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COATINGS

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OPACIFICATION OF GLAZES FOR HOUSEHOLD MAJOLICA

I. A. Levitskii,[1,2] S. E. Barantseva,[1] A. I. Poznyak,[1] and E. O. Bogdan[1]

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A compounded mixture of fritted white, bright, glass ceramic, glaze coating for household majolica in the system $Na_2O–K_2O–CaO–B_2O_3–Al_2O_3–ZrO_2–SiO_2$ is developed. The structure of the coating is distinguished by homogeneity and uniformity of the distribution of the crystalline formations over the entire volume of the glaze. The physical and chemical properties of the glaze coating (CLTE = $(50.2 – 50.5) \times 10^{-7}$ K^{-1}, thermal resistance 150°C, whiteness 80 – 82%, brightness 87 – 89%, microhardness 5350 – 5400 MPa) attest an appropriate ratio of the crystalline and glassy phases in the glass ceramic coating formed.

Key words: majolica, glass formation, opacified glaze, crystallization, phase composition, migration, food environments.

The assortment of majolica largely depends on their decorative and user properties imparted by a glaze coating. In addition, the possibilities of ceramics in this range of properties are quite broad, and sometimes even unique.

Most majolica in the Republic of Belarus is manufactured by Belkhudozhkeramika JSC. Most articles manufacture by this enterprise that reflect the distinctive character and national color of Belarus are exported, so that the quality requirements are more stringent. Mostly utilitarian articles are produced, including tableware and teaware, intended not only for food storage and preparation but also for use in catering and restaurants.

The aim of the present investigation was to develop a compounded mixture of fritted, white, bright, glass ceramic, glaze coating for majolica for household use. The specifics of its usage are tied to repeated washing in dishwashers by jets of hot water (45 – 80°C) under pressure 0.03 – 1.0 MPa as well as possible temperature differentials in the dishwasher chamber to 40 – 50°C [1]. Aside from high decorative-aesthetic characteristics (brightness, whiteness) the glaze coatings are required to meet tough physical and chemical specifications, viz., thermal stability owing to the dilatometric matching of the linear thermal expansion coefficients (CLTE) in the system ceramic base – glaze coating.

[1] Belorussian State Technological University, Minsk, Republic of Belarus.
[2] E-mail: keramika@belstu.by.

Glass ceramic coatings on ceramic significantly expand not only the sphere of application but also the implementation of new technical and functional properties of the articles. As a rule, they comprise compositions whose main properties are due to a crystalline phase or complex of phases, micron in size and uniformly distributed in the glass matrix, formed in the course of heat treatment [2].

Zirconium dioxide makes it possible to obtain an opacified coating; its mechanical action is the subject of a number of foreign and domestic works predominately in the field of fritted coatings [3 – 5]. Detailed experimental and theoretical studies have made it possible to draw the well-grounded conclusion that the dissolved opacifier crystallizes out of the melt in the form of a finely disperse phase (in most cases zircon), which makes the opacification process more efficient than by introducing when the composition is milled. In addition, the degree of opacification of the glaze is determined not so much by the high content of the crystalline phase as by its total surface area. Therefore the smaller the particles, the greater the light scattering from the particles and, correspondingly, the greater the opacification of the glaze are [4].

A preliminary investigation was conducted for compositions in the system $Na_2O–K_2O–CaO–B_2O_3–Al_2O_3–ZrO_2–SiO_2$ in the content range of the main oxides 50 – 70% SiO_2, 5 – 20% Al_2O_3, and 5 – 12% ZrO_2 with variation steps 5.0% for silicon dioxide, 2.5% for zirconium dioxide, and 5% for aluminum oxide, the total content of zinc, boron, calcium, and alkali-metal oxides remaining constant at about 20%.[3]

Analysis of the results showed that to obtain opacified coatings the glass frits should be synthesized in the range of compositions with a limited range of the indicated components and their variation step reduced to 1.25%. This is associated with the fact that the problem of the present work was not only to obtain high-quality opacified coatings but also to take account of the economic aspects associated with the content of expensive and refractory oxides.

In this connection the glaze coatings were synthesized in the same system, and the total content of zinc, boron, calcium, and alkali-metal oxides was 30%. The composition range of the experimental glass frits is presented in Fig. 1.

The glasses were synthesized at temperature 1450 – 1470°C and granulated by casting into water. The glaze slip was obtained by wet milling of the raw material composition with a definite content of the glass frit, clay component, water, and saltpeter in a Speedy mill (Italy) for 50 min with quenched cullet : milling bodies : water ratios 1 : 1.2 : 0.9. An investigation of the glass formation process conducted in temperature gradient 1000 – 1100°C made it possible to evaluate the degree of opacification of the coatings, coverage, and decorative-aesthetic characteristics, specifically, the brightness and whiteness of the glazes.

