Al_2O_3), and 14% water (H_2O) (Moshnyakova, 2017:105).

Quartz is among the most abundant minerals in the Earth's crust, serving as a rock-forming component in most igneous rocks, and it also appears in mineral mixtures and silicates. Quartz constitutes up to 12% of the Earth's crust in its free form, and overall accounts for more than 60% of its SiO_2 content (Vdovina E.V., 2007: 103).

Cristobalite (SiO_2) is a common ceramic mineral, often formed as a neo-mineral from quartz or clay materials. Another significant mineral is mullite - a silicate-class compound with a general formula of $mAl_2O_3 \cdot SiO_2$, where m varies across a broad range, including fractional values. Mullite forms upon heating kaolinite to approximately 950°C and is a primary component in synthetic ceramic granite. Hematite, a widely distributed iron oxide mineral (Fe_2O_3), is often present as an accompanying component. Iron oxides, in combination with other metal oxides, impart colors ranging from pink to brown to ceramic granite and contribute to the formation of high-quality decorative surface finishes upon heating (Shakelford, 2008: 201; Moshnyakova, 2017: 101; Martín-Márquez, 2010: 1599).

Currently, the production of ceramic granite involves high-temperature firing, during which tiles are thermally processed to a cold state within 60-90 minutes. This rapid heating promotes the formation of new crystalline phases through complex chemical reactions involving kaolinite, illite, mica, and feldspars. As a result, part of the quartz remains unaltered, while metakaolinite - formed from the dehydration of kaolinite - transforms into mullite ($3Al_2O_3 \cdot 2SiO_2$).

Rapid firing of ceramic granite is accompanied by intensive phase transformations. The starting minerals - kaolinite, illite, mica, feldspars - undergo complex chemical reactions that result in new crystalline phases. Specifically, the dehydration of kaolinite leads to the formation of metakaolinite, which subsequently transforms into mullite, while part of the quartz remains embedded in the final structure (Romero, 2015).

The chemical reactions occurring during the high-temperature processing of ceramic granite raw materials underpin the formation of its structure and properties. Kaolinite, the primary component of the raw mixture, undergoes dehydration and subsequent condensation to form mullite. The resulting mullite is the main component of ceramic granite, contributing to its high strength, hardness, thermal resistance, and wear resistance (Adyrbayev, 2017: 131).

The mullite formation reaction can be represented as follows:

$$Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \xrightarrow{500°C} Al_2O_3 \cdot 2SiO_2 + 2H_2O \xrightarrow{980°C} \text{Si-Al(spinel)} + SiO_2 \xrightarrow{1200°C} 3Al_2O_3 \cdot 2SiO_2 + SiO_2 \text{ (amorphous)} \quad (1)$$

As the temperature reaches 1200°C, additional chemical transformations occur, leading to the formation of new crystalline phases that define the final composition of the ceramic product.

Due to a lack of Al_2O_3 in the original material, amorphous SiO_2 is released during thermal treatment. To enhance mullite formation, supplementary Al_2O_3 should be added to the mixture. The thermodynamic feasibility (ΔG) of mullite-forming reactions, including those leading to $3Al_2O_3 \cdot 2SiO_2$ and other compounds in the 25-1200°C range, must be investigated.

To date, the production of ceramic granite utilizing microsilica - an industrial byproduct of silicon manufacturing - as an active component has not been extensively studied, nor has its effect on the physical and mechanical properties of ceramic granite. Incorporating microsilica as a silicon-containing additive allows for the optimization of the phase composition and microstructure of the material, thereby enhancing its strength and hardness. The physical and chemical properties of the resulting ceramic granite samples were thoroughly characterized using a wide array of analytical techniques. The findings demonstrate the scientific relevance and promising potential of microsilica application in the production of high-performance ceramic materials (Yessimov, 2020:355; Lewicka, 2010:582).

Materials and methods of research. To produce high-strength ceramic products, a study was conducted on the effect of microsilica on the structure and properties of ceramic granite.

