

**МЕТАЛЛИЗИРОВАННЫЕ ГЛАЗУРИ ДЛЯ ДЕКОРИРОВАНИЯ КЕРАМОГРАНИТА
НА ОСНОВЕ СЫРЬЕВЫХ МАТЕРИАЛОВ РЕСПУБЛИКИ БЕЛАРУСЬ****А.Н. Шиманская, Р.Ю. Попов, А.В. Поспелов**

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*Настоящее исследование посвящено изучению возможности получения металли-
зированных нефритованных глазурей для керамогранита с использованием сырьевых ма-
териалов Республики Беларусь. В состав глазурной композиции входили глина легкоплав-
кая, кварцевый песок, доломит, каолин и оксид меди. Полученный в производственных
условиях ОАО «Березастройматериалы» глазурованный керамогранит обладал металли-
зированной поверхностью темно-серой цветовой гаммы. В процессе исследований изучены
физико-химические свойства синтезированных образцов в соответствии с требованиями
действующих международных стандартов, результаты которых показали, что темпе-
ратурный коэффициент линейного расширения глазурей составляет $(65,9-73,4) \cdot 10^{-7} \text{ K}^{-1}$,
микротвердость – 5090–6570 МПа, степень износостойкости – 1–2, термическая стой-
кость – $150 \pm 5 \text{ }^\circ\text{C}$. Структура глазурных покрытий исследовалась с помощью рентгенофа-
зового анализа и сканирующей электронной микроскопии. Установлено, что преобладаю-
щей фазой в покрытии является стекловидная. Кристаллическая составляющая пред-
ставлена анортитом и теноритом, количество которых зависит от состава глазурной
композиции. Благодаря присутствию кристаллической фазы глазурованный керамогра-
нит отличается относительно высокой степенью износостойкости. Для изучения пове-
дения экспериментальных глазурей в процессе термообработки применялся нагреватель-
ный микроскоп и дифференциальный сканирующий калориметр. Определены характери-
стические температуры (спекания, образования сферы и полусферы, плавления), а также
краевой угол смачивания и усадка глазурей в температурном интервале 500–1400 °С. Вы-
явлено, что увеличение содержания оксида меди от 12,5 до 22,5% способствует сниже-
нию температуры спекания на 10–50 °С. Однако основное влияние на поверхностное
натяжение расплава глазури в интервале температур 1050–1200 °С оказывает количе-
ство доломита.*

Ключевые слова: металлизованная глазурь, нефритованная глазурь, керамогранит, смачива-
ющая способность, износостойкость, тенорит

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**METALLIZED GLAZES FOR THE DECORATION
OF PORCELAIN STONEWARE USING RAW MATERIALS OF THE REPUBLIC OF BELARUS**

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The aim of this research was to study the possibility of obtaining metallic (metallized) raw glazes for porcelain stoneware using the raw materials of the Republic of Belarus. Fusible clay, quartz sand, dolomite, kaolin and copper oxide were used to prepare the glazes. The glazed porcelain stoneware obtained under the industrial conditions of BerezaStroimaterialy JSC had dark grey surface with a metallic appearance. The research on the physico-chemical properties of the synthesized samples was carried out under the requirements of existing international standards. The temperature coefficient of linear expansion of glazes was $(65.9-73.4) \cdot 10^{-7} \text{ K}^{-1}$, resistance to surface abrasion (PEI) – 1–2, resistance to thermal shock – $150 \pm 5 \text{ }^\circ\text{C}$. The structure of glaze coatings was characterized by X-ray diffraction analysis and scanning electron microscopy. The glassy matrix was established to be the predominant phase. Anorthite and tenorite were the crystalline components. Their amount varied depending on the glaze composition. Due to the crystalline phases, glazed porcelain stoneware has a relatively high degree of resistance to surface abrasion. A hot-stage microscope and differential scanning calorimeter were used to study the melting behavior of the experimental glazes. The characteristic temperatures (sintering, sphere, half-sphere, fusion), as well as the contact angle and shrinkage of glazes in the temperature range of 500–1400 °C were determined. It was found that an increase in the content of copper oxide from 12.5 to 22.5 % contributes to a decrease in the sintering temperature by 10–50 °C. However, the prevailing influence on the surface tension of the glazes at temperatures 1050–1200 °C had the percentage of dolomite.