It should be noted that a glaze coating was deposited on an intermediate majolica part after the first (glaze-free) firing at 860 – 880°C; the experimental temperature gradient for the firing of the coatings is directly related with the technological parameters of glaze synthesis in production.

The results of the investigation of glass formation and the technological characteristics of the glass frits confirmed that the optimal glaze coating obtains by using the composition N-2 (see Fig. 1), which according to the criteria indices satisfies the specifications for opacified glazes for household majolica.

The formation of the glass ceramic coating N-2 was studied by a complex method, including x-ray phase analysis performed with a Bruker diffractometer and JEOL JSM 56-LV (Japan) scanning electron microscope, equipped with a JED 2201 system for electron-probe energy dispersive local chemical analysis. The Joint Committee on Powder Diffraction Standards 2003 international card file and the DIFFRAC PLUS software (Bruker) were used to identify the crystalline phases. The Win Ploter software in the Fill Prof Suite package was used to process the profiles in the diffraction patterns.

The results of the x-ray phase analysis of the coating samples heat-treated at 950°C attest the existence of an initial stage of formation of crystalline phases in small quantities and the intensity of the halo in the x-ray diffraction pattern attests presence of predominately a glassy phase. Heat-treatment at 1000°C results in the formation of a crystalline phase of zircon $ZrSiO_4$ in amounts sufficient for at-

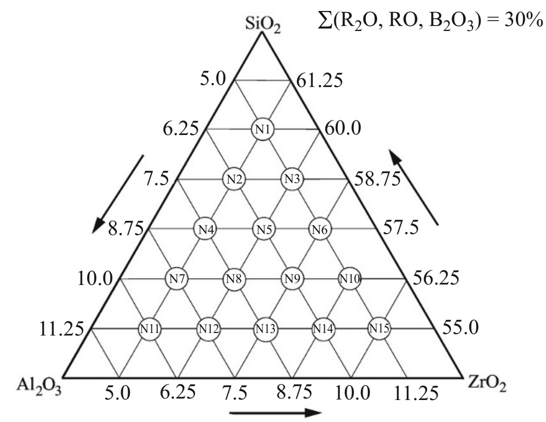

Fig. 1. Range of experimental compositions of opacified glaze coatings with the content of the silicon, zirconium, and aluminum oxides varying in steps of 1.25%.

taining the required opacification effect. The phase composition of the coating heat-treated at 1100°C is characterized by more distinct characteristics peaks due to zircon in the x-ray diffraction pattern. In addition, reflections due to aluminum silicate of the type β-Al_2SiO_5, which can be attributed to andalusite, are present.

The quite strong light scattering and, correspondingly, opacification as well as the weak halo in the x-ray diffraction pattern attest to a practically complete crystallization process owing to not only the formation of two crystalline phases but also their synergetic contribution to the activation of the process leading to a glass ceramic structure of the coating [4].

Zircon crystallizes in the tetragonal system, forming bipyramidal and prismatic crystals, possesses Mohs hardness 7 – 8 and is characterized by diamond-like brightness. Andalusite crystallizes in the rhombic system, forming thick-plate and columnar crystals, and is distinguished by a glass-like brightness and possesses Mohs hardness 7.5 [6 – 8]. The characteristic peaks due to andalusite on the diffraction patterns are superposed on the zircon reflections; however, at heat-treatment temperature 1100°C they differentiate quite clearly, which confirms its presence in glass ceramic glaze.

The following conclusions were drawn on the basis of the data from electron microprobe chemical analysis in different local regions of the surface, at points of crystalline formations and glassy phase of the glaze coating N-2, formed at annealing temperatures 1000 and 1100°C with 15-min soaking (Table 1).

The silicon oxide content on the surface of coatings fired at 1000 and 1100°C differs because of the somewhat lower degree of crystallization and, correspondingly, higher content of glass-forming SiO_2 in the first case. The chemical composition of the crystalline formation taking account of the stoichiometric ratio SiO_2/ZrO_2 in zircon confirms the presence of $ZrSiO_4$ in the opacified coating, and taking account of the stoichiometric ratio Al_2O_3/SiO_2 in andalusite the presence of β-Al_2SiO_5 [6, 7].

[3] Here and below the content by weight, %.