The production of ceramic granite replicates the natural granite formation process in a technologically enhanced and time-compressed manner. However, artificial ceramic granite exhibits significantly superior properties compared to natural granite. In the manufacturing process, the recipe-based components are mixed and pressed using hydraulic presses under high pressure, followed by firing in roller kilns. The firing stage is the final phase of the technological cycle. Due to the higher homogeneity of the raw mixture in terms of chemical and mineralogical composition (compared to natural granite), and the specific firing technology, the resulting material achieves water absorption below 0.5% and a flexural strength of no less than 35 N/mm², in accordance with EN 14411:2009. Firing is one of the fundamental operations in the production of ceramic granite. During firing, the ceramic material is formed as the raw materials transform into new crystalline and amorphous phases, imparting the necessary properties: mechanical strength and hardness, low porosity and water absorption, and chemical resistance. Firing involves heating the material - transferring energy within the kiln - for a certain period and with a specific intensity, allowing controlled physicochemical changes to occur in the material. The composition of the raw material mixture was analyzed using a JSM-6490LV scanning electron microscope equipped with an INCA Energy-350 energy-dispersive microanalysis system and the HKL Basic system for structure and texture analysis of polycrystalline samples. Additional physicochemical analysis methods were also used, including X-ray diffraction (XRD) with a DRON-3 instrument and differential thermal analysis (DTA) (Kulinich, 2000:372; Sanchez, 2006:2533).

The ceramic mass for ceramic granite production contained clay components (kaolinite and white-firing clays), feldspar, and a silicon-containing component (microsilica). The composition was as follows (by weight percentage): kaolinite clay 32-34%, kaolin 24-26%, feldspar 23-25%, white-firing clay 5-17%, and microsilica 2-5% (Darkhan, 2023).

Special attention was given to the influence of the flux - feldspar - and microsilica, a byproduct from LLP «Tau-Ken Temir», on sintering behavior and phase formation, as well as to the influence of the particle size distribution of the components on reaction kinetics during firing. The chemical composition of the raw materials is shown in table 1.

Table 1 - Chemical composition of raw materials

	Raw materials	SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	MgO	K_2O	Na_2O	P_2O_5	CO_2
1	B-1 Clay (Berezovskoye deposit)	57.10	37.14	0.77	2.00	0.64	-	2.32	-	-	-
2	NK-5 Clay («Novoor Ceramic»)	41.76	24.42	1.33	0.92	-	-	1.20	-	-	30.13
3	Kaolin (Soyuznoye deposit)	29.60	11.51	-	-	39.17	-	4.31	5.10	-	10.30
4	Feldspar (Vishnevogorsk deposit)	64.28	32.50	0.68	0.70	0.39	-	1.45	-	-	-
5	Microsilica (by product of LLP «Tau-Ken Temir»)	93.23	2.62	-	1.23	1.20	0.42	0.43	0.88	-	-

As shown in table 1, the primary constituents of the raw materials are SiO_2 and Al_2O_3. During firing, these oxides form mullite - a mineral responsible for the strength and enhanced properties of ceramic granite.

All raw materials were separately dry-milled in a laboratory ball mill for 16 hours and then sieved through control meshes of 0.224, 0.125, 0.08, 0.063, and 0.04 mm. The materials were dosed using T-200 laboratory scales. Several compositions of ceramic masses were tested, all based on feldspar, kaolin, clays, and microsilica.

Test samples, sized 60×30×5 mm, were prepared by semi-dry pressing of powders with 8-11% moisture. The press-powder was granulated by sieving through a 1.0 mm mesh for even moisture distribution. The powder was conditioned for 24 hours in a desiccator. Specimens were pressed semi-dry on a laboratory hydraulic press at 400 MPa, then dried at 110°C in a drying oven. The final firing was carried out in a high-temperature electric furnace (LHT 02/16) at 1100-1300°C.

Several raw compositions of the ceramic granite mass were prepared for the study. The ceramic mass for producing ceramic granite, containing a clay component, kaolin, feldspar, and a silicon-containing component, includes kaolin and white-firing clays as the clay component, and microsilica as the active component (Adyrbaev, 2024: 6).

The raw composition of the ceramic granite mass is presented in table 2.

Table 2 – Raw composition of the ceramic granite mass

Component	Mass % Content			
	№1	№2	№ 3	№4
B-1 Clay	16	16	16	16
NK-5 Clay	24	24	24	24
Feldspar	33	33	33	33
Kaolin	26	25	24	23
Microsilica	1	2	3	4
Total,%	100	100	100	100

As seen in table 2, the main components of the raw mixtures are feldspar, kaolin, and clay. Microsilica constitutes 1-4% of the mixture.

To optimize the composition of the ceramic granite mass using microsilica, the influence of different ratios of the raw mixture components on the properties of the obtained samples was studied. The elemental composition (table 3) and structure of the microsilica (figure 1) were preliminarily investigated.