Key words: metallic (metallized) glaze, raw glaze, porcelain stoneware, wetting force, resistance to surface abrasion, tenorite

INTRODUCTION

Along with enhancement of the functional aspects of porcelain stoneware (hardness, resistance to surface abrasion, chemical resistance and etc. [1]) glazed layers are also responsible for aesthetic superficial effects. Therefore, in recent years, much attention has been paid to the development of the metallic (metallized) glazes of high decorative value [2-9]. In addition, these copper-containing glazes can have high antibacterial activity against *Staphylococcus aureus* and *Escherichia coli* strains [9].

The literature review shows that new metallic glaze compositions should meet the following requirements [2-4, 8]:

- precious metallic elements, raw materials which are costly and toxic should be avoided;
- glazes should be suitable for present-day single-fire porcelain stoneware manufacturing technologies and decoration techniques used in the sector;
- glazed porcelain stoneware must meet quality standards;
- raw glazes are cost-effective alternatives to fritted compositions;

– glazes should be environmentally friendly.

Generally, in order to give the single-fired porcelain stoneware glazes a metallic appearance MnO, CuO and CoO [8], CuO can be added [9], as well as stainless steel and a Ni-based superalloy belonging to the NiCoCrAlY alloys family [10], frit containing copper oxide [3] or Fe₂O₃ and P₂O₅ which are formed iron phosphate phase with modified structure [4].

It is important to note that Spain imported glazes by the enterprises of the Republic of Belarus to produce ceramic tiles.

The aim of the present work is to develop copper-containing raw glazes with a metallic luster for porcelain stoneware using the local raw materials of the Republic of Belarus; to investigate the sintering behavior of metallic raw glazes; to understand the effect the glaze components have on the formation of glaze

structure; to establish the impact of the component ratio on the glaze properties.

EXPERIMENTAL PART

The following commercial grade raw materials were used to prepare the experimental metallic glazes: fusible clay "Lukoml-1" (GOST 9169, Republic of Belarus) in amount of 37.5-47.5%¹, dolomite (group 1, grade A, class 4, GOST 14050, JSC "Dolomit", Republic of Belarus) – 20.0-30.0%, quartz sand OVS-020-V (GOST 22551, the branch "Gomel Mining and Processing Plant" of the OJSC "Gomelsteklo", Republic of Belarus) – 9.0-11.0% and kaolin KN-83 (GOST 19285, Ukraine) – 9.0-11.0%. 12.5-22.5% copper (II) oxide (analytical grade, GOST 16539) was chosen to give the glazes a metallic luster. Oxide compositions of the experimental metallic glazes are indicated in Table 1.

Table 1

Chemical composition of the metallic glazes (in %) under study

Таблица 1. Химический состав изучаемых металлизированных глазурей (%)

Composition	SiO ₂	CuO	CaO+ MgO	Al ₂ O ₃	Fe ₂ O ₃	Na ₂ O+ K ₂ O	TiO ₂
M1	47.09	14.62	15.87	14.52	4.28	3.03	0.59
M2	45.44	14.91	18.52	13.84	3.94	2.80	0.55
M3	43.71	15.20	21.28	13.14	3.60	2.56	0.51
M4	43.79	17.84	18.22	13.28	3.71	2.64	0.52
M5	43.88	20.36	15.29	13.41	3.82	2.71	0.53
M6	42.17	20.75	17.91	12.72	3.48	2.48	0.49
M7	40.71	26.02	14.71	12.32	3.37	2.39	0.48

The glaze slip was prepared by combined wet grinding of the raw materials in a ball mill (Speedy, Italy) to 0.1-0.3 % residue in the No. 0056 sieve with material : milling body : water ratio 1 : 1.5 : 0.5. The obtained suspension was applied to the ceramic stoneware bodies predried to 0.5% moisture content and coated with engobe by pouring method. It should be noted that production compositions of the porcelain stoneware tile mixes and engobe coating were used in the present research. The tiles glazed with the experimental compositions were fired in an RKK 250/63 gas-flame furnace (Italy) at temperature 1185±5 °C for 45±2 min under the extant conditions at Berezastroimaterialy JSC (Bereza, Republic of Belarus).