TABLE 1. Oxide Chemical Composition of Opacified N-2 coating

Index	Oxide content, wt.%						
	Na_2O	Al_2O_3	SiO_2	K_2O	CaO	ZnO	ZrO_2
Firing temperature 1000°C							
Local surface region	1.45	11.73	74.65	4.13	3.35	2.76	1.92
Firing temperature 1100°C							
Local surface region	3.43	14.04	68.68	4.05	4.20	4.69	0.92
Local point in a crystalline formation	0.36	10.38	57.76	2.66	3.98	4.67	20.19
Local point in the glass phase	–	14.58	68.40	3.03	4.22	6.40	3.36

The low content of alkaline metals and zinc in the crystalline formation could be associated with the capture of elements from the glassy phase by x-ray fluorescence flow. The practical identity of the chemical composition on the surface of the glaze and in the intercrystalline space at firing temperature 1100°C of the coating is characteristic. Thus, the temperature interval of formation of a high-quality glass ceramic coating of the new glaze developed, which equals 1000 – 1100°C, was determined. For this reason, taking account of the economic aspects of the energy resources there is a possibility of picking the temperature of glass formation for majolica from different ceramic bodies, differing by the composition and temperature of biscuit firing and glaze firing.

The electron-microscopic image of the surface of samples of a glaze coating, fired in a gradient temperature interval 1000 – 1100°C, specifically, at firing temperatures 1000, 1040, 1070, and 1100°C, presented in Fig. 2, made it possible to interpret as follows the process leading to the formation of the glass ceramic structure.

Active crystallization occurs at 1000°C and the amount of crystalline formations of zircon practically secures opacification of the coating. As the heat-treatment temperature increases from 1000 to 1040°C, further quantitative growth of crystalline formations and reduction of the glass phase content are observed. This process continues actively at 1070°C. The coating structure at 1100°C is distinguished by uniformity and homogeneity of the distribution of the crystalline formations over the entire volume of the glaze. The physical and chemical properties of the opacified coating (CLTE $(50.2 – 50.5) \times 10^{-7}\ K^{-1}$, thermal stability 150°C, whiteness 80 – 82%, brightness 87 – 89%, microhardness 5350 – 5400 MPa) attest an appropriate ratio of the crystalline and glassy phases in the glass ceramic coating formed.

The electron-microscopic investigation of the surface of a fresh fracture surface completely formed at 1100°C of glass ceramic glaze coating, presented in Fig. 3, is of great interest for interpreting the process and particularities of the formation of a polyphase structure of an opacified coating, represented by crystalline formations and a micro-heterogeneous and gas phase.

Under ×500 magnification (Fig. 3*a*) it is evident that the crystals of the opacifying phases are distributed uniformly, grouping in the ring- and oval-shaped aggregates as well as in irregular polyhedra joined with one another along the

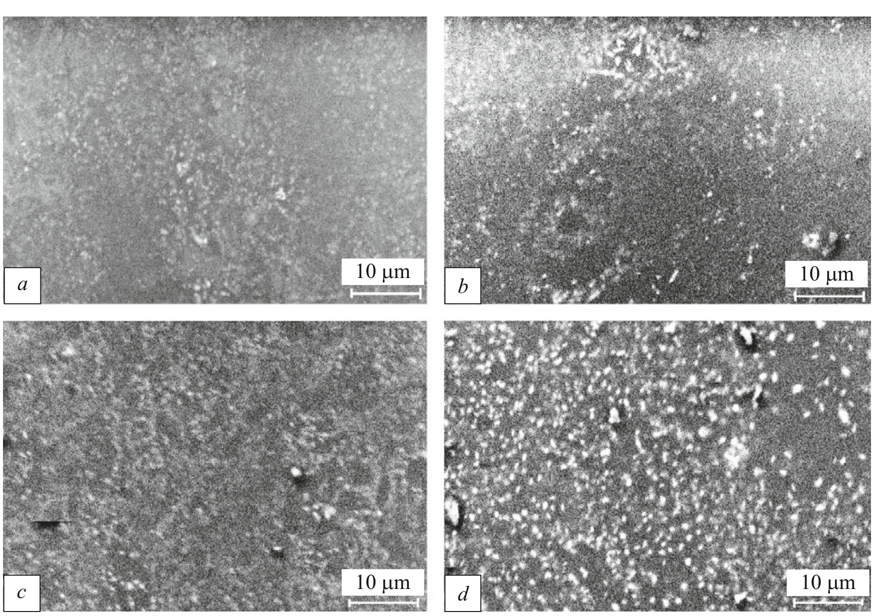

Fig. 2. Electron-microscopic image of the surface of an N-2 coating obtained at different firing temperatures: *a*) firing temperature 1000°C; *b*) 1040°C; *c*) 1070°C; *d*) 1100°C.