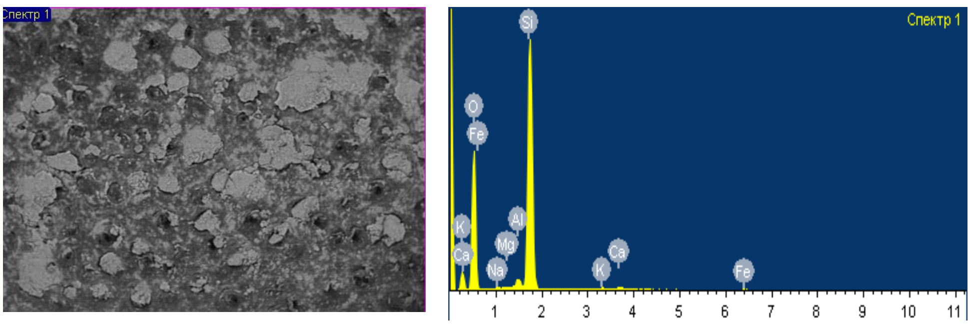


Figure 1 - Structure and microanalysis of microsilica according to SEM data

Table 3 - Elemental composition of microsilica

Elemental composition of microsilica, %								
O	Na	Mg	Al	Si	K	Ca	Fe	Total
58.10	0.57	0.22	1.21	38.09	0.31	0.75	0.75	100

As seen from figure 1 and the data in table 3, microsilica mainly contains silicon, aluminum, sodium, calcium, and iron.

Results. The firing process of the ceramic granite mass is conducted by gradually increasing the temperature up to 1200ºC (1473K) for 60-90 minutes. A particular scientific interest is the thermodynamic feasibility (ΔG) of the mullite formation reaction - $3Al_2O_3{\cdot}2SiO_2$ and other compounds in the temperature range of 25-1200ºC (298-1473K). Information regarding the joint decomposition of the minerals - feldspar, kaolin, clays, microsilica, and thermodynamic analysis of the reactions involved is absent in the literature. An interesting aspect is the study of changes in the Gibbs free energy (G°) in the temperature range of 298-1573K.

To assess the feasibility of reactions 2-7, let's calculate the Gibbs free energy. The Gibbs free energy (ΔG°) was calculated using the HSC-51 software package developed by the Finnish metallurgical company Outokumpu. For calculations, the Reaction Equations subroutine was used, as well as reference data for ΔH° and S° for various compounds (Zubekhin, 2014: 52).

The changes in the Gibbs free energy (ΔG°) with temperature (T) were calculated for the reactions:

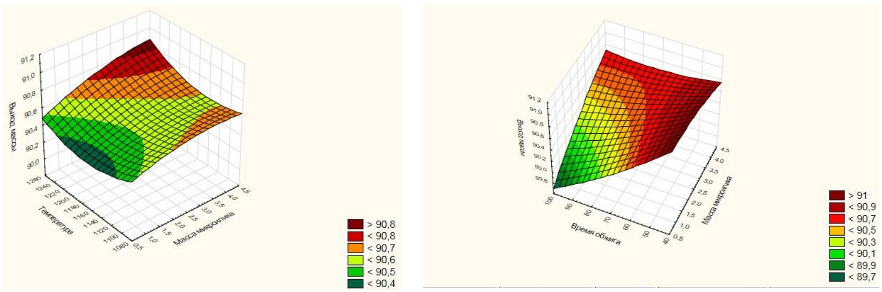
$$Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O = Al_2O_3{\cdot}2SiO_2 + 2H_2O \quad (1)$$
$$3(K_2O{\cdot}Al_2O_3{\cdot}6SiO_2) = 3Al_2O_3{\cdot}2SiO_2 + 3K_2SiO_3 + 13SiO_2 \quad (2)$$
$$3(Na_2O{\cdot}Al_2O_3{\cdot}6SiO_2) = 3Al_2O_3{\cdot}2SiO_2 + 3Na_2SiO_3 + 13SiO_2 \quad (3)$$
$$Na_2O{\cdot}K_2O{\cdot}Al_2O_3{\cdot}10SiO_2{\cdot}8H_2O = Na_2O{\cdot}K_2O{\cdot}Al_2O_3{\cdot}10\,SiO_2 + 8H_2O \quad (4)$$
$$3(Na_2O{\cdot}K_2O{\cdot}Al_2O_3{\cdot}10SiO_2) = 3Al_2O_3{\cdot}2SiO_2 + 3Na_2SiO_3 + 3K_2SiO_3 + 22SiO_2 \quad (5)$$
$$Al_2O_3{\cdot}2SiO_2 + 2Al_2O_3 = 3Al_2O_3{\cdot}2SiO_2 \quad (6)$$