The investigation of the samples obtained after firing included the luster determination using a FB-2 photoelectronic brightness meter and uviol glass. The coloring parameters L*, a*, and b* of the glazes were measured via a ColorEye XTH Spectrophotometer (USA). L*, a*, b* analyses were made three times for each glazed tile. Within this method L* is the lightness axis (black (0) – white (100)), a* is the green (-a*) –

red (+a*) axis, and b* is the blue (-b*) – yellow (+b*) axis. Color differences (ΔE*) were also calculated as

$$\Delta E = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad [11]. \quad (1)$$

Resistance of glazed tiles to surface abrasion was determined with an abrasimeter ISO 8 (Italy) in accordance with EN ISO 10545 – Part 7, resistance to thermal shock – EN ISO 10545 – Part 9. The coefficient of linear thermal expansion (CLTE) was measured with a DIL 402 PC electronic dilatometer (Netzsch, Germany) within 20-400 °C (EN ISO 10545 – Part 8) and the Vicker hardness – with a Wolpert Wilson Instruments (Germany) apparatus.

The melting behavior of the tested glazes were carried out using a hot-stage microscope Misura 3.0 (Expert System Solutions, Italy). The prepared and dried glaze slip was used to make the test samples. The next step was to press 5 mm high cylindrical shaped pellets of 2 mm in diameter. The measurement was taken at a heating rate of 10 °C/min within 500 to 1400 °C temperature range.

¹ Here and below, the weight content, wt. %

X-ray diffraction (XRD) analysis was performed on X-ray diffractometer D8 ADVANCE setup (Bruker, Germany), differential scanning calorimetry (DSC) – with the device DSC 404 F3 Pegasus calorimeter (Netzsch, Germany). A JSM-5610 LV scanning electron microscope with an EXS JED-2201 JEOL chemical analysis system (Japan) was used to investigate the microstructure of matured specimens.

RESULTS AND DISCUSSION

The firing result indicated that the glaze surfaces appeared to have different shades of grey: dim grey (glazes M1, M6), greenish grey (glazes M2–M4), mouse grey (glaze M5), bluish grey (glaze M7). Table 2 presents the colorimetric values of samples. Amongst the studied glazes, M4 having the highest L*, a*, and b* values was selected as the reference sample of the studied system and ΔE* was controlled according to this glaze. In fact, there wasn't strong dependence between the shades of grey and content of colorants (copper and iron oxides). In the authors' opinion, the color of the glazes was determined by the firing atmosphere. However, it is quite difficult to control the atmosphere at fast firing.

Table 2
Colorimetric analysis of the metallic glazes under study
Таблица 2. Результаты колориметрического анализа изучаемых металлизированных глазурей (%)

Glazes	L*	a*	b*	ΔE*
M1	44.26	0.75	1.85	5.69
M2	46.80	1.13	4.55	2.03
M3	48.34	0.82	5.52	1.02
M4	48.33	1.83	5.68	–
M5	42.66	0.11	-0.69	8.70
M6	45.73	-0.22	-0.35	6.88
M7	47.80	1.18	3.75	2.10

Physical-chemical properties of the experimental metallic glazes are shown in Table 3.

Table 3
Average values of physical-chemical properties of the synthesized glaze coatings
Таблица 3. Усредненные значения физико-химических свойств синтезированных глазурных покрытий

Glazes	CLTE, $\alpha \cdot 10^7$, K ⁻¹	Micro-hardness, MPa	Luster, %	PEI
M1	65.9	6570	100	2
M2	68.7	6000	100	2
M3	73.4	6010	100	2
M4	69.4	5970	90	2
M5	66.5	5650	60	2
M6	70.7	5550	82	1
M7	66.9	5090	40	1

The coefficient of linear thermal expansion of glazes (Table 3) is similar to the CLTE of the biscuit – $(75-78) \cdot 10^{-7} \text{ K}^{-1}$. Thus, the glaze layers are under compressive stress what provides high heat resistance – $150 \pm 5 \text{ }^\circ\text{C}$ and higher mechanical strength of ceramic tiles.