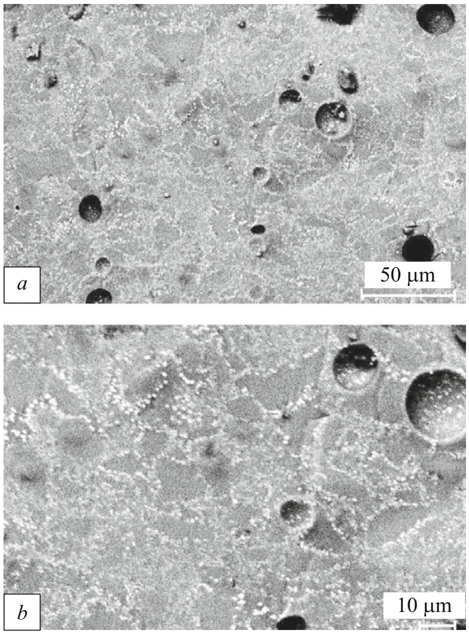

Fig. 3. Electron-microscopic image of a fracture surface of opacified N-2 glaze obtained at firing temperature 1100°C: *a*) ×500; *b*) ×1000.

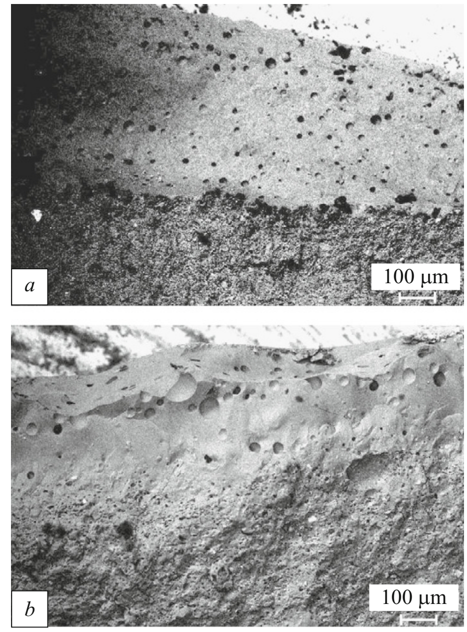

Fig. 4. Electron-microscopic image of a fracture surface in the system ceramic matrix – contact layer – glaze coating (×100): *a*) firing temperature 1000°C; *b*) firing temperature 1100°C.

common sides. The visually supposed amount of crystalline formations could be 25 – 30%.

Under ×1000 magnification individual bipyramidal or prismatic crystals of zircon $ZrSiO_4$ as well as sparsely distributed columnar crystals of andulasite β-Al_2SiO_5 are differentiated in aggregates.

Characteristically, in accordance with the classical ideas about crystallization processes in multicomponent glassy systems [9] the most active and easily occurring processes are formation of crystalline phases on interfaces, in this case a gas phase and a glassy phase, as well as on the surface of the pores, where intense concentration of crystalline formations is observed.

This is also observed on the boundaries of the crystalline and glassy phases in the form of continuous accumulations of crystals, contouring aggregates of different configuration (close to oval, polyhedra, rings of irregular asymmetric type and form). This picture of the glass ceramic structure is characteristic of many zirconium-containing opacified coatings and is described in detail in the literature [2].

It is known [10] that the strength of the adhesion of a glaze coating to a ceramic skull is largely due to the character of the contact layer formed. An electron-microscopic image of a fracture surface in the system ceramic matrix – contact layer – glaze coating is presented in Fig. 4.

It was found that in the formation interval of a glass ceramic coating (1000 – 1100°C) the quite sharp boundary between the ceramic and glaze layers, whose thickness equals 700 – 800 μm according to the scale in the electronic photograph, is smoothed. The significant number of pores at 1000°C (Fig. 4*a*) attests continuing glass-formation and crystallization processes.

The structure of the coating obtained by firing at 1100°C (Fig. 4*b*) corresponds to a glass ceramic coating, and the number of pores decreases sharply. Owing to active diffusion processes and the chemical interaction of the coating and ceramic base of the contact layer is not differentiated and comprises a metamorphic zone, which gives adequate adhesion strength.

In summary, the opacified glaze N-2 developed in the system Na_2O–K_2O–CaO–B_2O_3–Al_2O_3–ZrO_2–SiO_2 meets in terms of the decorative-aesthetic characteristics, physical-chemical properties, and sanitary-hygienic indices the specifications of the normative-technical documentation.

The samples of majolica with an opacified coating, which are fabricated under the conditions at Belkhudozhkeramika JSC, were tested in the Minsk City Center for Hygeine and Epidemiology for migration of zinc and boron in standard solutions of lactic, citric, and acetic acids and aluminum in water extract. The data obtained confirmed the absence of migration of the substances presented, which attests the suitability of the glass ceramic coating for decorating majolica and their large-scale use in catering and public eateries with a large flow of ceramic dishware through dishwashers.

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