The thermodynamic characteristics of the Gibbs free energy (ΔG°) in the temperature range 25-200ºC (298-473K) for all reactions 2-7 show that the ΔG° values, calculated using the HSC software, are negative (ΔG° = -5400 to -52700 J/mol), indicating the feasibility of reactions forming $Al_2O_3{\cdot}2SiO_2$ and $Na_2O{\cdot}K_2O{\cdot}Al_2O_3{\cdot}10SiO_2$. In the temperature range 25-300ºC (298-573K), for reactions 3, 4, and 5, the ΔG° values are also negative, indicating that reactions forming $3Al_2O_3{\cdot}2SiO_2$, K_2SiO_3, Na_2SiO_3, and $SiO_2$are possible. In all reactions, the primary mineral, mullite – $3Al_2O_3{\cdot}2SiO_2$, is formed. In the temperature range 298-973K, reaction 7 may proceed through the interaction of the mineral $Al_2O_3{\cdot}2SiO_2$formed in reaction (2) Al_2O_3in the microsilica, leading to the formation of secondary mullite – $3Al_2O_3{\cdot}2SiO_2$, which is indicated by the negative Gibbs free energy value (ΔG° = -2700 J/mol). Further temperature increase to 1473K may lead to the melting of low-melting minerals. Therefore, the preliminary thermodynamic calculations using a computer in the temperature range 298-1573K suggest the feasibility of reactions (3-7) forming primary and secondary mullite -$3Al_2O_3{\cdot}2SiO_2$, as well as low-melting silicates Na_2SiO_3, K_2SiO_3, andSiO_2.

For the production of ceramic granite by pressing from semi-dry powders, a slip casting technology was used to prepare the mass. The tests were conducted in laboratory conditions. Pre-dried components were selected in a specific percentage and ground in a laboratory ball mill. The resulting mass - the slip - consisted of particles of sufficiently fine and uniform fractions. The prepared slip was then dried and ground to a powder-like consistency, and water (5-6% by weight of the powdered material) was added for subsequent molding. The samples were dried in a drying oven at 110ºC and fired in a high-temperature electric furnace LHT 02/16 at 1100-1300ºC (Brykov, 2011:147; Ryshchenko, 2008: 81).

Optimization of the mixture compositions and firing process parameters for achieving the required degree of mullite formation was carried out using the Statistica-10 program. Graphs were constructed showing the relationship between mass yield and mullite formation degree with respect to time and temperature, which are presented in Figures 2 and 3.

Figure 2 shows three-dimensional images of the function surface depicting the degree of mass yield from mullite with respect to temperature and firing time.

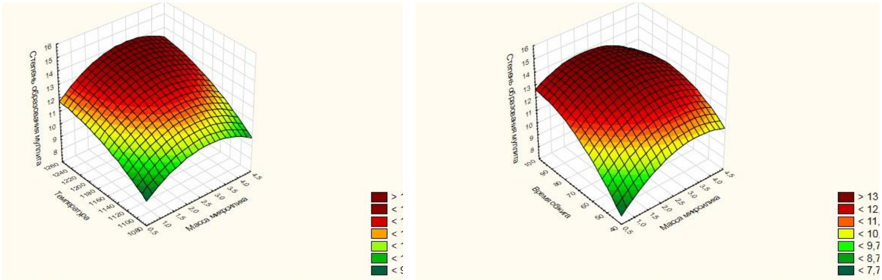


a) b)

Figure 2 - Dependence of mullite mass yield on firing temperature (a) and time (b)

As shown in Figure 2, the three-dimensional surface plot (highlighted in red) demonstrates that the highest yield of mullite mass is observed at a firing temperature of 1250ºC, reaching 90.8% (a), and at a firing duration of 40 minutes, the yield reaches 91.0% (b).

Figure 3 presents three-dimensional surface plots illustrating the degree of mullite formation as a function of firing temperature and duration.