The properties of the synthesized glaze coatings depend on their microstructure. XRD patterns of the experimental metallic glazes show a wide band corresponding to the glossy matrix and diffraction peaks associated to the two crystalline phases (anorthite and tenorite). The amount of fusible clay mainly influences on the precipitation of anorthite. It can be noted if the fusible clay content was low (glazes M3, M4, M7 – 37.5-40.0%) the intensity of anorthite reflection decreases up to a minimum. Introducing 47.5% fusible clay in glaze M1, by comparison, resulted in an increase of amount of anorthite crystals (Fig. 1). This is due to the following: clay minerals and their amorphous thermal decomposition products (metakaolin or alumina and silica) along with CaO formed as a result of decarbonization of dolomite have an increased reactivity. This phases reacted to form anorthite $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ during the firing. It should also be noted that the percentage of Al_2O_3 and SiO_2 was maximum in glaze M1 (Table 1). Intensity of the diffraction peaks of tenorite is determined by the content of copper (II) oxide.

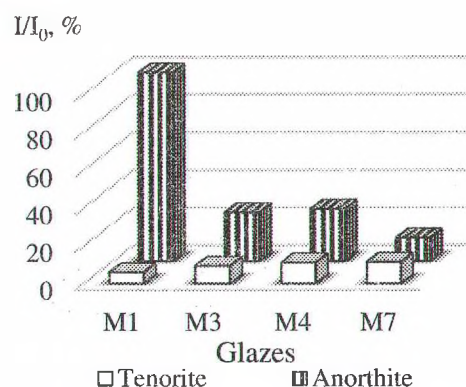


Fig. 1. Relative intensity of the diffraction peaks of anorthite ($d = 0.3195 \text{ nm}$) and tenorite ($d = 0.2327 \text{ nm}$) identified in the synthesized glazes
Рис. 1. Относительная интенсивность дифракционных максимумов анортита ($d = 0,3195 \text{ нм}$) и тенорита ($d = 0,2327 \text{ нм}$), идентифицированных в синтезированных глазурях

The predominant phase in the glazes was glassy matrix (Fig. 2). Complex dendritic patterns varying in size ($20-100 \mu\text{m}$) distribute irregularly on the surface of glazes. Energy dispersive x-ray spectroscopy allowed to determine that the elongated prismatic crystals forming these aggregates were tenorite. The

chemical composition at point 1 (Fig. 2), %: CuO – 46.83, SiO₂ – 30.49, Al₂O₃ – 15.36, MgO – 2.54, CaO – 4.78. The metallic luster of glazes was related to the copper compounds [8].

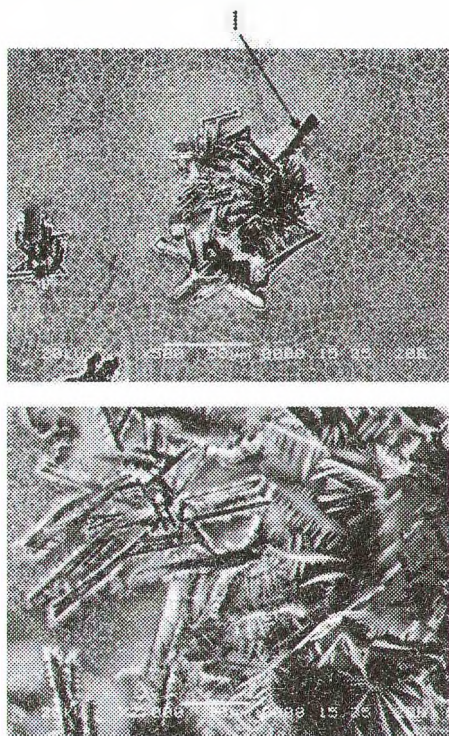


Fig. 2. SEM micrographs of the glaze M4

Рис. 2. Электронно-микроскопические снимки глазури М4

The nature of the devitrified crystals and amount of crystalline phase affect the microhardness and resistance to surface abrasion of glazes [12-14]. According to [15], Mohs' hardness of tenorite is 3.5-4.0, anorthite – 6.0. Therefore, the value of mechanical properties of synthesized glaze M1 was considerably better (Table 3).