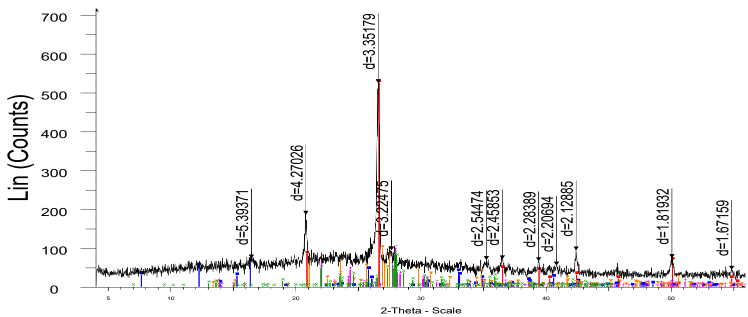


c) d)

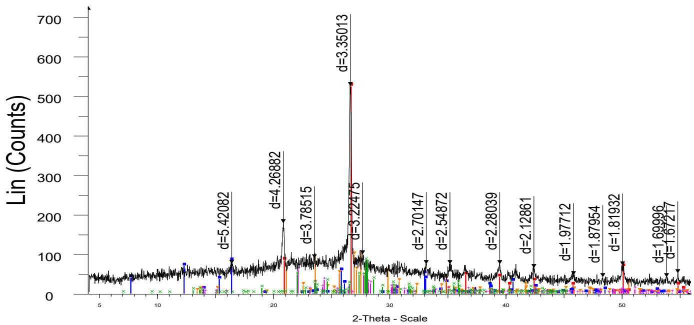
Figure 3 - Dependence of the degree of mullite formation on firing temperature (c) and time (d)

As shown in figure 3, the three-dimensional surface plot (highlighted in red) indicates that the highest degree of mullite formation is observed at a firing temperature of 1250ºC, exceeding 14.0% (c), and at a firing duration of 90 minutes, exceeding 13.0% (d).

The high physico-mechanical properties of the laboratory tile samples are attributed to the achievement of optimal chemical and mineralogical composition parameters (with microsilica content ranging from 1 to 4%) and the structure of the synthesized mass compositions (figures 4 and 5).

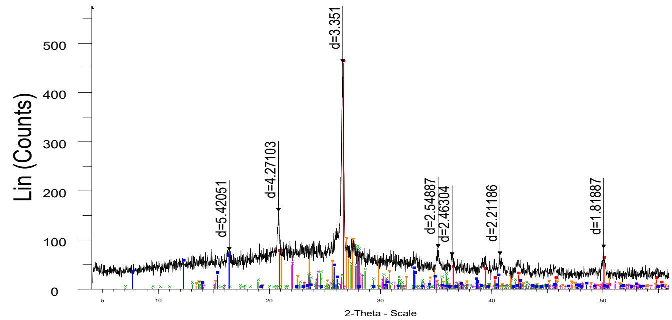


Sample №1

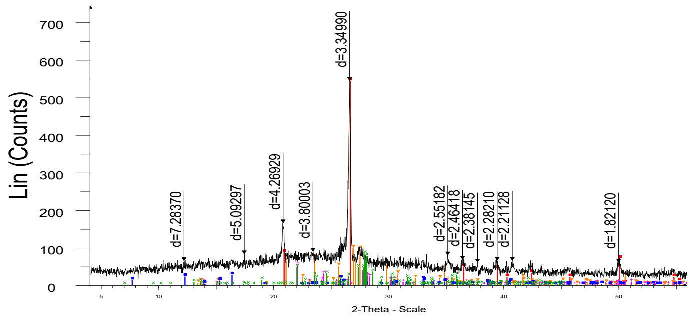


Sample №2

Figure 4- Diffractograms of samples № 1 and № 2



Sample № 3



Sample № 4

Figure 5-Diffractograms of samples №3 and №4

Figures 4 and 5 show that the samples contain silicon oxide, mullite, and the minerals -anorthite, albite, as well as hematite. X-ray diffraction (XRD) analysis of the obtained samples indicates that the diffractogram of the optimal composition of sample № 1 of the synthesized ceramic granite (Figure 4) displays peaks with intensities (d/n = 5.41049, 3.34996 Å) corresponding to mullite ($3Al_2O_3 \cdot 2SiO_2$), and peaks with intensities (d/n = 4.26383; 3.34998; 2.13111; 1.81733 Å) corresponding to quartz (SiO_2).

The investigation of physicochemical processes accompanying the formation of new mineral and liquid phases revealed the potential of using microsilica as a silicon-containing raw material. The samples exhibit a fairly dense structure (figure 6).

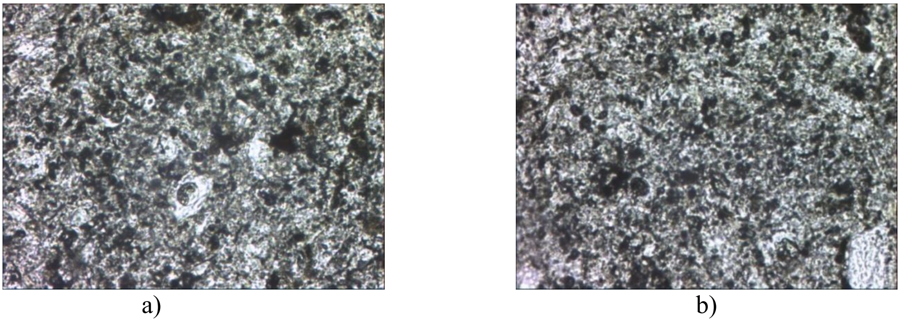


Figure 6-Microstructure of ceramic granite produced with microsilica:
(a) - mass with 1% microsilica addition,
(b) - mass with 2% microsilica addition.

Microstructural analysis revealed the presence of clearly distinguishable feldspar relics composed of a glassy phase and mullite. Sample (a) exhibits a more porous structure, whereas sample (b) displays a denser structure due to a higher content of mullite crystals and glassy phase. Quartz grains are surrounded by rims of high-silica glass and pores of various shapes and sizes. The micrographs of the fracture surfaces show a glassy matrix interspersed with uniformly distributed submicroscopic mullite crystals. Mullite regions corresponding to the original feldspar particles, as well as partially decomposed masses of clay substances, are clearly identifiable. A distinctive feature of the feldspar relics is the presence of large mullite needles growing inward from the surface in the direction of chemical composition changes due to alkali diffusion. Figure 7 presents the microstructure of the resulting ceramic granite (sample №. 1).

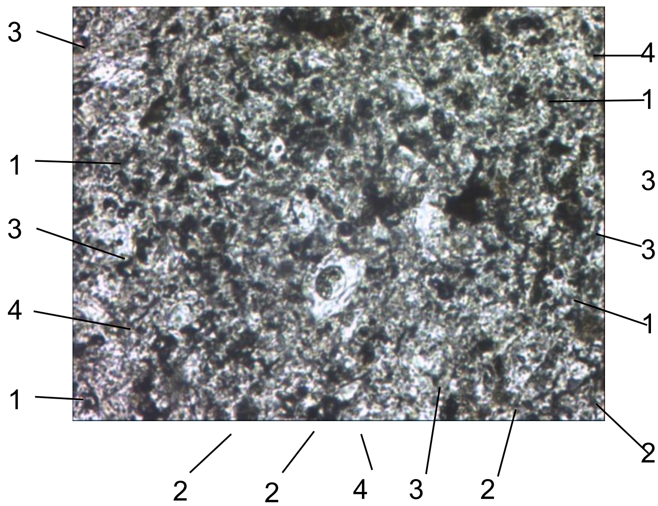


Figure 7 -Microstructure of ceramic granite (sample № 1) produced with microsilica addition (magnification ×1000):
1 - quartz, 2 - clay residues, 3 - mullite, 4 - corundum

As shown in figure 7, the sample produced with microsilica addition exhibits a needle-like morphology of mullite crystals (3) in the range of 14-15%, as well as corundum crystals (4) in the range of 2-4%, quartz (1) in the range of 22-26%, and a glassy phase. The mullite crystals have a thickness of 25-36 nm and a length ranging from 5 to 16 µm, classifying them as mid-sized mullite.

Thermal analysis was carried out using a Q-1500 derivatograph (MOM, Hungary) with a sensitivity of 200 and a heating rate of 7.5 °C/min (figure 8).