To form a smooth, flat layer, the glaze must have adequate properties (fusibility, viscosity, surface tension and wetting ability) within the ceramic tile firing. When developing glazes designed for the ceramic products which had been obtained at a certain temperature, the following characteristic glaze temperatures are determined with a hot-stage microscope [16-19]:

- sintering – the temperature at which finely milled glaze particles sinter together;
- softening – the temperature at which the sample shape begins to round;
- sphere – the temperature at which the height-width ratio is equal to 0.9–1.0;
- half-sphere – the temperature at which the sample height is equal to the half of the initial height;
- fusion – the temperature at which the sample height is equal to one-third of the initial height.

The hot stage microscopy analysis results for the glazes are given in Fig. 3. Locations of the characteristic sample shapes for the sintering, sphere, half sphere and fusion points are indicated in the curves. The sintering point varied from 1010 to 1060 °C, half sphere – 1100-1170 °C, fusion – 1120-1200 °C depending on the glaze composition. The plateau that indicates the formation of the crystals (presumably of anorthite) for glazes was between 850 and 1010 °C (Fig. 3). The obtained data was also found to correlate well with data collected by DSC.

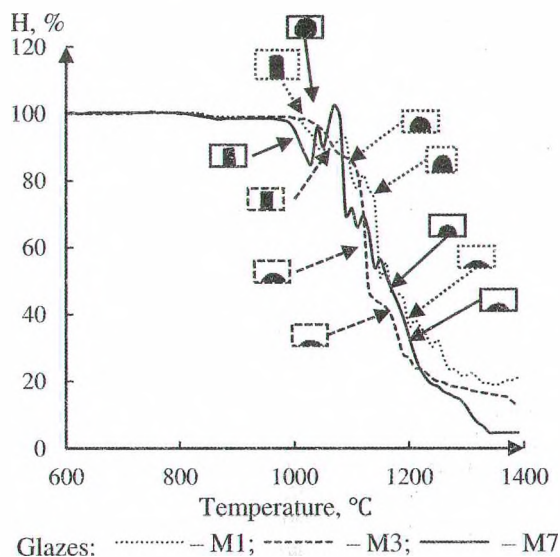


Fig. 3. Evolution of sample height (H) and shape as a function of temperature

Рис. 3. Изменение высоты и формы образца (H) в зависимости от температуры

The distinctive feature of M1 and M7 was the characteristic temperature point corresponding to sphere. There are several points of view on the formation of sphere during heating of glazes. T. Kronberg and L. Hupa [20] reported that during firing glazes consist of fusion and crystalline phase, thus the formation of the sphere typical for molten phases does not appear for them. Ch. Venturelli [19] notes that the glaze shape for amorphous systems is controlled by the surface tension. Thus, high surface tension glazes reach the sphere point.

According to Fig. 3, copper oxide lowered the sintering point, M7 had 10-50 °C lower initial sintering temperatures than others. Dolomite was more effective at high-temperature ranges (1050-1200 °C), the difference between M1 and M3 fusion point was 40 °C. In addition, melting behavior of the experimental metallic glazes depends on the content of other components, liquid composition change or microstructural evolution during the sintering.

The contact angle is the measure of the glaze capacity to wet the ceramic body (wetting force). If it is greater than 90°, the glaze does not wet the ceramic body [21]. Contact angles measured for the studied glazes at 1200 °C were as follows: M1 – 53°; M3 – 35°; M7 – 53°. So glaze M3 had the greater "ability" to wet the surface due to the smaller contact angle. Analyzing the obtained data, it can be concluded that the percentage of dolomite had a prevailing influence on the surface tension and wetting ability of the experimental glazes within 1050-1200 °C temperature range. In the authors' opinion, oxides of calcium and magnesium being part of dolomite increased glaze melt fluidity. This results in reduced surface tension (absence of sphere point in Fig. 3) and contact angle.

CONCLUSIONS

As a result of the conducted investigation the possibility of obtaining metallic raw glazes for porce-

lain stoneware using the raw materials of the Republic of Belarus was shown.

It was established that the developed glazes were suitable for present-day decoration techniques and single-fire manufacturing technologies for porcelain stoneware. Moreover, the glazed porcelain stoneware with the appropriate technical characteristics was provided.

The developed glaze could replace the imported ones and later reduce the net cost of porcelain stoneware and dependence of ceramic tile producers on imports.

The authors declare the absence a conflict of interest warranting disclosure in this article.

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