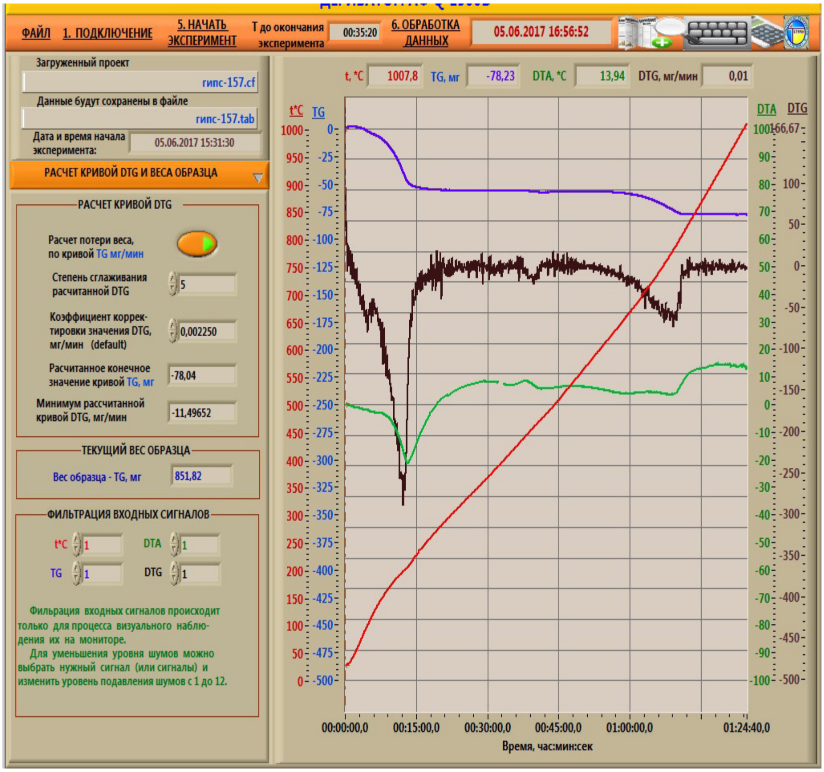


Figure 8 - DTA curve of microsilica

Samples for thermal analysis were obtained by quartering a representative 3 kg sample, which was ground to the required particle size and thoroughly homogenized. Portions of 2 g were then weighed on technical scales with a sensitivity of 10 mg for thermal analysis.

The derivatogram (figure 8) of the microsilica reveals the following main regions: Low-temperature region (up to 200°C): This region corresponds to the dehydration of microsilica, i.e., the removal of adsorbed water from its structure. Dehydration is accompanied by a loss of sample mass and an endothermic effect on the DTA curve. High-temperature region (200-1500°C): This region encompasses a series of phase transitions and chemical reactions occurring in the microsilica. The most significant feature is a high-temperature exothermic effect, which corresponds to the crystallization of the amorphous phase of microsilica into quartz. Interpretation of DTA of microsilica: The low-temperature endothermic effect indicates the amount of adsorbed water in the microsilica. The high-temperature exothermic effect provides insights into the degree of crystallinity of the microsilica. The higher the intensity of this effect, the more crystallized the microsilica is (Tereshchenko, 2000:31).

The developed composition of the ceramic granite mass was determined through analysis of fusion curves on phase diagrams, physicochemical and structural transformation studies in multicomponent systems during firing, and technological experiment results. The physical and mechanical properties of the ceramic granite samples are presented in table 4.

Table 4 - Physical and mechanical properties of ceramic granite samples

Indicator	Physical and mechanical properties of the samples			
	M-1	M-2	M-3	M-4
Firing shrinkage, %	9.16	11.12	11.02	10.36
Mechanical strength (flexural), MPa	40.4	41.5	40.8	40.6
Water absorption, %	0.029	0.023	0.025	0.026
Frost resistance, number of cycles ≥	104	107	106	105
Abrasion resistance, g/cm³ ≤	0.18	0.17	0.18	0.19

As seen from table 4, among the various compositions of ceramic granite masses, sample M-1 demonstrates the highest performance indicators. Experimental data indicate that the addition of microsilica improves the flexural strength of ceramic granite to 41.5 MPa (exceeding the standard), reduces water absorption to 0.023%, and increases frost resistance to 107 cycles. It also results in an increase in firing shrinkage to 11.12%.

The use of microsilica as a silica-containing component in ceramic granite mixtures yields a beneficial effect, significantly improving the physical and mechanical properties of the synthesized material beyond standard requirements (figure 9).

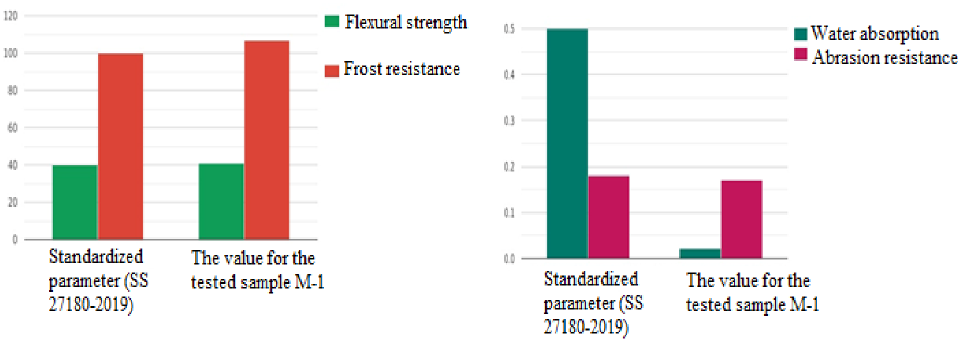


Figure 9 - Physical and mechanical characteristics of the samples

As shown in figure 9, the physical and mechanical test results of the ceramic granite demonstrate a flexural strength of 41 MPa (exceeding the standard), a reduction in water absorption to 0.023%, and an increase in frost resistance to 107 cycles. Additionally, the data indicate improved dimensional stability and enhanced shrinkage of the ceramic granite. The process flow diagram for the preparation of ceramic granite is presented in Figure 10.

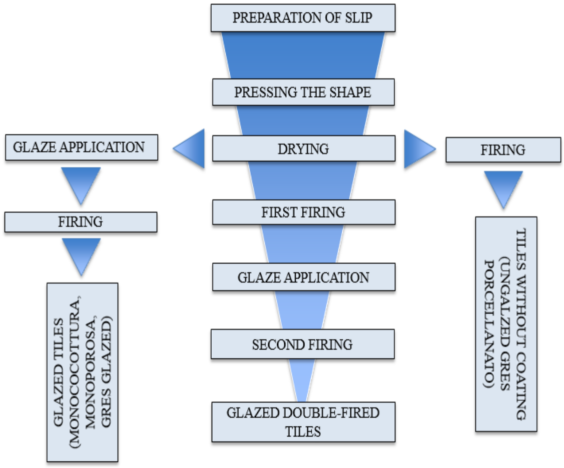


Figure 10 - Process flow diagram of ceramic granite production

As shown in figure 10, the preparation and production of ceramic granite includes the following stages: raw material mixing, mold pressing and drying, first firing, glaze application, second firing, and the resulting finished ceramic granite. The process also allows for the production of unglazed tiles as well as glazed tiles with homogeneous firing. This provides flexibility in manufacturing tiles based on the intended purpose and specific requirements of ceramic granite (Nori, 2010).

Discussion. According to the test results, composition M-1 was identified as the optimal formulation. The study demonstrated that the incorporation of microsilica as a silica-containing component in the ceramic granite batch leads to a significant enhancement in the physical and mechanical properties of the final product. The fine-grained structure of microsilica contributes to improved cohesion within the ceramic matrix, positively influencing both the strength and durability of ceramic granite. This approach opens new opportunities for the development of high-performance construction materials based on industrial byproducts. Microstructural analysis revealed clearly distinguishable relic feldspar fragments composed of glassy phase and mullite crystals. Quartz grains are surrounded by zones of high-silica glass, as well as pores of varying shape and size. Fracture surface micrographs show a glassy matrix permeated by uniformly distributed submicron mullite crystals. Mullite regions, corresponding to the original feldspar particles, are clearly identifiable, along with remnants of partially decomposed clay masses.

Conclusion. This study investigated the effect of microsilica addition on the phase composition and properties of ceramic granite. As an active silica additive, microsilica was introduced into the batch to improve the physical and mechanical performance of the final product.

Various ceramic compositions were developed by varying the content of microsilica while maintaining a fixed ratio of kaolin, feldspar, and white-firing clay. The samples were fired at temperatures ranging from 1200 to 1300 °C. The phase composition and microstructure of the resulting materials were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM). It was found that the addition of microsilica increases the flexural strength of ceramic granite to 41.5 MPa (above the standard), reduces water absorption to 0.023%, improves frost resistance to 107 cycles, and increases shrinkage to 11.12%. The results demonstrate that microsilica, when used as a silica-containing component, enables effective control over the phase composition and structure of ceramic granite, thereby enhancing its performance characteristics. A process flow diagram of the ceramic granite production process is presented. The findings contribute to expanding the potential for developing new high-efficiency ceramic materials.

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